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Transfer of Organochlorine Pesticide Residues into Cigarette Smoke as a Function of Tobacco Blends and Filter Types*

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INTRODUCTION

To prevent excessive treatment of tobacco plants and crops with pesticides, several countries have prescribed maximum levels for pesticide residues. In view of these legal measures, the laboratories of the industry made a considerable effort to analytically assess pesticide residues in tobacco and in smoke.

By systematically monitoring the leaf crops, it has been established that the trend is towards less pesticide residues in general, and an almost complete absence of those substances the use of which on tobacco crops has been prohibited in the tobacco-producing countries.

Although governmental regulations refer only to the pesticide residues remaining in the manufactured tobacco products** (cigarettes, cigars and pipe tobacco), this study investigates the fate of these substances during smoking, in particular their transfer from the tobacco into the smoke, and their retention by commercial cigarette filters.

EXPERIMENTAL

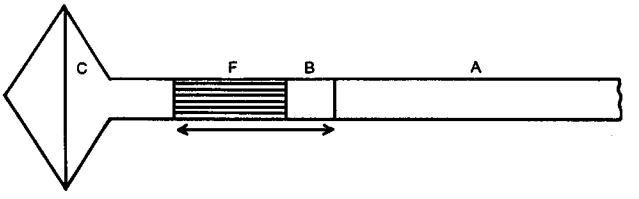
Objectives of the Study

a)
Determination of the transfer of pesticides into the smoke from four different types of tobacco blends, keeping constant cigarette paper and filter (cellulose acetate : 5.0/45,000 Y): American, Maryland, Virginia and Oriental blends.

b)
The effect of filters was tested on American blend cigarettes tipped with the following four types of filters: cellulose filter, cellulose acetate filter I 5.0/45,000 Y, cellulose acetate filter II 2.1/36,000 Y, and a charcoal filter in the plug-space-plug configuration.

Figure 1. Definition of terms.

A: Amount of pesticides in the tobacco filler to be smoked.
B: Amount of pesticides in the tobacco part of the cigarette butt.
F: Amount of pesticides in the smoke retained by the cigarette filter.
C: Amount of pesticides in the smoke retained by the Cambridge filter pad.



Transfer Rates (T)

Transfer into cigarette filter:

$$T_F = 100 \frac{F}{A} \quad [\%]$$

Transfer into mainstream smoke:

$$T_C = 100 \frac{C}{A} \quad [\%]$$

Total transfer:

$$T_t = 100 \frac{F + C}{A} = T_F + T_C \quad [\%]$$

Pesticide retention (R) by the filter:

$$R_F = 100 \frac{F}{F + C} \quad [\%]$$

Extraction

The pesticides were extracted and determined according to the *Coresta*+ Recommended Method No. 2 relating to the determination of organochlorine pesticide residues in the tobacco (2a, 2b, 4). The cigarettes all had a total length of 85 mm, with a 20 mm filter. They were conditioned,

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** Except for Yugoslav government, which refers to pesticide residues in tobacco smoke.

+ Cooperation Centre for Scientific Research Relative to Tobacco, Paris.

selected on a weight and pressure drop basis and smoked according to the *Coresta* Standard Method Nr. 10 (1) on a Borgwaldt RM 20/CS smoking machine. The smoke was trapped on a 92 mm diameter Cambridge filter disc. In one instance, when the retention of nicotine by the charcoal filter had to be determined, the direct *Coresta* Standard Method No. 13 (3) was used.

The pesticides were extracted separately from the Cambridge disc and the cigarette filter (5, 10, 11). Because of the very low quantities of pesticides to be dealt with in cigarette smoke, 20, 40 or 60 cigarettes had to be smoked to determine all those pesticides that had been found in the tobacco.

The final determination of the pesticides was performed by gas chromatography under the following conditions:

Gas chromatograph:	Hewlett-Packard 5750
Detector:	Electron capture Ni-63
Column:	Glass, 4 m × 2 mm (1.5% SP-2250 + 1.95% SP-2400/Supelco, 100–120 mesh)
Temperatures:	Injector: 225 °C Detector: 270 °C Column: 205 °C (isothermal)
Carrier gas:	Helium (40 ml/min)
Auxiliary gas:	Argon-methane (90:10): 90 ml/min
Internal standard:	Mirex

The following pesticides were studied:

α-BHC
γ-BHC (lindane)
Aldrin
o,p′-DDE
α-Endosulfan
p,p′-DDE
Dieldrin
o,p′-TDE
Endrin
o,p′-DDT
p,p′-TDE
β-Endosulfan
p,p′-DDT
Endosulfan sulfate

Methodological Considerations

As shown in Table 1, several of the pesticides determined in the cigarette blends were present in very low concentrations or could not even be detected. Calculation of transfer rates and of retention by filters could, therefore, not be done on individual substances, but had to be based on the total pesticides present. When determined in smoke, the total pesticide figures also include those substances which were not originally present in tobacco, but were formed by partial chemical degradation upon smoking.

In some of the experiments, the cigarette blend was spiked with an additional amount of pesticides, i.e. approx. 10 µg/cigarette per substance, applied by injection into the cigarettes. The recovery rates of the injected pesticides from tobacco showed that the injection method was acceptable.

Table 1. Pesticide residues (ppm) in cigarette tobacco blends.

Component	Tobacco type			
	Maryland blend	Virginia blend	Oriental blend	American blend
α-BHC	n.d.	n.d.	0.16	0.08
γ-BHC (lindane)	n.d.	n.d.	0.35	0.21
Aldrin	n.d.	n.d.	n.d.	0.01
o,p′-DDE	n.d.	n.d.	n.d.	n.d.
α-Endosulfan	0.02	n.d.	n.d.	0.04
p,p′-DDE	0.13	0.13	0.18	0.25
Dieldrin	0.02	n.d.	n.d.	0.04
o,p′-TDE	0.67	0.13	0.01	0.35
Endrin	0.015	0.03	n.d.	0.05
o,p′-DDT	0.20	0.15	0.30	0.51
p,p′-TDE	3.37	0.91	0.07	1.75
β-Endosulfan	0.05	0.03	0.05	0.15
p,p′-DDT	0.96	0.99	1.60	3.35
Endosulfan sulfate	n.d.	n.d.	n.d.	n.d.

n.d.: not detected.

RESULTS

The average total pesticide transfer rate was 17% (Table 2); it appeared to be independent of the tobacco type (American blend, Maryland, Virginia, Oriental).

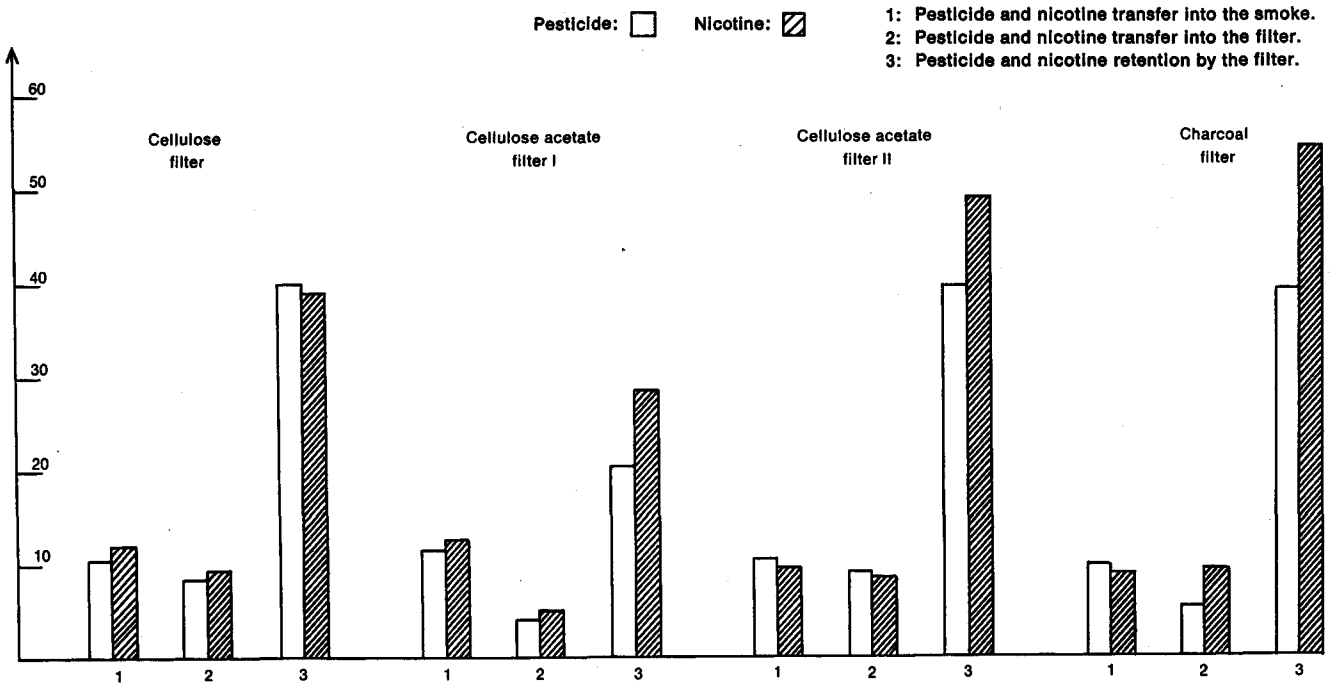
However, as shown in Table 3 and Figure 2, the percentage of retention by the cigarette filters depended on the efficiency of the filters used, according to the type of filter. The retention by the cellulose acetate filter II was comparable to the retention by the cellulose filter. The latter showed comparable retentions for both total pesticides and nicotine. In both the low and high pressure drop cellulose acetate filters, however, the pesticide retention is lower than the nicotine retention. The charcoal filter retained comparable proportions of pesticides to the cellulose and the cellulose acetate II filters, but proportionally more nicotine.

When cigarettes spiked with additional pesticides were used, it was found that the activated charcoal did not retain pesticides from the smoke stream. This observation is based on identical retentions by the plug-space-plug filters with empty vs. carbon-filled cavities (see Table 4). Pesticide transfer rates were observed to be higher in

Table 2. Mean transfer and retention of pesticides from various tobacco blends.

	American blend	Maryland blend	Virginia blend	Oriental blend
Transfer into the smoke (%)	13	12	12	13
Total transfer (%)	17	16	16	17
Retention by filter (%)	23	25	25	23

Figure 2. Mean transfer of pesticides and nicotine and retention in various filter types.



spiked than in non-spiked cigarettes. It is hypothesized that injected pesticides are not integrated into the tobacco substance and are more readily volatilized. Results obtained from spiked cigarettes were therefore not used to calculate the pesticide transfer, but only to determine the retention by the filter of those pesticides present in very low concentrations in tobacco.

Degradation of Pesticides during Smoking

Although no o,p'-DDE was present in the tobacco, its occurrence in the smoke was confirmed. Both o,p'-DDT and p,p'-DDT were partially degraded to o,p'-DDE and p,p'-DDE, respectively (6, 7, 8). The average degradation yield for both p,p'-DDT and o,p'-DDT was 3%, of which 2.5% was recovered in the smoke and 0.5% in the filter.

Transfer of Pesticides to the Tobacco Butt

The transfer of pesticides into the tobacco part of the cigarette butt is calculated according to the following formula:

$$\text{Transfer into butt (\%)} = \frac{\text{B after smoking} - \text{B before smoking}}{\text{A}} \times 100.$$

Actual results were surprising in that fewer pesticides were determined in the tobacco part after smoking than before smoking. There was an average negative transfer of 4%. Individual pesticides and degradation products (e.g. o,p'-DDE) however differed somehow in behavior.

There is no doubt that there is a zone where the temperature facilitates the volatilization of the pesticides during smoking. This zone is not the same for all the pesticides; it depends in each case on the boiling point and degradation temperature (9).

The following phenomena are likely to occur in sequence or simultaneously during burning: Volatilization and transfer of the pesticides, partial degradation and transfer of the degradation products, eventually followed by total decomposition in the cigarette coal. This was confirmed by the absence of any trace of pesticides in the cigarette ash.

Table 3. Mean transfer of pesticides and nicotine and retention in various filter types.

		Cellulose filter	Cellulose acetate filter I	Cellulose acetate filter II	Charcoal filter
Pesticide transfer into the smoke	(%)	11	13	11	10
Nicotine transfer into the smoke	(%)	15	15	9	8
Pesticide transfer into the filter	(%)	7	3	7	6
Nicotine transfer into the filter	(%)	9	5	8	9
Pesticide retention by cigarette filter	(%)	39	19	39	38
Nicotine retention by cigarette filter	(%)	38	25	47	53

Table 4. Pesticide retention by charcoal filter.

Component	Retention (%)	
	Cavity with charcoal	Empty cavity
p,p'-DDT	39	39
p,p'-TDE	39	38
o,p'-DDT	39	39
o,p'-TDE	38	38
p,p'-DDE	34	35
o,p'-DDE	36	35
Mean value	38	37

SUMMARY

The transfer during smoking of pesticides contained in tobacco into the smoke and the filter of cigarettes was investigated.

The overall transfer into the mainstream smoke was 17 %. It was found to be independent of the type of the tobacco blend (American, Maryland, Virginia and Oriental).

The pesticide retention of the following four filters was investigated: cellulose filter, cellulose acetate filter with low and high pressure drop, and a charcoal filter, characterized by nicotine retentions of 38 %, 27 %, 48 % and 54 %, respectively. The corresponding pesticide retentions found were 40 %, 21 %, 39 % and 38 %, i.e. lower than the nicotine retention in the cellulose acetate, and significantly lower in the charcoal filter.

A 3 % degradation of p,p'-DDT and o,p'-DDT contained in tobacco to p,p'-DDE and o,p'-DDE respectively, was also observed. The pesticides initially contained in the tobacco part of the cigarette butt decreased during smoking. This appears to be the result of some initial condensation of substances carried through by the smoke stream (as indicated by the presence of pesticide degradation products), followed by strong desorption during the very last puffs.

ZUSAMMENFASSUNG

Es wurde untersucht, inwieweit im Tabak enthaltene Pestizide während des Abrauchens in den Rauch und in den Filter der Cigarette übergehen.

Es zeigte sich, daß der Gesamtübergang der Pestizide in den Hauptstromrauch 17 % ausmacht und von der Art der Tabakmischung („American blend"-, Maryland-, Virginia- und Orient-Tabak) unabhängig ist.

Die Pestizidretention folgender vier Filterarten wurde untersucht: Cellulosefilter, Celluloseacetatfilter mit niedrigem und hohem Zugwiderstand und Kohlefilter. Die Nikotinretention dieser Filter betrug 38, 27, 48 bzw. 54 %. Für die Pestizidretention ergaben sich die Werte von 40, 21, 39 bzw. 38 %, d. h. sie war im Celluloseacetatfilter niedriger und im Kohlefilter erheblich niedriger als die Nikotinretention.

Es wurde auch beobachtet, daß sich im Tabak enthaltenes p,p'-DDT und o,p'-DDT zu 3 % zu p,p'-DDE bzw. o,p'-DDE abbaut. Die anfangs im Tabakteil des Cigarettenstummels vorhandene Pestizidmenge nahm während des Abrauchvorganges ab. Dies scheint durch eine anfängliche Kondensation von Substanzen bedingt zu sein, die durch den Rauchstrom transportiert werden (was auch das Vorhandensein von Pestizidabbauprodukten zeigt); mit den letzten Zügen erfolgt anschließend eine starke Desorption.

RÉSUMÉ

Nous avons procédé à une étude sur le transfert et la rétention des pesticides présents dans le tabac lors du fumage.

Il s'avère que le taux de transfert total des pesticides dans la fumée principale ne dépend pas du type de mélange utilisé (Américain, Maryland, Virginie et Orient), et est égal à 17 %.

Pour étudier la rétention des pesticides, nous avons comparé 4 filtres différents, à savoir: le filtre en cellulose, le filtre en acétate de cellulose à faible et haute résistance au tirage, et le filtre à charbon. Les résultats obtenus sont de 40 %, 21 %, 39 % et 38 %, résultats que nous pouvons comparer à ceux de la rétention de la nicotine par ces mêmes filtres, à savoir: 38 %, 27 %, 48 %, et 54 %.

Nous avons constaté une dégradation de 3 % de p,p'-DDT et o,p'-DDT présents dans le tabac en p,p'-DDE et o,p'-DDE respectivement. En étudiant ce que deviennent les pesticides initialement présents dans la partie tabac du mégot, nous avons constaté une diminution de leur teneur après fumage, ainsi que la présence de produits de dégradation. Ceci permet de conclure à une déposition initiale dans cette partie de la cigarette, suivie d'une forte désorption lors des dernières bouffées.

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