

## TRACE ORGANIC CONTAMINANTS INCLUDING TOXAPHENE AND TRIFLURALIN IN COTTON FIELD SOILS FROM GEORGIA AND SOUTH CAROLINA, USA

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### Introduction

The availability of inexpensive elemental chlorine together with the development of industrial chlorination procedures in the twentieth century led to the production of a wide range of chlorinated organic compounds for commercial applications. Because of their persistence, bioaccumulation and toxic potentials, production and usage of several chlorinated compounds have been banned or restricted in the United States. However, there has been an ongoing debate about the primary sources of emission of organochlorine compounds in recent years. Countries such as India and Mexico continue to use DDT and HCHs for agriculture and to combat malaria<sup>1,2</sup>. This can contribute 'fresh' emissions into the environment. Another potential source is emission from historically contaminated soil or sediments. Agricultural soils in the United States are suspected to be an important source of organochlorine pesticides that were used historically in large quantities<sup>2</sup>. It has been hypothesized that pesticides used historically in agriculture in the southern United States are being volatilized to the atmosphere and likely contributing to the long-range transport of these compounds<sup>3-5</sup>. Georgia and South Carolina are major cotton growing regions in the United States. DDT and toxaphene were used widely to control pests in cotton fields. Over 85% of toxaphene use in the United States was in cotton-growing states from Texas through Georgia. Only 1-4% of its use occurred in the upper Midwest, including the Great Lakes Basin<sup>6</sup>. DDT was used until 1972 and toxaphene was used until 1990. Relatively high concentrations of toxaphene found in the Great Lakes water have been attributed to the atmospheric transport of toxaphene from the southern United States<sup>6</sup>.

Trifluralin ( $\alpha$ -, $\alpha$ -, $\alpha$ -trifluoro-2,6-dinitro-N,N-dipropyl-p-toluidine) is a selective, pre-emergence nitroaniline herbicide most commonly used in cotton cultivation. Half-lives of trifluralin in soils vary from 45 days to 8 months<sup>7,8</sup>. Very few studies have reported the occurrence of trifluralin in soils. In this study, we determined the concentrations of organochlorine pesticides including DDT and its derivatives (p,p'-DDE, p,p'-DDD and p,p'-DDT), HCHs ( $\alpha$ -,  $\beta$ -,  $\gamma$ ,  $\delta$ - isomers) HCB and toxaphene and trifluralin in soils collected from cotton fields in Georgia and South Carolina. Further, soils were also tested for the presence of polychlorinated biphenyls (PCBs), sixteen priority polycyclic aromatic hydrocarbons (PAHs) and nonylphenol (NP).

### Materials and Methods

Surface soils (0-10 cm) were collected from 32 cotton fields: 16 from South Carolina on 14 November, 1999 and 16 from Georgia on 4 December, 1999 (Table 1). Cotton was the standing crop when samples were collected. Samples from several locations in a given field were pooled to obtain a representative sample. Samples were transferred to pre-cleaned I-Chem glass jars and stored at -20°C until extraction. Soil moisture content was determined by weighing soils before and after drying for ~ 20 h at 100°C. Total organic content (TOC) of the soil samples was analyzed. Pesticides, PCBs, PAHs and NP were analyzed following methods described elsewhere<sup>9</sup>.

### Results and Discussion

Toxaphene and trifluralin were the most commonly detected pesticides in soils. Concentrations of toxaphene in cotton soils from South Carolina ranged from 3.3 to 2500 ng/g, dry wt (mean: 277) whereas

**Table 1.** Concentrations of trifluralin, and toxaphene,  $\Sigma$ DDT,  $\Sigma$ HCH and  $\Sigma$ PAHs (ng g<sup>-1</sup> dry wt.) in cotton field soils from South Carolina (SC) and Georgia (GA), USA.

Location	TOC (%)	Trifluralin	Toxaphene	$\Sigma$ DDT	$\Sigma$ HCH	$\Sigma$ PAHs
SC soil #1	0.67	41.0	26.6	3.62	<0.1	8.2
SC soil #2	0.57	35.8	3.3	0.11	<0.1	6.4
SC soil #3	0.69	50.1	63.2	0.31	<0.1	13.9
SC soil #4	1.06	17.8	75.8	3.68	<0.1	27.1
SC soil #5	0.68	3.3	10.4	2.93	<0.1	<5
SC soil #6	1.48	67.7	2500	14.3	0.39	138
SC soil #7	1.54	212	48.5	1.50	0.19	34
SC soil #8	1.59	109	26.2	4.03	<0.1	8.3
SC soil #9	1.65	104	116	26.7	0.25	78.8
SC soil #10	1.21	176	99.0	11.5	<0.1	7.9
SC soil #11	0.77	176	100	11.3	<0.1	<5
SC soil #12	0.86	5.7	275	26.5	0.16	241
SC soil #13	0.97	16.6	698	44.8	0.54	<5
SC soil #14	1.27	574	286	15.9	<0.1	<5
SC soil #15	0.71	178	94.8	11.0	<0.1	14.0
SC soil #16	1.44	69.5	5.7	0.75	<0.1	26.0
GA soil#1	1.12	22.3	43.3	18.9	<0.1	16.5
GA soil#2	1.03	16.6	96.9	8.64	<0.1	49.3
GA soil#3	0.76	122	166	21.8	<0.1	19.6
GA soil#4	0.69	548	14.8	12.5	<0.1	<5
GA soil#5	0.57	1.0	138	25.4	<0.1	<5
GA soil#6	1.26	297	130	33.6	0.16	13.3
GA soil#7	0.92	197	12.1	1.16	<0.1	23.8
GA soil#8	0.56	1.0	76.2	9.36	<0.1	13.3
GA soil#9	0.75	323	112	19.9	<0.1	9.3
GA soil#10	1.01	269	56.6	0.88	<0.1	18.3
GA soil#11	0.68	7.1	269	22.8	0.49	11.0
GA soil#12	1.35	127	101	0.56	<0.1	189
GA soil#13	0.8	181	21.3	6.15	<0.1	6.70
GA soil#14	0.96	105	21.7	0.34	<0.1	6.90
GA soil#15	1.07	58.7	58.3	18.9	<0.1	7.70
GA soil#16	1.43	132	9.5	0.90	<0.1	24.1

Concentrations of PCBs, HCB and Nonylphenol were <5, <1 and <5 ng/g, dry wt., respectively.

those from Georgia ranged from 9.5 to 269 ng/g, dry wt (mean: 83) (Table 1). The highest toxaphene concentration, 2500 ng/g, dry wt, was found in a soil sample collected from Hampton County in South Carolina. This value was similar to the highest concentration of 2420 ng/g, dry wt, reported for a farm soil collected from southwestern Alabama in the late 1990s<sup>5</sup>. In general, the range of toxaphene concentrations found in soils from South Carolina are similar to those observed in farm soils in Alabama (<3-2420 ng/g, dry wt)<sup>5</sup>. Measured concentrations of toxaphene in soils were 10 to 100-fold greater than those observed in surface sediments from Grand Traverse Bay, Lake Michigan<sup>10</sup>. Occurrence of notable concentrations of toxaphene in soils has implications for atmospheric contamination by this compound by soil-air exchange. For a soil-air system in equilibrium, the concentration of a hydrophobic chemical is expected to be proportional to the organic carbon content of the soil. The wide variability in soil concentrations of toxaphene and the poor correlation with organic carbon suggest the soil burdens are largely dependent on the application history of toxaphene and the soil-air concentrations are not in equilibrium.

Of the various contaminants measured, trifluralin, a pre-emergence organofluorine herbicide, was the second abundant compound found in soils (Table 1). Concentrations of trifluralin in cotton field soils from

South Carolina ranged from 3.3 to 574 ng/g, dry wt (mean: 115) whereas those from Georgia ranged from 1 to 548 ng/g, dry wt (mean: 150) (Table 1). There was no significant difference in the concentrations of trifluralin in soils from Georgia and South Carolina ( $p > 0.05$ ). Trifluralin is applied as a pre-emergence herbicide during March-May. Occurrence of this herbicide in soils collected in November-December suggests its persistence in soils. Occurrence of trifluralin at concentrations of 50 to 130 ng/g, dry wt, has been reported in soils 30 months after the last application<sup>11</sup>. Concentrations of trifluralin in soils collected from vegetable farms in British Columbia varied from 55 to 310 ng/g, dry wt<sup>12</sup>. These values are similar those observed in this study. Trifluralin is strongly adsorbed to soil organic matter<sup>7</sup> and the adsorbed herbicide becomes inactive. Therefore, higher application rates are needed for soils rich in organic matter. Nevertheless, concentrations of trifluralin were not proportional to soil organic carbon. This suggests that, in addition to application rates, farm management practices such as tillage and irrigation and soil temperature play an important role in determining persistence of trifluralin in soils.

Residues of DDT were found in almost all of the soils (Table 1). Total concentrations of DDT (including DDE and DDD) ranged from 0.11 to 45 ng/g, dry wt (mean : 11) in soils from South Carolina and from 0.34 to 34 ng/g, dry wt (mean: 13) in soils from Georgia (Table 1). *p,p'*-DDE was the predominant metabolite of DDT, accounting for, on average, 69% of the total DDT concentrations. *p,p'*-DDT accounted for 33% of the total DDT concentrations. DDT concentrations were similar to those observed in soils from Alabama (mean: 50 ng/g, dry wt)<sup>5</sup>. The mean concentrations were 5 to 20-fold less than those observed in cotton field soils in India (mean: 1000; median: 280 ng/g, dry wt), where DDT was used until the late 1990s<sup>13</sup>. There was no significant relationship between the concentrations of total DDT and soil organic matter content. DDT was extensively used as an agricultural and vector control pesticide in the United States with peak production occurring in 1963. Usage of DDT was banned in the United States in 1972. However, DDT persists in soil for several years with reported half-lives ranging from 20-30 years<sup>14</sup>.

Concentrations of HCHs were less than 1 ng/g in all the soils. Among HCH isomers,  $\beta$ - and  $\gamma$ -HCH isomers were found in some soils. HCB, PCBs and NP were not detected at the detection limits of 1, 5, and 5 ng/g, dry wt, respectively (Table 1). The application sludge in agriculture can be a potential source for these compounds in soils. In addition, presence of these compounds as impurities in other chlorinated pesticide formulations and atmospheric deposition can contribute their occurrence in soils. The results our study suggest that contamination by HCB, PCBs and NP in cotton soils is not a significant concern.

Polycyclic aromatic hydrocarbons (PAHs) are a group of common environmental contaminants, originate from anthropogenic sources such as waste incineration, coal gasification and accidental oil spills as well as natural processes like fossil fuel and wood combustion. The total PAH concentrations ranged over 2 orders of magnitude from <5-241 ng/g dry wt (mean: 38 ng/g) (Table 1). Three of the 32 soils analyzed contained PAH concentrations greater than 100 ng/g, dry wt. Fluoranthene was the most commonly detected PAH in soils. In soils that contained PAH concentrations greater than 100 ng/g, pyrene, chrysene and benzo[b]fluoranthene were also found at notable levels.

These results suggest that the residues of organochlorine pesticides in cotton field soils in Georgia and Alabama varied 2-3 orders of magnitude. Toxaphene, trifluralin and DDT were the predominant pesticides detected in these soils. Concentrations of these pesticides were not proportional to organic carbon content, which suggests that the history of the pesticide usage and farm management practices play a major role in influencing residue levels. It is hypothesized that toxaphene and trifluralin residues in soils in Georgia and South Carolina are continually being volatilized to the atmosphere and likely to contribute to long-range transport as suggested earlier<sup>3,5</sup>.

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## References

1. Loganathan, B.G. and Kannan, K (1994). *Ambio* 23, 187-191.
2. Kannan, K., Tanabe, S., Giesy, J.P. and Tatsukawa, R. (1997). *Rev. Environ. Contam. Toxicol.* 152, 1-55.
3. Spencer, W.F., Singh, G., Taylor, C.D., LeMart, R.A., Cliath, M.M. and Farmer, W.J. (1996). *J Environ. Qual.* 25, 815-821.
4. Hoff RM, Strachan WMJ, Sweet CW, Chan CH, Shackleton M, Bidleman TF, Brice KA, Burniston DA, Cussion S, Gatz DF, Harlin K and Schroeder WH (1996) *Atmos. Environ.* 30, 3505-3527.
5. Harner, T., Wideman, J.L., Jantunen, L.M.M., Bidleman, T.F. and Parkhurst, W.J. (1999) *Environ. Pollut.* 106, 323-332.
6. James, R.R. and Hites, R.A. (2002). *Environ. Sci. Technol.* 36, 3474-3481.
7. Wheeler, W., Stratton, G., Twilley, R., Ou, L-T., Carlson, D. and Davidson, J. (1979). *J. Agric. Food Chem.* 27, 702-706.
8. Environment Canada/Agriculture Canada (1987). Pesticide Registrant Survey, 1986. Commercial Chemicals Branch, Environmental Canada, Ottawa.
9. Kannan, K., Kober, J.L., Kang, Y-S., Masunaga, S., Nakanishi, J., Ostaszewski, A. and Giesy, J.P. (2001). *Environ. Toxicol. Chem.* 20, 1878-1889.
10. Schneider, A.R., Stapleton, H.M., Cornwell, J. and Baker, J.E. (2001). *Environ. Sci. Technol.* 35, 3809-3815.
11. Corbin, B.R., McClelland, M., Frans, R.E., Talbert, R.E. and Horton, D. (1994). *Weed Sci.* 42, 438-445.
12. Szeto, S.Y. and Price, P.M. (1991). *J. Agric. Food Chem.* 39, 1679-1684.
13. Kawano, M., Ramesh, A., Thao, V.D., Tatsukawa, R. and Subramanian, A.N. (1992). *Intern. J. Environ. Anal. Chem.* 48, 163-174.
14. Dimond, J.B. and Owen, R.B. (1996). *Environ. Pollut.* 92, 227-230.