# A RADIAL DILUTION MODEL FOR THE DISTRIBUTION OF TOXAPHENE IN THE UNITED STATES AND CANADA BASED ON MEASURED CONCENTRATIONS IN TREE BARK

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## Introduction

The goal of this research was to investigate the distribution and transport of toxaphene in the U.S. and Canada by measuring toxaphene concentrations in tree bark collected in these two countries. We have developed a radial dilution model for toxaphene based on our data using spherical Euclidian distances from a central point in the southern U.S. We found good agreement with the model parameters generated using the tree bark and published air data.

## Materials and Methods

Tree bark samples were collected between the U.S. Gulf Coast to Yellowknife in the Northwest Territories and to Radisson in Quebec. Geographical coordinates were obtained at each location using an Eagle Explorer™ global positioning system. Bark was collected from three individual trees at each location. Approximately 15 to 30 g of bark was placed into a Soxhlet extractor and spiked with a known amount of $^{13}C_{10}$-γ-chlordane, the surrogate standard. Samples were extracted with 450 mL of 50 % hexane in acetone for 40-48 hours. After clean-up, the extracts were analyzed using an Agilent 5973 mass spectrometer operating in the electron-capture, negative-ionization, selected ion-monitoring mode using the program developed by Swackhamer et al. and modified slightly for use with our standards.[1, 2] A method blank and matrix spike were conducted alternately with each batch of extractions. No toxaphene was ever observed in the method blank, and the average recovery for the toxaphene matrix spike was 94 ± 6% (N = 11). The average recovery for $^{13}C_{10}$-γ-chlordane, the internal standard, was 86 ± 8 % (N = 11). Our method detection limit for toxaphene is 0.1 ng/extract.

## Results and Discussion

In general, the higher toxaphene concentrations (>20 ng/g bark) are found in the southern U.S. in a zone extending from approximately 32° N to 40° N, which is the region where most cotton was grown, and therefore, where significant quantities of toxaphene were used. Inside this zone, two extremely high concentrations of toxaphene were found in southeastern Missouri (300 ± 120 ng/g bark) and northwestern Mississippi (250 ± 70 ng/g bark). Because toxaphene has not been used for approximately two decades and because tree bark stays with the tree for 3-5 years, the possibility of direct application of toxaphene to the trees can be eliminated. Lower levels of toxaphene (<15 ng/g bark) were generally found outside the 32-40°N zone.

We expected concentrations to generally decline with distance moving north from the southern U.S. We saw this trend to the north, but surprisingly, we also saw it to the south. Toxaphene concentrations in bark between approximately 31° N and the Gulf Coast (and the Atlantic coast of northern Florida) show concentrations ranging from 2 and 6 ng/g bark. These values are relatively low given their close proximity to cotton growing regions as well as their close proximity to much higher measured values.

Toxaphene concentrations in northern U.S. and Canadian tree bark samples show values of < 1 to 5 ng/g bark with one exception, on the eastern side of James Bay (11 ng/g bark). These low levels are expected, given that toxaphene was never even licensed for use in Canada.

Although there is a rough spatial correlation between our tree bark toxaphene concentrations and the estimation of toxaphene use by Li et al.,[3] these results do not explain the low toxaphene concentrations in samples far removed from the southern U.S. sources or the very high concentrations in the vicinity of Memphis, Tennessee. Attempts to model our data with these estimated historical values did not produce a useful result, and we turned to a simpler approach.

Let's assume that there is a continuous point source of toxaphene in the center of a hemisphere and that this pollutant is carried by air movement uniformly in all directions (except down). This omni-directional assumption is acceptable only over the long-term and is based on the observation that the annualized wind roses are relatively symmetrical. Let's further assume that the average air velocity through the center of this hemisphere is constant and radially outward. At some distance $r$ from the center, the total mass of toxaphene ($\triangle M$) in a layer or shell of thickness $\triangle r$ is constant as a function of time and is given by $\triangle M = m_0 \triangle r$, where $m_0$ is a proportionality constant with units of, say, ng/km. The concentration as a function of radial distance in this layer or shell of thickness $\triangle r$ is given by $C(r) = \triangle M / \triangle V = m_0 \triangle r / \triangle V$, where $\triangle V$ is the volume of the layer or shell. Thus, for the limiting case as $\triangle$r becomes zero, $C(r) = m_0 / (dV / dr)$. F-or a hemisphere,

$$\frac{dV}{dr} = \frac{d}{dr}\left(\frac{4}{6}\pi r^3\right) = 2\pi r^2$$

Substituting this into the previous equation, we have $C(r) = m_0 / 2\pi\ r^2$.

Thus, a curve fitted to the data of the form

$$C(r) = a_0 r^{a_1}$$

(where $a$ and $a_1$ are fitted by non-linear regression methods) should show an $a_1$ value of -2. In essence, this is an inverse square dilution model.

Through examination of the historical toxaphene use data, we choose 35° N, 90° W (approximately Memphis, Tennessee) as our source location. In addition, this location is about halfway between the two high concentration samples discussed earlier. Using this location as the starting point, we calculated the Euclidian distance to each sample location accounting for the spherical geometry of the earth using D = arccos[(sin( p ) sin( a) + (cos( p) cos( a ) cos |δ λ|], where $D$ is the distance between two points on a sphere, $p$ and $a$ are the latitudes of the two points, and |δ λ| is the absolute value of the difference in longitude between the two points.

Tree bark toxaphene concentrations were plotted against these spherical Euclidian distances (see Figure 1, top), and a non-linear regression of concentration and distance gave $C = 2.77 \times 10^6 \times D^{-2.0\pm0.3}$. This regression is significant at the 99 % confidence level.

These results indicate that, for our data set, Memphis, Tennessee is the area from which toxaphene is moving outward as an inverse square function of distance. Of course, the city of Memphis itself is not emitting toxaphene, but it is being emitted from the agricultural areas in the vicinity. It is important to note that the exponent associated with D is a fitted parameter resulting from the non-linear regression. The exponent's fitted value of -2.0 ± 0.3 (standard error) verifies that our prediction of an inverse square model to describe radial dilution is correct.

The tree bark samples we collected received toxaphene through atmospheric transport; thus, the tree bark and air concentrations should be related. If our choice of Memphis as a central location was correct, then atmospheric concentrations of toxaphene should also follow an inverse square model with Memphis as the center. To test this supposition, we used 13 air concentrations from the literature and

from work done in our laboratory. The spherical Euclidian distances for these air samples were calculated with 35° N, 90° W as the center and plotted against the air concentrations (see Figure 1, bottom). The non-linear regression of the air concentrations against this spherical Euclidian distance using our radial dilution model gave $C = 2.3 \times 10^7 D^{-2.0 \pm 1.0}$. This regression is also significant at the 99% confidence limit. Although the error on the fitted exponent on D is larger than for the tree bark regression (± 1.0 versus ± 0.3), we are gratified that this exponent also has a value of -2.0, which verifies that our prediction of an inverse square model to describe radial dilution of toxaphene in air is correct.

Our attempt to model both the tree bark and atmospheric concentrations data sets using an inverse square dilution model with 35° N, 90° W as the source was successful. This is compelling evidence that our choice of Memphis, Tennessee (at approximately 35° N, 90°W) is a reasonable estimate of the center of the area from which toxaphene is moving radially.

Toxaphene use has been banned now for almost two decades. Our tree bark concentrations along with air measurements show that very high levels of toxaphene still exist in areas where it was originally used, and therefore, toxaphene will be emitted from these regions for many years. Li et al. estimate that annual emissions of toxaphene from southern U.S. agricultural regions maximized in 1977 at 11 kt, and by 2004, it will have decreased to 0.26 kt.[3] Therefore, it is reasonable to assume that the levels outside this region shoulddecrease as the levels in the southern U.S. decline over time. The transport of toxaphene to remote regions is still of concern, even as these levels decrease. It has already been demonstrated that toxaphene accumulates in biota that live in aquatic systems. The bioaccumulation of toxaphene in wildlife presents the possibility for biomagnification in species atn higher trophic levels, including humans. Our results, combined with other studies, demonstrate the need for continued study of toxaphene in these and other systems.

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**References**

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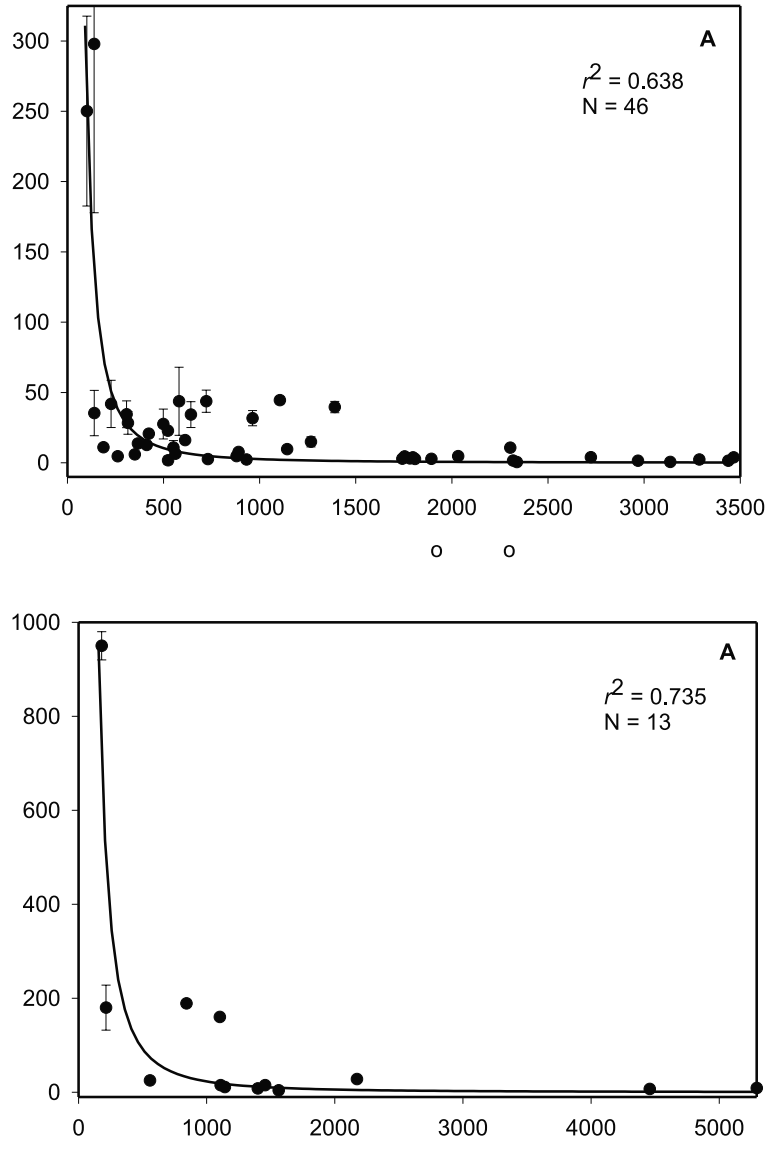


**Figure 1.** Toxaphene concentrations in tree bark as a function of spherical Euclidian distance from 35° N, 90° W. (bottom) Toxaphene concentrations in air as a function of spherical Euclidian distance from 35° N, 90° W. Error bars represent standard errors of the replicate tree bark measurements and of the air concentrations, where available. On the concentration scales, zero is offset slightly for clarity.