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TRANSPORT OF PESTICIDES TO THE SEA BY THE VISTULA RIVER

Contents: 1. Introduction, 2. Methods and materials, 3. Results and discussion; Streszczenie; References.

1. INTRODUCTION

Pesticides indicate considerable migrational properties in the environment. Applied to crops and forests they are carried into water bodies in a direct way by the wind, as well as indirectly with runoff [2—4, 8, 13] precipitation [10] and by infiltration [5]. Industrial and agricultural waste waters and accidental discharge from the washing of agrochemical devices or the throwing out of pesticide containers into the water are an other source of pesticide pollution of waters.

It was found, that persistent pesticides such as chlorinated hydrocarbons contribute to the surface water pollution throughout the year. The level of these fresh water pollutants does not usually exceed 1 ppb. It should however be emphasized, that even very low concentrations of the persistent pesticides in water can result in chronic toxicity for aquatic fauna, and may have a negative influence on reproduction and survival. Moreover, the tendency of these pesticides to accumulate and their relationship to lipids cause the biological concentration of pesticide residues. The other less persistent pesticides cause seasonal water pollution hazards i.e. for several weeks or months after their application during the course of intensive runoff. Local cases of water pollution at the acute toxicity level are usually connected with intensive rainfall or inappriopriate pesticide application.

Rivers which drain pollutants from their basins are the main source of sea contamination. Knowledge of the pesticide loads carried by these rivers is therefore of great importance in investigations on the accumulation of harmful substances in the marine environment, and the establishment of the balance of pollutants.

2. METHODS AND MATERIALS

During the period January 1972 — March 1974, investigations on pesticide occurrence in the lower Vistula River were carried out by the Institute for Meteorology and Water Economy in Gdańsk. The Vistula is the greatest river in Poland, it is over 1000 km in length and has a catchment area of about 172 thousand km², which constitutes about 60% of the total area of the country.

Average samples of water were collected twice a week from two Vistula cross sections during the whole period of investigations. Fig. 1 shows the location of sampling stations. Cross section I was located in the upstream of the River Nogat (the first Vistula River branch in its delta), and cross section II — on the main river bed upstream of the other branches: Szkarpawa River and the Dead Vistula River.

The subject of the investigations was organochlorine insecticides: DDT, DMDT (metoxychlor), γ-HCH (lindane) and chlorophenoxyacetic acid herbicides: 2,4-D and MCPA. They constituted about 90% of the total quantity of the pesticides used in the first survey year. Although in 1973 DDT was eliminated from the list of chemical plant protection means by law in Poland, supplies of DDT and its metabolites accumulated in the environment may still cause pollution of water resources. In addition to the organochlorine insecticide analysis of water and suspended solids the residues of these compounds were determined in fish. Gas-liquid and thin-layer chromatography were used for pesticides determination [1, 11, 12].

3. RESULTS AND DISCUSSION

The investigations have shown, that organochlorine insecticide concentrations in the lower Vistula River ranged from indeterminable quantities to 2.5 μg/l, the highest ones falling to DDT and its metabolites: DDD and DDE. Concentrations of over 1 μg/l occurred only in isolated cases, mainly during the period of treatment. The most frequently detected pesticide concentrations were at a level of several nanograms per litre on average. Increased concentrations were found in the spring and summer seasons, the highest ones occurring in May — July, this being due to the application of pesticides to crops, orchards and forests. Intensity of storm showers in summer increases pesticide drainoff from soil and

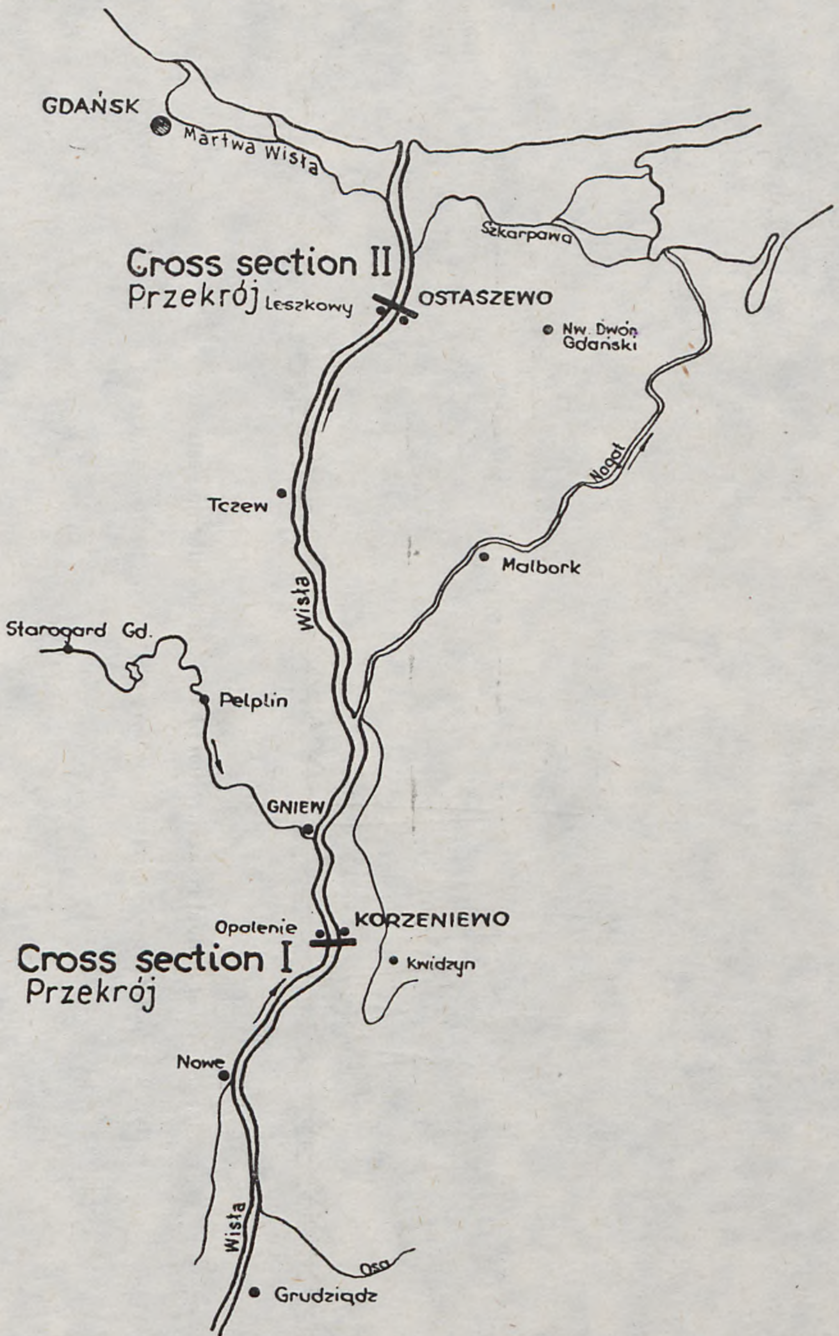

Fig. 1. Location of stations

Ryc. 1. Rozmieszczenie stanowisk badawczych

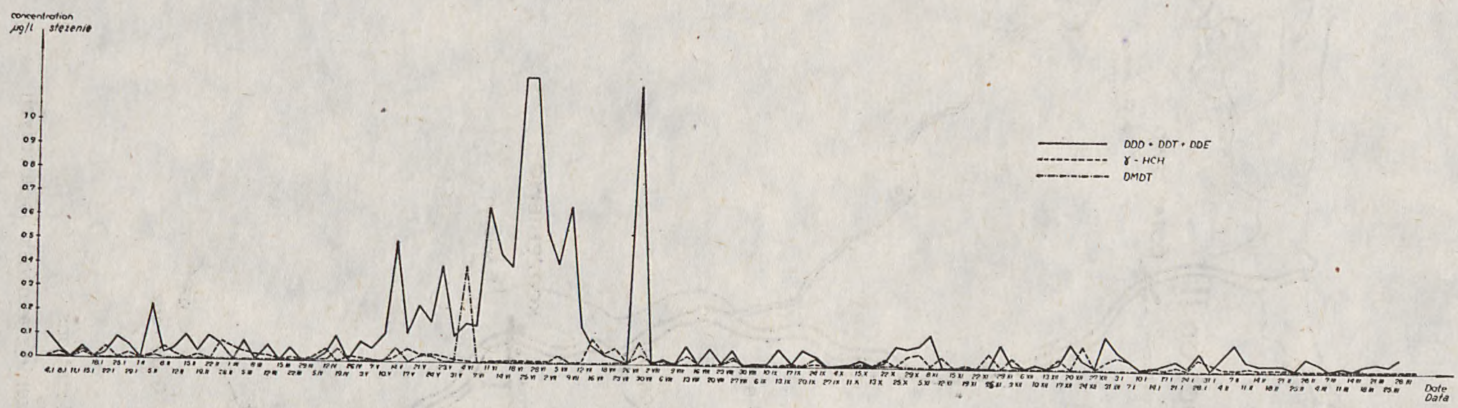

Fig. 2. Typical annual concentration plot of organochlorine pesticides

Ryc. 2. Typowy, roczny przebieg stężeń pestycydów chloroorganicznych plants, besides the direct migration of active substances into the waters. The lowest quantities of the pesticides under investigation were observed during the late autumn and winter months. Fig. 2 shows a typical run of organochlorine pesticide concentrations during a year (data for 1973 and the first quarter of 1974).

The highest quantities of DDT complex fell to pp'DDT, pp'DDD was the most often found metabolite of DDT. The ratio of pp'DDT/pp'DDD in 1972 was greater than in 1973. This can be explained by DDT withdrawal and degradation of DDT supplies accumulated in the water environment to pp'DDD, pp'DDE was found more rarely and in lower concentrations.

The average annual concentrations of insecticides attained the highest level in 1972. During the following years average concentrations of the DDT family and γ-HCH decreased by 30—80%, respectively, whereas DMDT concentration was low throughout the whole investigation period, and in 1974, no DMDT was detected at all. This fact was probably connected with the restriction of the application of chlorinated hydrocarbon in our country.

The organochlorine insecticide residues in fish were between hundredths and several ppm. At the same time pp'DDT was found in all samples, pp'DDD, pp'DDE and γ-HCH were also detected in the majority of fish examined, whereas DMDT was found in 60% of the samples. No correlation was revealed between the concentrations of the DDT family and γ-HCH in fish tissues and the season of the year. The average level was constant and depended on the species, weight and fat content of fish. The DMDT residues in fish were highest during the spring and summer. During the other seasons DMDT was either not detected or found in trace quantities. It was probably due to the lower durability of this pesticide in water and its easier excretion by organizms than is in the case of other pesticides. The maximum concentration of DDT in fish was calculated on the basis of the highest concentration found in fish tissue in relation to DDT concentrations most often found in water. The maximum residue concentration ratio was 1:100 000, which was in line with data [6] from other authors, and confirmed the usefulness of this determination as a criterium of water pollution by organochlorine insecticides.

In the Vistula, herbicides were recorded only sporadically in concentrations of up to 10 μg/l; the average being 0.3 μg/l. This was probably due to a lower durability of herbicides as compared with the other compounds investigated. No correlation was found between the concentrations detected and the flow or the season.

The pesticide concentrations determined in water were combined with water flow data measured in the cross sections investigated to calculate the weekly rate of transport of pesticide pollutants. The relation

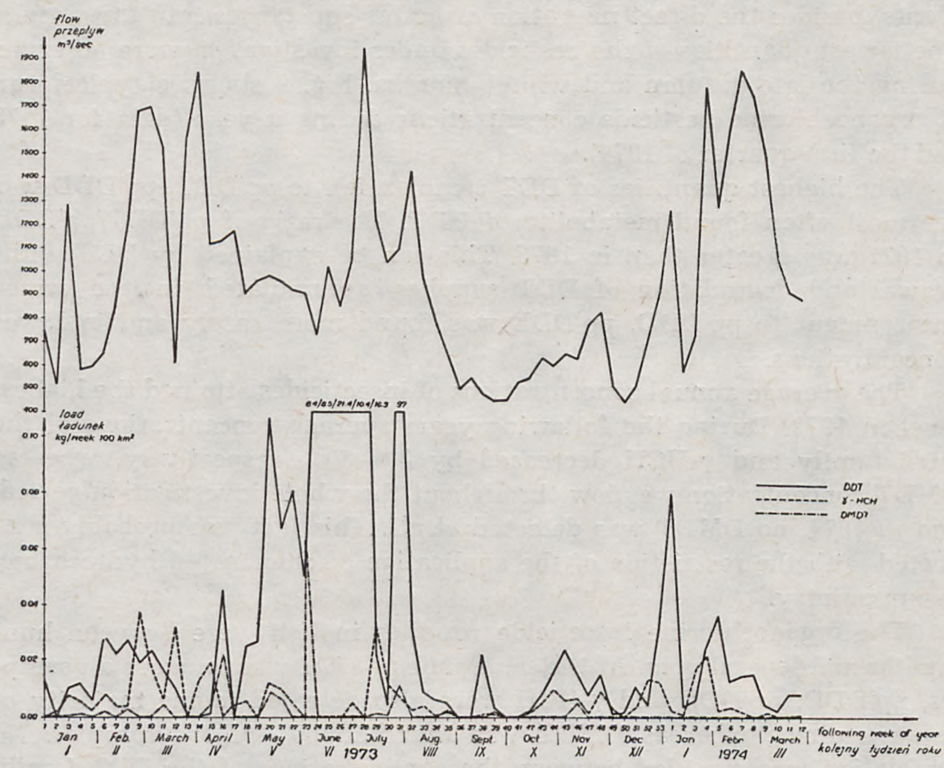

Fig. 3. Relation between the transport of organochlorine pesticides and the intensity of flow

Ryc. 3. Zależność pomiędzy transportem pestycydów chloroorganicznych a natężeniem przepływu

between the organochlorine pesticide transport and the intensity of flow (1973 data) is presented in Fig. 3. The average loads of pesticides in the watershed per week per 100 km² and the average weekly flows were put on the y-axis while the following weeks of the year on the x-axis. Although statistical calculations did not confirm the existance of any linear correlation between loads and flow, some relation between these parameters can be seen. Consistency of peaks and shape of curves was found in many cases, with the exception of the application period when the pesticide loads were the highest and irrespective of the flow intensity, which would indicate washing out of pesticides from treated soil into the water.

The total loads of polichlorine pesticides in particular seasons and years were similar for both cross sections investigated. During the following years the average annual loads of pesticides amounted to: DDT and metabolites — 2.446 and 2.081 kg/100 km² of watershed, γ-HCH — 0.666

and 0.338 kg/100 km^2, and DMDT — 0.165 and 0.035 kg/km^2, respectively. It can be seen that, as in the case of concentrations, the average annual loads of all polichlorine pesticides decreased by about 15—80% in 1973 in relation to 1972. This was probably due to the decrease in the application of these compounds by about 50%.

Comparing the global annual loads and the usage of particular pesticides (calculated on active substances) it was found, that only a small part of the plant protection agents applied penetrates into the running waters. In 1972 the Vistula River transported pesticide pollutants which constituted 0.85% DDT, 0.55% γ-HCH, and 0.085% DMDT, in relation to the total usage of these compounds in the Vistula River drainage basin. In 1973, this amounted to 3.7%, 0.22%, and 0.17%, respectively. The higher percentage of DDT and DMDT resulted from the fact that 1973 records of insecticides did not include the residue of both pesticides accumulated in previous years which were, in fact applied in the course of plant protection campaigns.

The share of particular insecticides in the total pollution of the lower Vistula in relation to the quantity of the compounds used indicated, that the highest percentage fell to DDT while the lowest — to DMDT. This is understandable considering the persistence of these pesticides and their tendency to accumulate which are highest in the case of DDT and lowest in that of DMDT.

Investigations on particular pesticides showed that only maximum short-term and sporadic concentrations of the DDT family reached the toxicity limit for the most sensitive aquatic organisms [7]. Normal pesticide concentrations did not constitute a direct threat to organisms although they often exceeded those permissible for surface waters (0.01 μg/l). γ-HCH and DMDT concentrations occurring throughout almost the whole year were found to be below normative levels (0.2 and 0.01 μg/l). Similar results were confirmed concerning pesticide residues in fish. The concentrations were the only ones to exceed the water protection standards (1 ppm in the wet mass) [9]. In the light of the criteria quoted, only DDT presents some threat to the ecosystems of the Vistula. As they are greatly diluted, the pesticide pollutants transported to the sea by the Vistula River cannot, in any case, directly endanger the marine organisms. However, each of the DDT loads, even the smallest, is accumulated in organisms and sediments, increasing the level of this insecticide in the marine environment. Fortunately, in 1974 the use of DDT was prohibited in Poland. The changed structure of pesticide application already caused a drop in the concentrations, as well as total loads of DDT in waters in 1973. This fact affords an optimistic prognosis for further years. The content of this compound, the most dangerous of the pesticides investigated, should gradually decrease in the surface waters.

Other less persistent pesticides such as chlorophenoxy herbicides do not constitute a threat to the estuarine waters of Vistula River, nor therefore to the sea. The estimated concentrations of these herbicides were not toxic for organisms and never exceeded the permissible limits. As these compounds have a relatively low durability they are probably the cause of harmful pollution only at the points of direct discharge.

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Streszczenie

W latach 1972—1974 Instytut Meteorologii i Gospodarki Wodnej przeprowadził badania nad występowaniem pestycydów w Dolnej Wiśle. W badaniach uwzględniono insektycydy polichlorowe (kompleks DDT, metoksychlor i lindan) oraz herbicydy pochodne kwasów chlorofenoksyoctowych (2,4-D i MCPA).

Stężenia insektycydów w wodzie sięgały 2,5 $\mu g/dm^3$; przeciętnie były rzędu kilku do kilkunastu nanogramów w litrze. Maksymalne stężenia przypadały na miesiące letnie, co było związane z okresem stosowania tych środków w rolnictwie. Średnie stężenia roczne były najwyższe w pierwszym roku badań, w następnych latach obniżały się o 30—80%, prawdopodobnie na skutek ograniczenia zużycia insektycydów polichlorowych w naszym kraju. Również średnie ładunki roczne przenoszone wodami Wisły obniżały się w kolejnych latach badań o 15—80%. Ilość pestycydów doprowadzanych do morza stanowiła niewielki procent rocznego zużycia tych środków w zlewni Wisły. W roku 1972 wynosiła 0,085—0,85% w zależności od związku.

Pozostałości insektycydów polichlorowych w ciele ryb wahały się od wartości niewykrywalnych do kilku ppm i zależały od gatunku i wieku ryby. Nie zauważono natomiast zależności pomiędzy stężeniem pestycydów a porą roku.

Herbicydy występowały w wodzie Wisły sporadycznie, średnie stężenie wynosiło około 0,3 $\mu g/dm^3$.

Spośród badanych pestycydów tylko DDT przedstawiał pewien stopień zagrożenia dla ekosystemu wodnego Wisły. Ładunek tego zanieczyszczenia wnoszony do morza ulega dużemu rozcieńczeniu i nie może bezpośrednio zagrażać organizmom morskim. Wycofanie DDT z użycia pozwala przewidywać stopniowe obniżanie się poziomu DDT i jego metabolitów w wodach powierzchniowych, a więc i dalsze zmniejszenie ładunku doprowadzonego do morza.

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