New DDT in North America? A Perspective 20 Years Later

Terry Bidleman[1], Fiona Wong[1], Henry A. Alegria[2]

[1]Meteorological Service Of Canada
[2]California Lutheran University

Introduction

This title, and article, were inspired by a classic paper written 20 years ago by Robert Rapaport and coworkers, "New" DDT in North America -- Atmospheric Deposition[1]. The authors analysed cores from peat bogs collected in the Great Lakes region and eastern Canada for residues of DDT to determine historical loadings and modern deposition in the early 1980s. They noted that, while total DDT residues (ΣDDT) peaked in the mid- to late-1960s, deposition in the late 1970s and early 1980s continued at a lower level and declined more slowly. Moreover, the composition of ΣDDT in recent peat layers was marked by a high proportion of "fresh" DDT (p,p'-DDT and o,p'-DDT) in comparison to stable DDT degradation products (DDDs and DDEs). These observations led the authors to suggest that DDT was undergoing air transport from ongoing use in Mexico and Central America, nearly a decade after its 1972 deregistration in the United States.

Contemporary levels of ΣDDT in the atmosphere of southern Mexico exceed average ambient air concentrations in the U.S. and Canada by an order of magnitude or more[2,3]. These measurements were made between 2000-2004, coincident and just after Mexico officially stopped using DDT for vector control. Some portion of this DDT may be influencing air concentrations in other parts of the continent, but there are other potential sources of DDT to be considered: air transport across the Pacific Ocean from Asia[4] and emission of soil residues from past usage in the U.S. and Canada[5-8]. The ratio of p,p'-DDT/p,p'-DDE (DDT/DDE) is often used to roughly gauge the age of residues; a high ratio implies current use of DDT while a low ratio suggests emission of old residues[1].

The availability of air data from a region where DDT has been recently used provides an opportunity for comparisons with the U.S. and Canada, where DDT has been banned for several decades. Objectives of the study are to: a) set bounds on proportions of DDT and DDE that are expected from emission of legacy residues, b) compare these limits with the proportions found in ambient air to determine if "new" DDT is present.

Materials and Methods

Sampling and analysis of DDT and other organochlorine pesticides in the ambient air of southern Mexico were carried out as described[2,3]. Briefly, air samples were collected with a glass fiber filter - polyurethane foam cartridge. After extraction and cleanup, the pesticides were determined by capillary GC - electron capture negative ion mass spectrometry, using isotopically labelled pesticides as recovery surrogates.

Levels of DDTs in the ambient air and soil of the U.S. and Canada were obtained from literature reports. Some air data were from long-term surveys involving regular high volume air sampling over one or more years, or deployment of passive air samplers to integrate air concentrations over a full year. Other data were from limited campaigns carried out over several months using active or passive samplers. Soil residue data collected since 1985 were from agricultural fields in British Columbia and Saskatchewan, Canada, California and the southern and midwestern U.S. states, Canadian orchards in British Columbia and Ontario, and forests in Maine which had been sprayed with DDT in the past. Due to limited abstract space, references to these soil and ambient air studies are available from T.F.B.

Comparisons of DDT compound profiles in soil and overlying air were made in agricultural and orchard regions of British Columbia[8], in the southern U.S.[5] and at one Ontario farm[7] by collecting air samples in close proximity to the soil. Fractionation of DDTs between soil and air was predicted from $(DDT/DDE)_{air} = (DDT/DDE)_{soil} \times P_{DDT}/P_{DDE}$ where P refers to the liquid-phase vapour pressure[9]. DDT proportions were expressed as $F_{DDT} = DDT/(DDT + DDE)$, since fractions are preferred to ratios for statistical purposes[10]. $F_{DDT} = 0.5$ corresponds to DDT/DDE = 1. The means and standard deviations in Figures 1 and 2 refer to the regional distributions of site-averaged F_{DDT}, not to individual samples.

Results and Discussion

Figure 1 shows F_{DDT} in regional soils and the predicted F_{DDT} in air due to soil emissions. F_{DDT} is lower in air due to the greater volatility of DDE[6,9]. The fractionation relationship (see above) was tested at sites in the southern U.S.[5], Ontario[7] and British

Columbia[8], and agreement between predicted and measured F_{DDT} was quite good (Figure 1).

F_{DDT} in soils varies due to soil management practices[6,11] and microbial activity which is responsible for DDT metabolism[12]. Regional average F_{DDT} in soils ranged from 0.32 − 0.88. The predicted average F_{DDT} in air from soil emissions ranged from 0.10 − 0.52. Measured regional average F_{DDT} in the ambient air of the U.S. and Canada (including the Arctic) varied from 0.25 − 0.44. The mean F_{DDT} was 0.64 in the air of southern Mexico.

Considering transport across the Pacific, the F_{DDT} in air samples collected at Taihu Lake, China [13] ranged from 0.24 − 0.52. The following F_{DDT} values were calculated from average air concentrations measured at Tagish, Yukon, Canada in 1993-94 when air transport was from India (0.06) and eastern Asia (0.16) [4]. Transport events from western North America resulted in lower air concentrations, but higher F_{DDT} ranging from 0.11 − 0.21 in winter and 0.57 - 0.74 in summer[4].

In conclusion, emission of DDTs from legacy residues in U.S. and Canadian soils can support $F_{DDT} \leq 0.5$ in air, and measured average F_{DDT} in ambient air of the U.S. and Canada are also generally <0.5. Although averaging below 0.5, F_{DDT} in the air of western Canada seems to be higher than in other parts of Canada and the U.S. (Figure 2 and measurements at Tagish [4], see above). Air samples from southern Mexico have $F_{DDT} > 0.5$. It is difficult to ascertain whether influxes of "new" DDT are raising the F_{DDT} signatures in ambient air (Figure 2) above the background expected from soil emissions (Figure 1), because the background is not well defined. Improving the ability to make "new" vs. "old" distinctions will require more information on soil signatures and how they vary regionally.

References

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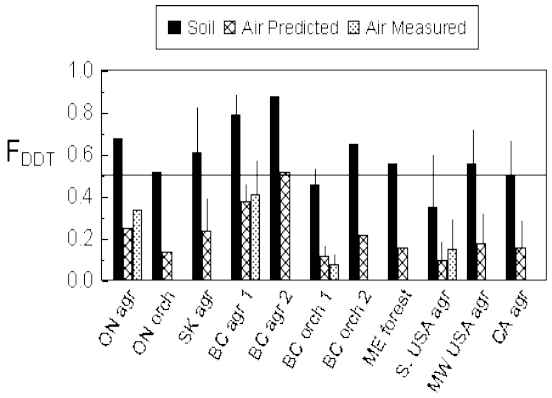

Figure 1. F_{DDT} in soils, predicted F_{DDT} in air due to soil-air exchange, and F_{DDT} measured in air-above-soil field experiments. The line at F_{DDT} = 0.5 is drawn to facilitate comparisons.

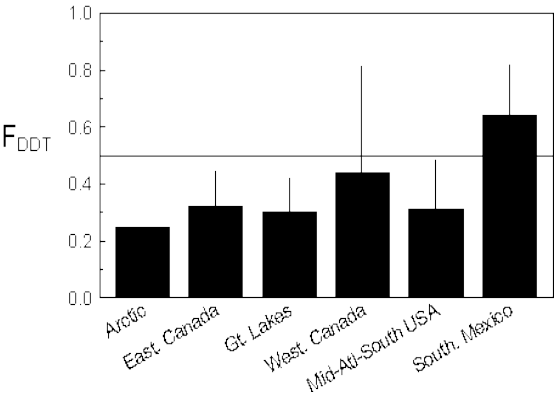

Figure 2. Mean and standard deviation of F_{DDT} in regional ambient air.