Distribution of Hexachlorocyclohexanes in Bivalve Mollusks

of U.S. Coastal Waters and the Great Lakes

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ABSTRACT

Hexachlorocyclohexanes (HCHs) are persistent organic pollutants (POPs) found throughout the world in air, water, soil, sediment and biota. NOAA's National Status and Trends Program (NS&T) Mussel Watch Project began monitoring for gamma-HCH (lindane) in 1986 and has analyzed over 1,600 samples of bivalve mollusks at more than 280 sites in US coastal waters including Alaska, Hawaii and Puerto Rico. Since 1995, nearly 450 bivalve tissue samples have been analyzed for alpha-HCH. Gamma-HCH is declining at some sites and increasing at none. There are insufficient years of data (6 years minimum) to evaluate alpha-HCH temporal trends. Mussel Watch sites range in latitude from 18° N (Puerto Rico) to 61° N (Alaska). The majority of declining gamma-HCH trends occurred along the Northeast Coast between 40° and 44° N latitude. Most of the eleven Alaskan sites exceed the 85th percentile of the alpha-HCH concentration. HCH concentrations were significantly correlated with several variables and although the correlation coefficients were weak the results provide further evidence for long-range transport and global fractionation of HCHs along a latitudinal gradient.

INTRODUCTION

Hexachlorocyclohexane (HCH) has eight isomers of which five dominate the commercial mixture technical HCH, a widely used post WWII pesticide, that typically contains 60-70% alpha, 5-12% beta, 10-12% gamma, 6-10% delta, and 3-4 % epsilon-HCH.

USE

•Technical HCH is banned in many countries but still used in parts of Asia, South America and Africa;

• North American use of technical HCH was banned in the 1970s, in favor of gamma-HCH (lindane), the isomer with the greatest insecticidal activity and still widely used around the world;

•World consumption of alpha and gamma-HCH between 1960 and 1989 has been estimated at 403,900 and 146,700 tons, respectively with the highest consumption of alpha-HCH between 0° and 30° N latitude, and gamma-HCH between 30° and 60° N (1). In the United States, gamma-HCH use decreased from 270 to 110 t/yr between 1980 and 1990 (2).

PROPERTIES

•Compared to other POPs such as DDT, HCH isomers are more water soluble and volatile which helps to explain their global distribution even to remote pristine regions of world;

•The gamma isomer is classified by the EPA as a possible human carcinogen, while the alpha isomer shows the greatest incidence of hepatic lesions and is a probable human carcinogen (EPA);

• Beta-HCH, the most environmentally persistent, metabolically active, and most often found in mammals has also been reported to have estrogenic effects (3).

OCCURRENCE & TRENDS

•Decreasing trends of HCHs have been documented in fish (4), seabirds (5), air (6);

•Latitudinal gradients have been reported for HCHs in tree bark (7), foliage (8), lichens (9), and sea water (10).

METHODS

The Mussel Watch Project, part of NOAA's National Status and Trends Program, monitors chemical residues in tissues from bivalve mollusks collected from US coastal waters (mussels or oysters) and the Great Lakes (zebra mussels). The program began in 1986 and has grown to over 280 sites, which are collected at regular intervals (biennially in winter for mollusks, less frequently for sediments). The sites are designed to describe national and regional distributions of contamination and to represent large coastal areas and to avoid small-scale patches of contamination, or "hot spots." Sites selected for monitoring are generally 10 to 100 km apart.

The bivalves (oyster or mussel) are collected by hand, tongs or dredge from each site. The soft tissue is removed from approximately 30 individuals and homogenized prior to extraction and cleanup. Analysis and quantitation for organochlorine compounds is performed by capillary gas chromatography with electron capture detection (GC/ECD). The sampling and analytical protocols are described in detail elsewhere (11, 12).

Spearman-Rank Correlation analysis was performed to identify variables which could be important in describing occurrence and distribution of HCH residues. All statistics and data manipulations were performed with SAS (SAS Institute Cary, NC).

RESULTS & DISCUSSION

TABLES 1 & 2 identify the Mussel Watch sites with alpha and gamma-HCH tissue residues which exceed the 85th percentile level (values below the MDL excluded). These are the highest 15 percent of the data and are used here to define "high" concentrations.

TABLE 1: Mussel Watch sites which exceed the 85th percentile (3.074ng/g dry wt) for gamma-HCH (lindane) in bivalve tissue. The latitudinal distribution of these sites are plotted in Figure 1c.

gamma-HCH	NST Site	General Location	State	Latitude	Longitude
15.333	DBHC	Delaware Bay	NJ	39.43	75.49
12.000	DBWB	Delaware Bay	DE	39.33	75.46
8.250	BBPC	Biscayne Bay	FL	25.52	80.33
7.113	NYSR	New York Bight	NJ	40.19	74.01
6.724	GBSC	Galveston Bay	TX	29.70	94.99
5.824	GBYC	Galveston Bay	TX	29.62	95.00
5.055	HRLB	Hudson/Raritan Estuary	NY	40.57	74.05
4.880	DBKI	Delaware Bay	DE	39.20	75.36
4.615	LIMR	Long Island Sound	NY	40.94	73.70
4.538	DBAP	Delaware Bay	NJ	39.38	75.45
4.456	BHDI	Boston Harbor	MA	42.36	70.97
4.346	DBBD	Delaware Bay	NJ	39.25	75.30
4.128	CBBO	Chesapeake Bay	MD	39.16	76.40
4.103	BHDB	Boston Harbor	MA	42.30	71.04
4.020	CBMP	Chesapeake Bay	MD	39.07	76.41
3.884	BBAR	Buzzards Bay	MA	41.58	70.86
3.884	PSNR	Pamlico Sound	NC	35.09	76.53
3.870	LIHR	Long Island Sound	CT	41.17	73.11
3.835	HRJB	Hudson/Raritan Estuary	NY	40.57	73.90
3.707	PSPR	Pamlico Sound	NC	35.30	76.44
3.705	LISI	Long Island Sound	CT	41.05	73.42
3.631	PLLH	Point Loma	CA	32.68	117.25
3.625	SFDB	San Francisco Bay	CA	37.50	122.12
3.537	LIHU	Long Island Sound	NY	40.92	73.43
3.501	LIHH	Long Island Sound	NY	40.86	73.68
3.460	NYSH	New York Bight	NJ	40.49	74.03
3.444	BBRH	Buzzards Bay	MA	41.54	70.93
3.427	PSEH	Puget Sound	WA	47.97	122.23
3.424	BBGN	Buzzards Bay	MA	41.48	71.04
3.380	GBTD	Galveston Bay	TX	29.50	94.90
3.324	UISB	Unakwit Inlet	AK	60.96	147.65
3.323	PSHC	Puget Sound	WA	47.83	122.69
3.283	PBPI	Penobscot Bay	ME	44.26	68.73
3.274	LIPJ	Long Island Sound	NY	40.96	73.09
3.270	WIPP	Whidbey Island	WA	47.91	122.38
3.228	RSJC	Roanoke Sound	NC	35.89	75.63
3.204	CBIB	Chesapeake Bay	VA	37.79	76.28
3.195	SJCB	St. Johns River	FL	30.38	81.44
3.074	PDSC	Point Delgada	CA	40.02	124.07
3.074	DBCH	Delaware Bay	DE	38.78	75.12

TABLE 2: Mussel Watch sites which exceed the 85th percentile (2.346 ng/g dry wt) for alpha-HCH in bivalve tissue. The latitudinal distribution of these sites are plotted in Figure 1b.

alpha-HCH	NST Site	General Location	State	Latitude	Longitude
18.091	GBYC	Galveston Bay	TX	29.62	95.00
6.312	YHFC	Yaquina Bay	OR	44.84	124.05
6.199	GBTD	Galveston Bay	TX	29.50	94.90
3.965	HMBJ	Eureka	CA	40.76	124.24
3.954	GHWJ	Gray's Harbor	WA	46.91	124.12
3.947	CBCH	Coos Bay	OR	43.35	124.33
3.878	GASH	Gulf of Alaska	AK	58.50	152.62
3.853	FBJB	Florida Bay	FL	25.21	80.53
3.777	GBOB	Galveston Bay	TX	29.28	94.84
3.704	NBDI	Narragansett Bay	RI	41.60	71.31
3.617	PSSS	Puget Sound	WA	47.52	122.39
3.416	NBPI	Narragansett Bay	RI	41.65	71.36
3.320	HRRB	Hudson/Raritan Estuary	NY	40.52	74.18
3.286	SGSG	Crescent	CA	41.75	124.21
3.145	PDSC	Point Delgada	CA	40.02	124.07
3.131	MBCB	Matagorda Bay	TX	28.67	96.38
3.030	PWKH	Prince William Sound	AK	60.69	146.58
3.005	JFCF	Strait of Juan de Fuca	WA	48.38	124.73
2.908	PWSH	Prince William Sound	AK	60.64	145.99
2.821	IBNJ	Imperial Beach	CA	32.59	117.13
2.816	GASL	Prince William Sound	AK	60.07	147.83
2.810	BPBP	Barber's Point	HI	21.32	158.12
2.793	BIPI	Beaufort Inlet	NC	34.72	76.68
2.763	CFBI	Cape Fear	NC	33.92	78.00
2.643	TBOT	Tampa Bay	FL	28.02	82.63
2.575	HRJB	Hudson/Raritan Estuary	NY	40.57	73.90
2.563	GBCR	Galveston Bay	TX	29.26	94.92
2.551	GBHR	Galveston Bay	TX	29.48	94.74
2.539	GAWB	Gulf of Alaska	AK	59.22	151.52
2.537	CBFM	Charlotte Harbor	FL	26.56	81.92
2.536	NBES	Nahku Bay	AK	59.45	135.34
2.533	PDPD	Point Dume	CA	34.00	118.81
2.439	HRUB	Hudson/Raritan Estuary	NY	40.69	74.04
2.411	BBAP	Buzzards Bay	MA	41.64	70.76
2.346	OSBJ	Oceanside	CA	33.20	117.39

ALPHA-GAMMA RATIOS

The alpha-HCH/gamma-HCH ratio (α/γ) has been used as evidence for long-range transport and global fraction of HCHs. The mean ratio for each site for years 1995 to 1998 ranged from 0.086 to 8.94 with a mean and standard deviation of 2.019 and 1.208, respectively. The ratio at Great Lakes sites ranged from 0.65 to 2.07 with a mean of 1.26 and standard deviation of 0.606. The ratio-latitude relationship is discussed further below.

TABLE 3. Spearman-Rank Correlation Analysis was used to identify environmental variables which might explain the tissue residues observed around the United States (East Coast, West Coast and "All Coasts" which included data from the Gulf of Mexico). These variables were latitude, size of the estuarine drainage area (EDA), size of fluvial drainage area (FDA), riverine discharge volume (Flow) at rivers near the site, and human population levels within 20 kilometers of the site.

• Significant correlations (in red) were weak, however comparisons of the magnitude and direction (±) of correlations between analytes (alpha, gamma, ratio) and coasts (East, West, All) is used here to identify the relative importance of environmental variables;

• Latitude was (+) correlated with alpha-HCH levels and the ratio (α/γ) in each data set (East Coast, West Coast, and "All Coasts") whereas, gamma-HCH was only correlated with latitude of the "All Coasts" data set (Table 3). This evidence, although weak, supports the notion of long-range transport and global fraction of HCHs;

• Human population was (-) correlated with alpha-HCH on the West Coast and (+) correlated with gamma-HCH on the "All Coasts" data sets which is consistent with the chemical properties of gamma- relative to alpha-HCH;

• River discharge (FLOW) was (+) correlated with gamma-HCH on the East Coast and "All Coasts" data sets which is consistent with the notion that gamma-HCH applied at the pesticide lindane should be found in the rivers as a result of runoff from agricultural use;

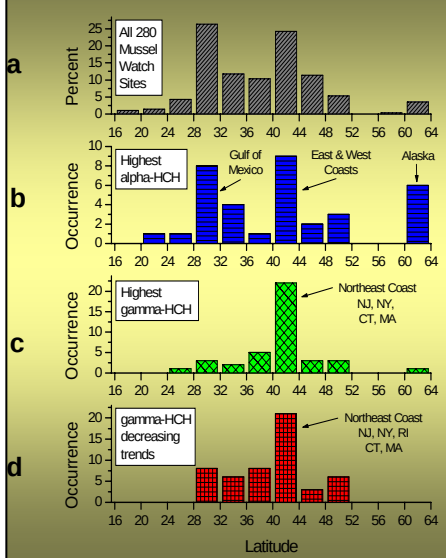
• Size (sq. mi.) of the estuarine drainage area (EDA) was (+) correlated with gamma-HCH on the East Coast and "All Coasts" data sets in contrast to the ratio (α/γ) which was (-) correlated.

TABLE 3. Spearman-Rank Correlation Analysis.

Coefficient / Prob > / Number of observations.

Coast	Analyte	Latitude	Population	FLOW	EDA	FDA
East Coast	alpha-HCH	0.394 0.0001 96	-0.006 0.950 94	-0.090 0.5483 47	-0.027 0.8457 55	-0.223 0.2442 29
	gamma-HCH	-0.017 0.8696 100	0.176 0.0838 98	0.471 0.0005 51	0.385 0.0026 59	-0.046 0.8030 32
	Ratio α/γ	0.309 0.0018 100	-0.022 0.8273 98	-0.227 0.1092 51	-0.363 0.0047 59	-0.184 0.3136 32
West Coast	alpha-HCH	0.374 0.0018 67	-0.373 0.0019 67	-0.070 0.7624 21	0.016 0.9442 21	-0.018 0.9597 10
	gamma-HCH	0.029 0.8075 74	0.118 0.3180 74	0.205 0.3368 24	0.138 0.5095 25	-0.063 0.8446 12
	Ratio α/γ	0.321 0.0056 73	-0.268 0.0221 73	-0.123 0.5776 23	0.053 0.8065 24	-0.321 0.3356 11
All Coasts	alpha-HCH	0.412 0.0001 260	0.022 0.7253 256	-0.039 0.6712 120	-0.048 0.5970 125	-0.167 0.1613 72
	gamma-HCH	0.180 0.0025 278	0.19443 0.0012 274	0.340 0.0001 133	0.184 0.0303 139	-0.038 0.7334 81
	Ratio α/γ	0.428 0.0001 276	0.079 0.1928 272	-0.109 0.2154 132	-0.233 0.0061 138	-0.368 0.0008 80

FIGURE 1



LATITUDINAL DISTRIBUTION

The latitudinal distribution of 280 Mussel Watch sites is compared with the distribution of sites with "high" alpha and gamma-HCH tissue residues. Mussel Watch sites and "high" alpha and gamma-HCH residues are not evenly distributed.

•FIGURE 1a: About 75 percent of all 280 Mussel Watch sites are between 28° to 48° N latitude with two regions, the Gulf Coast (28° to 32° N latitude) and the mid-Atlantic/mid-Pacific (40° to 44° N latitude), each accounting for about 25 percent o f the sites.

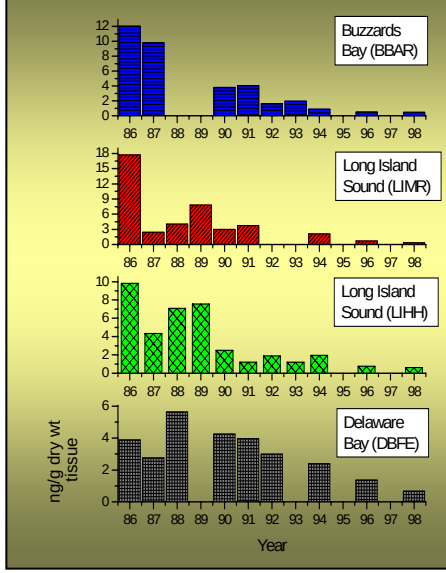
•FIGURE 1b: The latitudinal distribution "high" alpha-HCH concentrations (valves in Table 2) are plotted in Figure 1b. Three dominant regions are observed: the Gulf of Mexico (28° to 32° N latitude), mid-Atlantic/mid-Pacific (40° to 44° N latitude), and Alaska (60° to 64° N latitude).

•FIGURE 1c: In contrast to Figure 1b, the latitudinal distribution of "high" gamma-HCH (Fig 1c) is dominated by only one region, the mid-Atlantic Coast (40° to 44° N latitude) which includes the Northeast states NJ, NY, CT, and MA and accounts for 94 percent of the "high" gamma-HCH tissue residues.

FIGURE 1d: Of the 52 sites which show significant decreasing temporal trends of gamma-HCH, 27 (52%) were on on the Northeast Coast, 17 (33%) were on the West Coast and 8 (15%) were on the Gulf Coast.

The Gulf of Mexico (28° to 32° N latitude) has many "high" alpha-HCH residues (Fig 1b) but relatively few "high" gamma-HCH residues (Fig 1c). High alpha-HCH levels along the Gulf Coast suggests continued use of technical HCH in Central and South American counties. Similarly in Alaska, the greater incidence of "high" alpha-HCH and low incidence of "high" gamma-HCH is evidence for long-range transport.

FIGURE 2



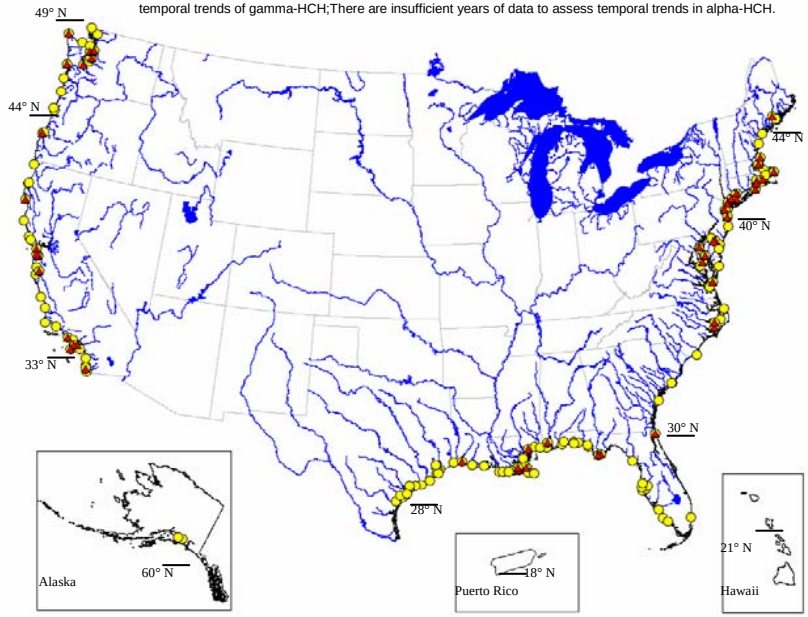
TEMPORAL TRENDS

FIGURE 2: Generally, temporal trends in gamma-HCH concentrations declined rapidly in the late 1980s and early 1990s but declining trends have leveled off in recent years particularly at sites in the Northeast.

The GREAT LAKES

Mean concentrations of alpha and gamma-HCH at twenty-six Great Lakes sites were low and uniformly distributed in contrast to other regions of the country. Alpha-HCH ranged from 0.460 to 1.770 ng/g (dry wt) with a mean and standard deviation of 1.242 and 0.406, respectively. Gamma-HCH levels ranged from 0.570 to 1.160 ng/g (dry wt) with a mean and standard deviation of 0.908 and 0.171, respectively. Alpha-HCH was detected at more than twice the frequency as gamma-HCH.

FIGURE 1 : Of the 280 Mussel Watch sites, 163 have 6 or more years of data (yellow circles). Fifty two of these (~20%) show significant (α<0.05) decline in gamma-HCH (red triangles).No sites showed increasing temporal trends of gamma-HCH;There are insufficient years of data to assess temporal trends in alpha-HCH.



CONCLUSION

Gamma-HCH levels in bivalve tissue collected from U.S. coastal waters declined rapidly in the late 1980s and early 1990s at nearly 20 percent of NOAA's Mussel Watch sites. The majority of these reductions occurred in the Northeast, most notably in coastal areas of NY, NJ, CT, and MA. Concentrations at these sites have leveled off in recent years. At present there are insufficient data to assess temporal trends of alpha-HCH. The occurrence of high levels of alpha-HCH are more broadly distributed in U.S. coastal waters than gamma-HCH which is consistent with its greater volatility and susceptibility to atmospheric transport.

The low levels of gamma-HCH and elevated levels of alpha-HCH in Alaska suggest long-range transport from distant sources. Based on current use estimates and environmental monitoring of technical HCH and gamma-HCH, the most likely source of these Alaskan residues is Russia and Southeast Asia. An important source of alpha-HCH to the conterminous United States is the Gulf of Mexico. High concentrations found here are likely due to recent use of technical HCH in Central or South America. Comparison of Mussel Watch HCH concentrations with latitude provides further evidence for global transport to the higher latitudes.

A new POPs elimination treaty is scheduled to be signed in early 2001. Although gamma-HCH is not on the initial list of 12 POPs, voluntary reductions seem likely. However, monitoring should continue in order to confirm whether or not all HCH isomers are declining and also to further define their movement and mechanisms of transport through the environment.

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