Impact of extensive use of organochlorine pesticides on climate

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1. Introduction

The mid-20th century surface cooling has been attributed to natural climate variability and sulphate aerosol from anthropogenic emissions that may reflect some sunlight back into space, thereby reducing the incoming radiation (1). The later has also been invoked to explain regional patterns of climate change in, for example, the southeastern United States and eastern China, the only regions in the global continents to exhibit reduced or little changed temperatures during the past century which is overwhelmed by pronounced cooling into the 1950s to the 1970s in the region compared with the rest of the world (1). The strong cooling during the mid-20th century and its impact on surface temperature trend in the past 100 years in the southeastern US has been puzzling the scientific community of climate research. We have noticed that the Northern Hemisphere cooling trend during the mid-20th century exhibits an inverse pattern (negative correlated) with extensive use of organochlorine pesticides (OCPs) after the second World War through the late 1970s, especially in the southeastern US (DDT and toxaphene, 2) and eastern China (DDT and Technical hexachlorocyclohexane, 2). To understand if the massive use of OCPs in the southeastern US might change the regional climate, using available OCPs historical usage data and soil residues we investigated the relationship between the use of OCPs in the US and strong cooling event occurring in the mid-20th century in the southeastern US. Evidence that identifies such the relationship is presented in this paper.

2. Trend of DDT and toxaphene usages and soil residues

The southeastern US was the largest user of DDT and toxaphene in the world from the 1940s to 1970s (2). Peak consumption occurred in 1966 for DDT and 1974 for toxaphene. It is estimated that 6.13×10^5 t of DDT (about 40% of the global total usage of this substance) was used in the US (mostly in the southeast US) after 1945 until its ban in 1972. During the 1960s and 1970s some use of DDT was replaced with toxaphene which became the most heavily used pesticide in the US until its restriction in 1982 (3). Toxaphene use in the US is estimated at 4.9×10^5 t between 1947 and 1986 (approximately 40% of the global total). Over 85% of the US use was for cotton-growing, primarily in the southeastern US (4). Figure 1 shows the time series of annual usages and soil residues of DDT and toxaphene in the US from 1947 – 2000 and the smoothed annual US air temperature anomalies from 1947 – 1998, compiled by the National Climate Data Center [NCDC, Baker] of the US National Oceanic and Atmospheric Administration (NCAR). The persistence and low volatility of these persistent organic pollutants (POPs) resulted in their accumulation in croplands where they are still detected and emitted at high concentrations decades after their use has ceased (5) as indicated in figure 1. It is of interest to note from figure 1 that the DDT and toxaphene usage and soil residue profile correspond inversely to the US temperature anomalies. Using these inventories we computed the linear trends of DDT and toxaphene use and the GISS surface temperature anomalies (6) from 1947 to 1976, the latter being the year when the use of toxaphene on the southeastern US cotton fields started to decline (3).

Figure 2a displays 30 years linear trend of toxaphene usage in the US. As shown, the massive use of toxaphene on croplands (mostly on cotton) was found in the six states of the southeastern US: Arkansas, Louisiana, Mississippi, Alabama, Georgia and South Carolina (3). The gridded maximum linear trend occurred in Alabama with an annual average of 40 t yr^{-1}. For DDT, there is no apparent trend over this time period as a

result of the marked decrease in it use after 1959. However, over the first 15 years (1945-1959) a maximum annually averaged trend about 30 t yr^{-1} is observed for Alabama. Figure 2b illustrates the trends of the temperature anomalies from March to August (the spring/summer seasons during which the two OCPs were applied and volatilized mostly) for the same period. As shown, the strongest cooling trend is found in the southeastern US, matching well with the increasing usage trend for toxaphene (figure 2a) and DDT.

3. Association of temperature drop with use of OCPs

As semi-volatile organic compounds that are sorbed to soil, OCPs undergo phase change from their supercooled liquid state to their vapor state to volatilization (soil-air emission). This is analogous to energy requirements associated with octanol-air partitioning – this partitioning constant (K_{OA}) and its temperature dependence (enthalpy, ΔH_{OA}) are well known for OCPs (7). When volatilization from soils occurs, the internal energy of molecules of a pesticide is increased which is manifested as absorption of that energy from the surrounding air molecules (endothermic), thereby leading to a decrease in air temperature. Relationships between DDT and toxaphene soil residues and temperature are assessed by linear correlation analysis using annual soil residues and the measured annual mean temperatures, derived from monthly "time bias corrected" average temperature ($\bar{t}$) for the US states (8) and the soil residues of the two OCPs averaged over each of the 6 states for 1947-1976. Results show good correlations with the exception of the state of Arkansas (Table 1).

To assess quantitatively the effect of DDT and toxaphene volatilization on the temperature, we assume that the OCPs and air are at a thermal equilibrium in the near surface regime. Thus, the increase in the enthalpy of OCPs associated with their volatilization ($\Delta H_{soil-air}$) results in an equal loss of heat from the surface air at a constant pressure, we then get

$$M_{pest}\Delta H_{soil-air} = -(m_{air}\ C_{Pair}\ \Delta T), \tag{1}$$

where M_{pest} is the mass of a pesticide and m_{air} is the mass of air associated with the surface compartment (with 0.1 m height above the ground surface subject to the roughness length over a cotton field), respectively. ΔT is the temperature drop due to volatilization. In Eq. 1, we first calculate the energy required for volatilization by multiplying the mass (M_{pest}, moles) of chemical by its enthalpy of soil-air transfer ($\Delta H_{soil-air}$) which we know is similar to known octanol-air partitioning enthalpies (i.e. ΔH_{OA}) - 88 kJ mol^{-1} for DDT and 86 kJ mol^{-1} for toxaphene (7). Masses of chemical emitted from the control volume of 1 m[2] by 0.1 m deep are calculated from residue data and an annual decay (loss) rate of 9% of total soil residues due to volatilization for DDT and 8% for toxaphene (i.e., 8-9% of soil residues are volatilized annually into air). The decay (loss) rate is obtained based on results of a numerical study of DDT and toxaphene soil residue concentrations over soil depth 0.1-10 cm across North America using the CanMETOP (Canadian Model for Environmental Transport of Organochlorine Pesticides, 9). Furthermore, in Eq. (1) masses are converted to moles using the molar masses of DDT and toxaphene which are 354.5 g mol^{-1} and 414 g mol^{-1}, respectively. C_{Pair} in Eq. (1) is the heat capacity of dry air at constant pressure (= 1.006 kJ kg^{-1} K^{-1}) and the mass of air near the surface was estimated over each cell at the 1[o] × 1[o] resolution subject to the air density 1.2 kg m^{-3}. It is noted that in Eq. (1) that although the surface compartment with 0.1 m height was defined, the estimated ΔT can be extended to a higher level in the atmosphere using the well-know similarity boundary-layer theory.

Using the 1[o] × 1[o] gridded annual soil residues of DDT and toxapene over the period 1947 to1976 and knowing that $\Delta H_{soil-air}$ is similar to ΔH_{OA} (8) we compute the linear trend of ΔT due to volatilization using Eq. (1). Figure 3 shows the sum of the linear trends of ΔT for DDT and toxaphene, which are statistically significant at the 0.01 level. As demonstrated in figure 1, there is a similarity in the spatial patterns between the linear trends of ΔT due to volatilization and the use of DDT and toxaphene. The strongest temperature decrease occurs in

Alabama, the State with the greatest use of DDT and toxaphene during this period (3). These findings are confirmed by the measured temperature data (Table 1) for the 6 States that exhibited the greatest cooling trend.

The 30 year cooling trends in the observed temperature, collected from the "time bias corrected" average temperature (8), in the top 6 states range from -0.53 (Arkansas) to -1.25^{o}C (Alabama). Whereas, the estimated decreasing trends of the temperature drop computed by Eq. (1) averaged over each state range from -0.023 (Arkansas) to -0.058^{o}C (Alabama). A direct quantitative link between the derived temperature drop from Eq. 1 and local climatic variations has not been established. Besides, the influence of other OCPs that were used in the southeastern US are not accounted for this study due to the lack of their usage data. Our current dataset shows that the minimum and maximum trends from both measured temperature and the estimated temperature drop in the two states correspond fairly well to the usage and soil residues of DDT and toxaphene in these two states. The peak value in Alabama is comparable to the temperature anomaly trend for the same period as shown in figure 2b. Given that the global mean forcing from sulfate aerosol was estimated to yield a decreasing in the global mean surface temperature change $\Delta T_s = -0.11^{o}$C (10), our analyses suggest that the surface cooling due to the volatilization of OCPs is likely of equal importance as the one contributed by other anthropogenic forcing such as sulfate aerosol (1, 10).

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Table 1 Linear correlations between the soil residues of toxaphene and DDT and 'time bias corrected' average temperature ($\bar{t}$), trend of $\bar{t}$, and summed trend of ΔT due to volatilization of DDT and toxaphene by (1) for 1947 – 1976 in the six states of the southeastern US.

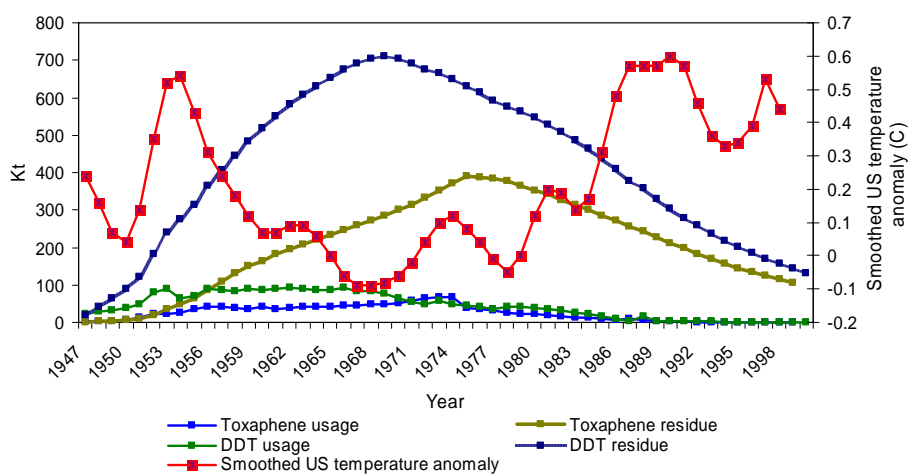| States | Correlation between residue and $\bar{t}$ | | | | Trend | |
	Toxaphene		DDT			
	rr	p	rr	p	$\bar{t}$	$\Sigma\Delta$T
Alabama	-0.62	0.0003	-0.64	0.0001	-1.25	-0.058
Arkansas	-0.36	0.0572	-0.24	0.2067	-0.53	-0.023
Mississippi	-0.54	0.0024	-0.54	0.0023	-0.98	-0.039
Louisiana	-0.59	0.0007	-0.57	0.0016	-0.94	-0.045
South Carolina	-0.54	0.0025	-0.56	0.0023	-0.94	-0.050
Georgia	-0.57	0.0011	-0.65	0.0001	-1.11	-0.035

Figure1. Annual usage and soil residues of DDT and toxaphene (kilo tonnes) for 1947 - 2000 and smoothed US annual temperature anomalies (^{o}C) for 1947 - 1998.
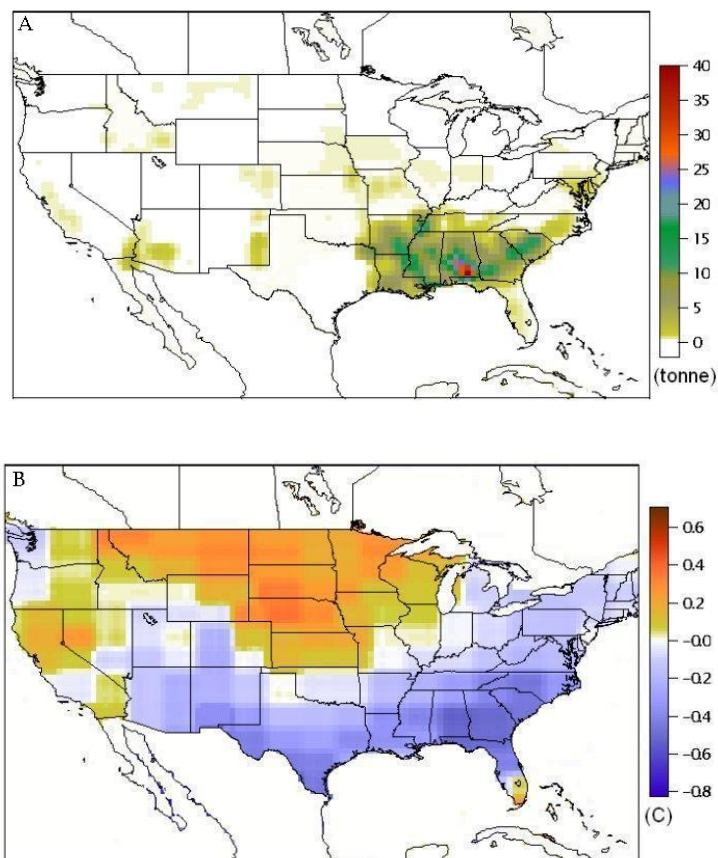
Figure 2. (a) Trends of annual toxaphene usages (tonne yr^{-1}) in the US for 1947-1976. (b) GISS derived surface air temperature anomalies from March to August (^{o}C) for the same period.
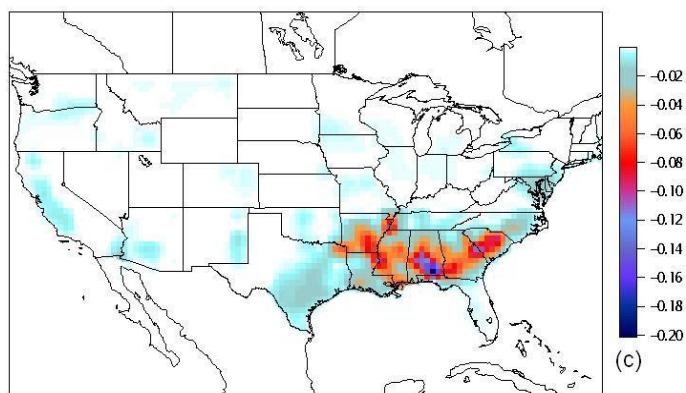

Figure 3. Sum of linear trend of temperature drop ΔT due to volatilization of DDT and toxaphene computed by Eq. 1.