A NUMERICAL ASSESSMENT OF IMPACT OF NEAR-SOURCE, LOCAL SOURCE AND REEMISSION ON THE BUDGET OF ?-HEXACHLOROCYCLOHEXANE OVER THE GREAT LAKES AND ST. LAWRENCE ECOSYSTEM

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INTRUDUCTION

Presence of γ-HCH in the Arctic and the Great Lakes ecosystem owes essentially to the atmospheric transport following its application to agricultural lands. Deposition of pesticides to the Great Lakes is also thought to have significant contributions from local sources and long-range transport over regional and even global scales. After ban in the United States in the 1980s, major sources of γ-HCH in North America have been identified only in Canada where γ-HCH is still used as a pesticide for treatment of canola and corn seeds (Waite et al., 1999; Poissant and Koprivnjak, 1996). In the last ten years, the Prairie Provinces canola fields (Saskatchewan, Alberta and Manitoba) of Canada have become the largest source of γ-HCH in North America. Concern is raised for the impact of γ-HCH application in Canada on the Great Lakes due to γ-HCH's sufficient toxicity and presence in water, sediments and aquatic biota of the Great Lakes ecosystem. The consideration of global scale long-range transport may help to distinguish important pathways of pesticides, but the contribution from trans-boundary transport in such a scale to pesticide distribution is difficult to assess and may not be significant. In reality, near- and local-sources, if they exist, always dominate the magnitude and distribution of concentration of a pesticide. In this study, an attempt is made to use a coupled atmospheric dispersion and soil-air, water-air exchange model to assess contributions from long-range transport in a regional scale, local emissions, and reemission to the budget and loadings of γ-HCH over the Great Lakes and the St. Lawrence ecosystem. Two numerical experiments are conducted for the summer season (June − August) and winter season (December 1997 − February 1998) of 1998 respectively by using the same emission inventory of γ-HCH.

COUPLED ATMOSPHERIC TRANSPORT, SOIL-AIR, AND WATER-AIR EXCHANGE MODEL

The atmospheric transport model employed in this investigation is a three-dimensional regional scale dispersion model, which has been used in previous studies of heavy metal deposition to the Great Lakes and other North American regions. The model equation is written as:

$$\partial c / \partial t = -\mathbf{v} \cdot \nabla c - w\, \partial c / \partial Z + \nabla(\mathbf{k}\nabla c) + \mathbf{n}(E + S) / m_a \qquad (1)$$

where χ is the mixing ratio of a pesticide, $\mathbf{k}$ is the second-rank tensor characterizing turbulence eddy diffusivity, $\mathbf{n}$ is the molecular mass of a pesticide, m_a is the air mass near the surface, and E and S are the surface fluxes at model grids due to emission and deposition. Removal of a chemical (say, γ-HCH) by reaction in air (via OH radical or other mechanisms) is not included in the model, because the residence time for the model grid cell (a few hours) is very small compared to typical half-life of atmospheric reaction processes (~ 10 to 1000 days) for oranochlorine pesticides (Brubaker and Hites, 1998). The model has a horizontal resolution of 35 km × 35 km (5 km sub-grid scale, Ma and Daggupaty, 2000) with 130 × 75 grids, and covers the most area of Canada and central and northern United States (figure 1). There are 12 vertical model levels from the surface to 7 km. The meteorological data that are used to drive (1) are

objectively analyzed data from the Global Environmental Multi-scale Model (GEM) of CMC (Canadian Meteorological Center).

The soil-air exchange model uses a dynamic, three soil layer, fugacity-based model (Harner, et al, 2001). The model is described and used to determine the extent of dis-equilibrium and magnitude of the soil-air transfer. The soil is treated as three well-mixed layers. In each layer, chemical loss mechanisms include volatilization, leaching, degradation and diffusion. Important transport processes in the air compartment include gas-phase absorption to soil, deposition and atmospheric processes, such as advection and diffusion. The water-air exchange is simulated with a two-film model (Liss and Slater, 1974).

Two numerical experiments were carried out for assessments of long-range transport and reemission of γ-HCH. In these two experiments, γ-HCH emission sources (Figure 1) in Ontario and Quebec cornfields are included and excluded, respectively, thereby to identify the contributions of major sources of γ-HCH in Prairie Provinces to γ-HCH budget over the Great Lakes and St. Lawrence ecosystem. The experiments are performed for the winter and summer season of 1998 in order to test sensitivities of long-range transport and reemission processes to the ambient atmospheric conditions. In subsequent discussions, these two experiments are referred to as EXP1 (with all emission sources) and EXP2 (excluding emission sources in the provinces of Ontario and Quebec). Assessments of the effects of reemission on air concentration in the summer and winter season are made using the results from the EXP1.
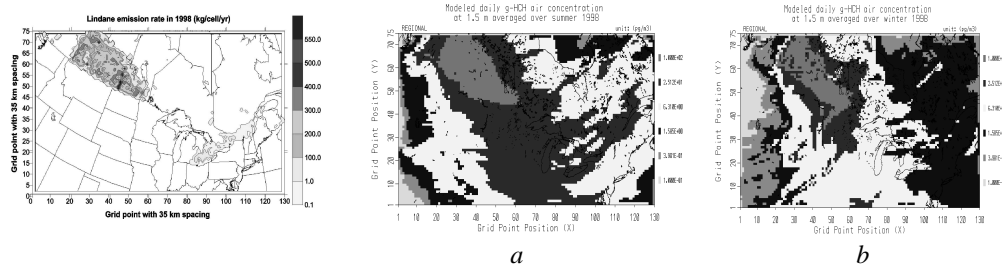

a   b

Figure 1. γ-HCH annual emission rate in 1998

Figure 2. Modeled daily air concentrations of γ-HCH from EXP 1 at 1.5 m averaged over June-August of 1998 (a) and December 1997-February 1998 (b).

RESULTS AND DISCUSSIONS

Reemission
Modeled daily γ-HCH air concentrations from EXP 1 at 1.5 m averaged over June-August 1998 and December 1997-February 1998 are illustrated in Figure 2. Higher air concentrations are observed over the Great Lakes and the St. Lawrence valley during the summertime than the wintertime. Modeled soil concentrations at 1-10 cm below the ground surface (so-called reservoir layer, Harner et al, 2001) in the same region are also higher during the summertime than the wintertime, especially near the upper Great Lakes (lakes Superior and Michigan). Because background soil concentration is not introduced in present numerical studies, the soils in most regions around the Great Lake and the St. Lawrence valley are contaminated by the deposition of γ-HCH in the atmosphere transported from the sources. The reemission can be estimated by soil/air fugacity ratio f_s/f_a, where f_s and f_a are the soil and air fugacities, respectively. $f_s/f_a > 1$ represents net transfer out of soil (volatilization) and values < 1 indicates the opposite (deposition). Estimated fugacity ratios in the summer and winter at selected grid

points are displayed in Figure 3. Among 8 grid points, 2 grid points are chosen at source grids and the rest taken at downstream grids of the sources. As shown, in most cases, the fugacity ratios are less than 1 either in the winter or summertime, except for the source grids (34,66) and (93,18) where strong emissions (and hence the strong γ-HCH residues in soil) occur so that the net transfer of γ-HCH was soil-to-air both in the winter and summer. The strongest soil-to-air transfer takes place in the summer at the grid (34,66), corresponding to the larger emission amount at the two selected source grids (317.9 kg yr^{-1}). This seems to suggest that air concentrations in the weak source region (with small γ-HCH soil residues) in Ontario and Quebec may not be generated mainly from local sources but transported largely from the upstream source region in the Prairie Provinces. The rest grids are located at downwind of the source regions in the Prairie Provinces between the upper Great Lakes and the St. Lawrence valley (grid (110,25)) at the downwind of Ontario and Quebec cornfields. As shown in Figure 3, at all these grids the fugacity ratios are far less than 1, indicating downward transfer of γ-HCH due mostly to deposition.
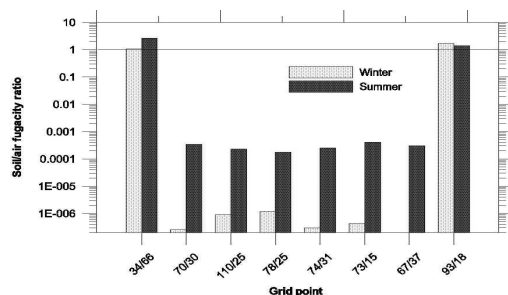

Figure3. Soil-air fugacity ratios at 1-10 cm (reservoir layer) below the ground surface in the summer and winter of 1998 at selected surface grid points.
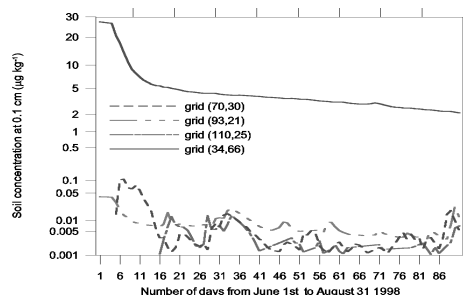
Figure 4. Time series of soil concentration at 0.1 cm at four model grids during the. summertime of 1998

Effects of near- and local-sources
To evaluate the effects of long-range transport and local sources on the changes in soil concentration, Figure 4 illustrates daily variations of soil concentration at 0.1 cm at four model grids during the summertime of 1998. Among them, two grids are within the source region in Saskatchewan (34,66) and Ontario (93,21). The rest two lie between lakes Michigan and Superior (70,30), and at the St. Lawrence valley (110,25). As shown, the soil concentration at grid (34,66) decreases monotonically with time due to volatilization, in agreement with Harner et al's result (2001). Because there are no other sources and because this study assumes clean air and soil in the upstream of the prairie source region, the variation of soil concentrations in this source region is dominated by soil-air exchange processes (deposition, absorption and volatilization). γ-HCH soil concentrations are re-volatilized into the air through soil removal process, which is then transported, with the substance remained in the air, to downwind regions.
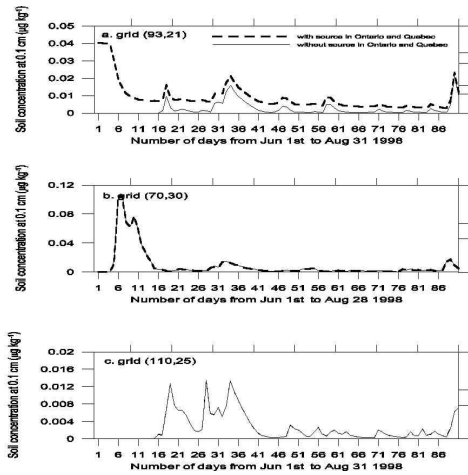
Figure 5. Modeled daily g-HCH air concentrations at selected grid points from EXP1 and EXP2 for summer 1998.
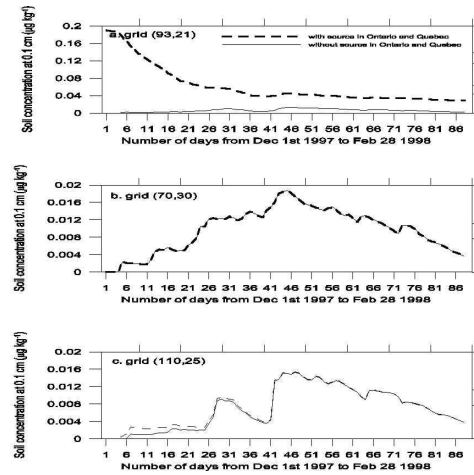
Figure 6. Same as fig. 5 but for winter 1998

Figure 5 displays temporal trends of soil concentration at 0.1 cm in the summer of 1998, generated from EXP1 and EXP2, respectively. At the source grid (93,21), soil concentration at 0.1 cm from EXP1 decreases rapidly during the first several days, whilst in EXP2 (no sources in Ontario and Quebec) the soil concentration remains zero during the first several days and then responds quickly to changes in air concentrations due mostly to long-range transport from the upstream sources (in the prairie region) and show the same trend to that from EXP1. In the downstream (the Great Lakes and the St. Lawrence valley) of the both γ-HCH source regions in the Prairie Provinces and Ontario and Quebec (grids (70,30) and (110,25)), the soil concentrations at 0.1 cm from both EXP1 and EXP2 are almost identical. The modeled mean daily γ-HCH averaged over the summer and winter seasons show (Tables 1 and 2) that the differences of modeled γ-HCH concentrations to the all five lakes between the two experiments are so small that can be neglected, and apparently the upper Great Lakes, which relatively close to the major sources in the prairie region canola fields, receive much more γ-HCH than lakes Erie and Ontario, which are adjacent to the sources in Ontario cornfields. This suggests that the γ-HCH emissions in the prairie region make major contribution to the γ-HCH budgets over the Great Lakes. Temporal variation of soil concentrations at 0.1 cm in the wintertime is illustrated in Figure 6. Compared with the summer trend, EXP2 yields considerably lower soil concentration at the source grid (93,21), whilst EXP1 yields larger values of the soil concentration, which corresponds to the air concentration. At the downstream grids (70,30) and (110,25), the both experiments obtains almost identical results, but the predicted soil concentrations reach their largest values in the mid-winter, compared to the summer cases in which the peak values of the soil concentration appear in the early summer. Compared with summer results, EXP2 produces lower γ-HCH concentration in lake Ontario (PPT) than EXP1 in the wintertime (Table 2).

Table 1. Modeled and measured seasonal *g*-HCH concentration at 1.5 m averaged over June 1st - August 31st 1998. Measured data are collected from IADN monitoring stations*.

		\u03b3-HCH (pg m^{-3})						
Sites		PPT	BNT	STP	SBD	EGH	CHI	BRR
Modeled	I	25.866	18.300	19.841	28.046	24.330	25.618	29.119
	II	25.524	18.241	19.520	27.982	24.322	25.613	29.100
Measured		19.0431	15.205	27.792	42.470	48.485	28.085	30.033

Table 2. Same as Table 1 but for December 1st 1997 - February 28 1998*.

		\u03b3-HCH (pg m^{-3})						
Sites		PPT	BNT	STP	SBD	EGH	CHI	BRR
Modeled	I	4.222	4.740	4.805	4.837	8.484	9.270	10.246
	II	3.550	4.464	4.472	4.581	8.478	9.248	10.243
Measured		2.899	3.524	5.504	6.497	5.509	13.574	1.044

* PPT: Point Petre, at model grid (101,23); BNT: Burnt Island, at grid (87,29); STP: Sturgeon point, at grid (96,18); SBD: Sleeping Bear Dunes, at grid (78,25); EGH: Eagle Harbor, at grid (74,35); CHI: Chicago, at grid (73,16); BRR: Brule River, at grid (67,34). I and II denote EXP1 and EXP2, respectively.

CONCLUSIONS

Two numerical experiments were carried out using the γ-HCH emission inventories with and without sources in Ontario and Quebec cornfields. In the regions with relatively strong γ-HCH emissions, γ-HCH transfers from the soil to the air either in the wintertime or in the summertime. Downward transfer of γ-HCH (from the air to the soil) was found around the Great Lakes and the St. Lawrence valley in the both seasons. In this ecosystem, the soil receives much less γ-HCH during the wintertime than the summertime due primarily to weak deposition and soil-to-air exchange processes. Overall results show that the sources in canola fields in the prairie region make major contributions to γ-HCH budget in the atmosphere over the Great Lakes and the St. Lawrence ecosystem. Modeled γ-HCH concentrations agree well with measurements.

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