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CHLORINATED HYDROCARBONS (PESTICIDES AND POLYCHLORINATED BIPHENYLS — PCBs) IN THE ATMOSPHERE OF LJUBLJANA

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Airborne particulate matter was continuously sampled from the atmosphere of the residential town area of Ljubljana for 45 days and trapped on a filter. Some chlorinated hydrocarbons (pesticides and PCBs) were determined by GLC after solvent extraction followed by concentration and clean-up of the oily residue. The PCB concentration in the particulate matter in the atmosphere was 1.3 ng/m³ and the concentration levels of the total DDT, dieldrin, alpha-, gamma-, delta-HCH and heptachlor epoxide were 0.86, 0.03, 0.08, 0.05, 0.03 and 0.01 ng/m³ respectively. Such a level of chlorinated hydrocarbons in the atmosphere is considered of little or no consequence to public health.

The presence of chlorinated hydrocarbons (pesticides and PCBs) in the atmosphere represents a possible exposure route to mankind and may be explained by the worldwide use of these relatively stable compounds. Clorinated pesticides and PCBs are dispersed from the local area of usage (from agricultural areas, household use, industrial waste) and they are present in very low concentrations all over the world. It is fairly certain that during spray applications half of the pesticide is dispersed into the atmosphere (1, 2, 3). Air transport is probably the principal way by which the largest amounts of pesticides are dispersed into the environment. The presence of chlorinated hydrocarbons in the air has been confirmed by several authors. DDT residues in airborn dust particles collected over the Atlantic ocean in the West Indies contained 8×10^{-5} ng/m³ (4), and the total DDT (in particulate matter and gaseous form) was 2×10^{-2} ng/m³. In the uncontaminated region of the Central

Europe (1) the DDT concentration in the air is about 0.3 ng/m³ and the corresponding lindane and α-HCH concentration below 0.1 ng/m³ (5). In urban areas (6), especially where spraying is conducted regularly, the estimated values range from 1 to 21 ng/m³ and in some agricultural regions they could even reach 1000 ng/m³ (3, 7).

PCB residues in the marine atmosphere are over 0.2 ng/m³ (4); in the continental region the values are higher and in industrial regions near the source of contamination (8), they can be over 1000 ng/m³. In the USA the average concentration of PCBs in the atmosphere is about 100 ng/m³ (9). Since there are no data on the pollution of the atmosphere by chlorinated hydrocarbons in Yugoslavia, the purpose of this work was to determine the level of chlorinated hydrocarbons in the atmosphere of the city of Ljubljana.

EXPERIMENTAL

Air was pulled through a Viledon P-15/500 filter (Viledon, Weinheim GFR) for 45 days during October and November 1975. The sampling station was located on the »ISKRA« building (8 m above the ground) in the centre of Ljubljana. Through 1 cm² of the filter surface 450 m³ of air was passed. Afterwards the filter was cut into strips and extracted for 12 hours with ether-petrolether-benzene (10 + 20 + 1) in a Soxhlet extractor. The extract was dried through a Na_2SO_4 column and concentrated in a rotovapor to dryness. The oily residue was cleaned-up through an alumina column (4 g Al_2O_3, activity grade III. from Woelm, was slurried with hexane into a 1 cm diameter column). About 50 mg of the oily extract diluted in 1 ml hexane was transferred to the column and eluted with 20 ml hexane. Further clean-up of the extract was conducted in two parallel ways:

1. Ethanolic hydrolysis in 2% KOH followed by CrO_3 oxidation in acetic acid as previously described (10). The chromatogram from extract after hydrolysis was used for dieldrin and heptachlor epoxide determination as well as for confirmation of the total DDT (in DDE form). PCB residues were determined after the oxidation of the extract and clean-up through florisil column eluted with petroleter.

2. On a H_2SO_4 — SO_3 (6% SO_3) celite 545 column eluted with hexane. The eluate was passed through florisil column as described in the FDA method (11). The method was used for the determination of DDT and HCH groups.

The retention time of some pesticides interferes with PCB chromatographic pattern. The residue values are calculated by comparison of chromatograms after two destructive clean-up procedures.

The PCB level is an average value calculated by relating the height of every peak (12) in the sample of air extract (we used 14 peaks) to the corresponding peak in the standard (Fig. 1). As a standard, we used mixed Aroclor 1254 — 1260 (1 + 1).

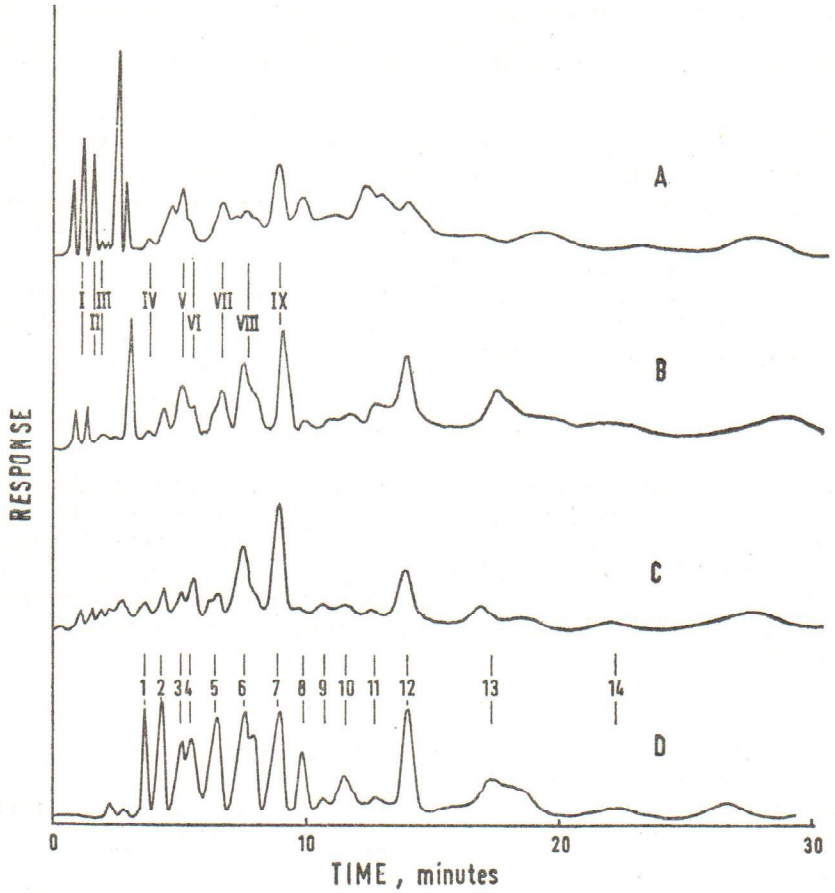

Fig. 1. *Gas chromatograms (glass column packed with 2.5% QF-1 + 2.5% DC-200 — on 100—120 mesh Varaport 30). Conditions are given in the text.*

A. Air extract after alumina and florisil clean-up

B. Alcoholic saponification of air extract with subsequent oxidation with CrO_3 and florisil clean-up

C. Sulphuric acid treatment and florisil clean-up of air extract

D. PCB standard Aroclor 1254—1260 (1 + 1). The PCB peaks used for the PCB quantification are numbered 1 to 14.

The retention time of organochlorine pesticides are numbered I to IX: I, α-HCH; II, γ-HCH; III, δ-HCH; IV, heptachlor epoxide; V, p,p'-DDE; VI, dieldrin; VII, o,p'-DDT; VIII, p,p'-DDD; IX, p,p'-DDT.

Identification of chlorinated hydrocarbons was accomplished on a Varian Mod. 1700 GL chromatograph equipped with two columns having different resolution characteristics. The instrument parameters were as follows:

Columns glass 6 foot x 2 mm (i. d.), packed with 2.5% QF — 1 + 2.5% DC — 200 on Varaport 30 (100 — 120 mesh) and 1.5% SP — 2250 + 1.95% SP — 2401 on Chromosorb W (80 — 100 mesh).

The detector was an electron capture (Sc — ^{3}H), the carrier gas prepurified nitrogen, flow rate 60 ml/min. Temperature: column 195° C, injector 205° C and detector 240° C.

In order to check the method of clean-up, we spiked the heavy petroleum with chlorinated hydrocarbons and made parallel blank analyses. Recovery for individual components was 75—90%.

RESULTS AND DISCUSSION

Chlorinated hydrocarbons in the extracted oily residue from air varied from 35.5 ppm (for PCBs) to 0.3 ppm (for heptachlor epoxide). The data in Table 1. are expressed as the concentration of chlorinated hydrocarbons in air. We have analyzed only the particulate matter trapped on the filter. Since gaseous forms of chlorinated hydrocarbons were probably not efficiently trapped (13), actual atmospheric levels could be considerably higher than reported here.

Table 1

Pesticide and PCB levels (ng/m³) in the atmosphere of Ljubljana

α-HCH	γ-HCH (lindane)	δ-HCH	dieldrin	heptachlor epoxide	p,p'-DDT
0.08	0.05	0.03	0.03	0.01	0.20

p,p'-DDE	p,p'-DDD	o,p'-DDT	Total DDT	PCB
0.36	0.11	0.14	0.86	1.3

Another effect might increase the level of chlorinated hydrocarbons in the particulate form. In the region of air sampling amorphous carbon was present in black smoke emission. These particles are a powerful adsorbent of some gaseous chlorinated hydrocarbons in air.

The content of chlorinated hydrocarbons was higher than in the atmosphere over the Atlantic ocean (4). Our values are the same as those in uncontaminated Central Europe (1).

Chlorinated hydrocarbons in Ljubljana have not been used for some years. Agricultural areas near Ljubljana are small. In the city even now the use of PCBs is very limited. The level of chlorinated hydrocarbons in the air of Ljubljana could not be explained as originating from local sources but rather as coming from other regions.

The daily average intake of chlorinated hydrocarbons from the air is below the level which could have any influence on their total daily intake. Daily intake of DDT from food is 7.4 μg/day (14): in 22 m^3 of air which one on average inhales daily there is 0.018 μg DDT. Here the resorption level in digestive system and lung is not considered. It has been stated (15) that in organisms — man in this case — there is an internal equilibrium between the amount of chlorinated hydrocarbons present in the fatty tissue — in the blood — in the lung and that in the air. On the basis of this assumption, we can state from the data on the contamination of the inhabitants of Slovenia (16) that they exhale more chlorinated hydrocarbons which originate from the food they eat than they inhale. However we cannot neglect the role of the respiratory route as a source of human exposure to chlorinated hydrocarbon, even if the doses are low because the exposure time is long.

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References

1. *Junge, C. E.:* Pure Appl. Chem., *42* (1975) 95.
2. *Van Dyk, L. P., Visweswariah, K.:* Residue Rev. *55* (1975) 91.
3. *Lewis, R. G., Lee Jr, R. E.,* in: Air pollution from pesticides and agricultural processes, ed. R. E. Lee Jr., CRC Press, Cleveland, Ohio, 1976, p. 5.
4. *Bidleman, T. F., Olney C. E.:* Science, *183* (1974) 516.
5. *Herzel, F., Lahmann E.:* Gesundh. Ing., *93* (1972) 202.
6. *Wheatley, G. A., in:* Environmental pollution by pesticides, ed. C. A. Edwards, Environm. Science Research, Vol. 3, Plenum Press, London, 1973, p. 365.
7. *Spencer, W. F.:* Residue Rev., *59* (1975) 91.
8. *Fujiwara, K.:* Sci. Total Environ., *4* (1975) 219.
9. *Kutz, F. W., Yang H. S. C.* Nat. Conference on PCBs, Chicago, Nov. 19—21, 1975.
10. *Trotter, W. J.:* J. Ass. Offic. Anal. Chem., *58* (1975) 461.
11. Pesticide Analytical Manual, vol. I., Food and Drug Administration, Washington, D. C. (rev. 1975)
12. *Chau, A. S. Y., Sampson, R. C. J.:* Envir. Lett., *8* (1975) 89.
13. *Klockow, D.:* Z. Anal. Chem., *282* (1976) 269.
14. *Ragaci, V., Malnerščič, S., Jan, J.:* Zdrav. vestn. (in press)
15. *Galley, R. A. E.:* Chem. and Ind. (London), (1974) 179.
16. *Jan, J.:* Zdrav. vestn., *44* (1975) 233.

Sažetak

KLORIRANI UGLJIKOVODICI (PESTICIDI I POLIKLOROBIFENILI — PCB) U ATMOSFERI GRADA LJUBLJANE

U soliteru »Iskra« u Ljubljani neprekidno smo 45 dana usisavali vanjski zrak kroz filter. Filter je zadržao čestice aerosola. U tom smo aerosolu tehnikom plinske kromatografije identificirali neke stabilne organskofosforne spojeve (pesticide i poliklorirane bifenile). Našli smo da je koncentracija PCB 1,3 ng/m³, a ukupnog DDT (p,p'-DDE, p,p'-DDE, p,p'-DDD i o,p'-DDT), dieldrina, alfa-, gama-, delta-HCH i heptaklor epoksida 0,86; 0,03; 0,05; 0,03; 0,01 ng/m³. Količina organoklornih spojeva u zraku ne prelazi količinu koja bi znatno utjecala na ukupni dnevni unos u čovjeka.

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