ANNA BRZEZIŃSKA
TERESA BOGACKA
REGINA TAYLOR
ANNA TRZOSIŃSKA

Institute of Meteorology and Water Management
Marine Branch — Gdynia

INPUT OF MERCURY COMPOUNDS WITH THE VISTULA WATERS

Contents: 1. Introduction. 2. Materials and methods of investigations, 3. Results and discussion; Streszczenie; references.

1. INTRODUCTION

Mercury, particularly in the form of organic compounds, is one of the most hazardous components of the aquatic environment, mainly because of its toxicity and progressing accumulation in the consecutive links of the food-webs of aquatic organisms [8]. According to bibliographic sources [10, 16], the natural level of mercury in the marine environment varies from 0.01 to 0.1 micrograms per litre.

Man's activities, mostly the increasing application of chemical substances have given rise to a higher level of mercury in the environment [13]. The principal sources of mercury in the hydrosphere are sewage from the chemical industry (electrolytic production of chlorine), electrical, cellulose, pharmaceutical, as well as other industries, and the products of coal and oil combustion. The present pollution of some European and American surface waters amounts to several micrograms of mercury per litre, while the amounts of mercury accumulated in fish often exceed those permitted by the standards for purposes of consumption (0.5 mg per kg in the Anglosaxon countries and 1 mg per kg in Sweden); bottom sediments at the sewage outfalls can reach as much as hundreds of milligrams per kg [10].

So far, information about the mercury contents in Polish surface waters is very limited [3, 4]. This paper presents the first systematic studies of the mercury contents in the Vistula water. The results obtained

give a certain insight into the level as well as variation of mercury concentrations in four cross-sections of the Vistula during the years 1974 to 1976.

2. MATERIALS AND METHODS OF INVESTIGATIONS

Water was taken from the Vistula in the period from September 1974 through October 1976 in the following cross-sections:

Kraków (Cracow)	— 69 km downstream from source
Warszawa (Warsaw)	— 509 km downstream from source
Kiezmark	— 926 km downstream from source
Świbno	— 941 km downstream from source.

The samples were taken once a week in the three first cross-sections and three times a week in the Świbno cross-section, about 20 cm below the surface. They were preserved with concentrated nitric acid [7] and were stored at 0—4°C until the time of analysis. During the first year of the study several series of different fish species were also sampled from the lower Vistula.

Mercury compounds in unfiltered water samples were determined by cold vapour flameless atomic-absorption spectrophotometry. The inorganic mercury compounds were determined directly, while the total mercury contents were found after mineralization at room temperature with a concentrated nitric and sulphuric acids, potassium permanganate solution and potassium persulphate solution [1—3]. The reagents were commercial mercury-free or were purified in the laboratory. Blanks were determined in each case. Mercury concentrations were measured by means of a Perkin-Elmer Coleman MAS-50 analyser or Beckman atomic-absorption spectrophotometer, model 1272. The detection limit calculated for both instruments as the standard deviation of ten measurements in the reagents taken as a blank was respectively 10 ng and 2 ng for total mercury and 5 ng and 1 ng for inorganic mercury. The precision of the measurements was evaluated from separate series of ten determinations in the Vistula waters with different mercury concentrations. The coefficient of variation, computed for the 0.95 confidence level was 5 to 10 per cent for concentrations range of 0.1—1 μg Hg/l and approached 50 per cent for concentrations around the detection limit. The accuracy of the measurements was found from mercury determinations in seven samples used as references at the U.S. Enviromental Protection Agency laboratories. In all cases the relative error did not exceed 5 per cent.

The same procedures and equipment were used for determination of total mercury in fish. The mean sample of the whole fish body was hot-mineralized using a mixture of nitric and sulphuric acids with the addition of hydrogen peroxide, and processed by the Jeffus method [11]. The results were calculated for the wet mass.

3. RESULTS AND DISCUSSION

In the period of 1974—1976 the concentration of total mercury in the cross-sections of the Vistula River varied from 0.09 to 5.60 μg per litre. The mean concentrations were 1.01, 0.89, 0.83 and 0.85 μg per litre for the upper, central, lower and estuary cross-sections respectively. The average concentrations decreased with the distance from the river's source. The decrease was small, however, so the statistical analysis has not indicated any essential differences in mercury contents at the various cross-sections (Table 1). The average concentrations in the upper (Cracow) and lower Vistula (Kiezmark and Świbno) were five to six times lower than those permitted for the purity class II waters, assumed for the river

Table 1
Tabela 1

Statistical evaluation of mercury concentration (μg/l) in the Vistula, 1974 to 1976
Statystyczna ocena wyników pomiarów stężeń rtęci (μg/l) w wodach Wisły w latach 1974—1976

River cross-section and mercury form Przekrój rzeki i forma rtęci	Number of samples Liczba prób	Concentration Stężenie		Standard deviation σ_x Odchylenie standardowe σ_x	Percent of data in the range $\bar{x} \pm \sigma_x$ Liczba danych w zakresie $\bar{x} \pm \sigma_x$ %
		weighted mean $\bar{x}$ średnie ważone $\bar{x}$	modal or (most frequent)* modalne lub (najczęściej występujące)*		
Kraków (Cracow)					
total mercury	79	1.02	0.57	0.74	80
inorganic mercury	79	0.31	0.28	0.30	95
organic mercury	79	0.68	(0.30 / 0.70)	0.69	91
Warszawa (Warsaw)					
total mercury	74	0.89	0.63	0.59	85
inorganic mercury	74	0.28	0.24	0.30	96
organic mercury	74	0.60	0.36	0.57	92
Kiezmark					
total mercury	90	0.83	0.64	0.48	77
inorganic mercury	90	0.28	0.29	0.28	100
organic mercury	90	0.57	0.37	0.42	83
Świbno					
total mercury	216	0.84	0.77	0.71	87
inorganic mercury	216	0.42	0.13	0.55	72
organic mercury	216	0.42	(0.10 / 0.50)	0.33	92

* Variants of two most numerous classes.
Warianty dwóch najliczniejszych klas.

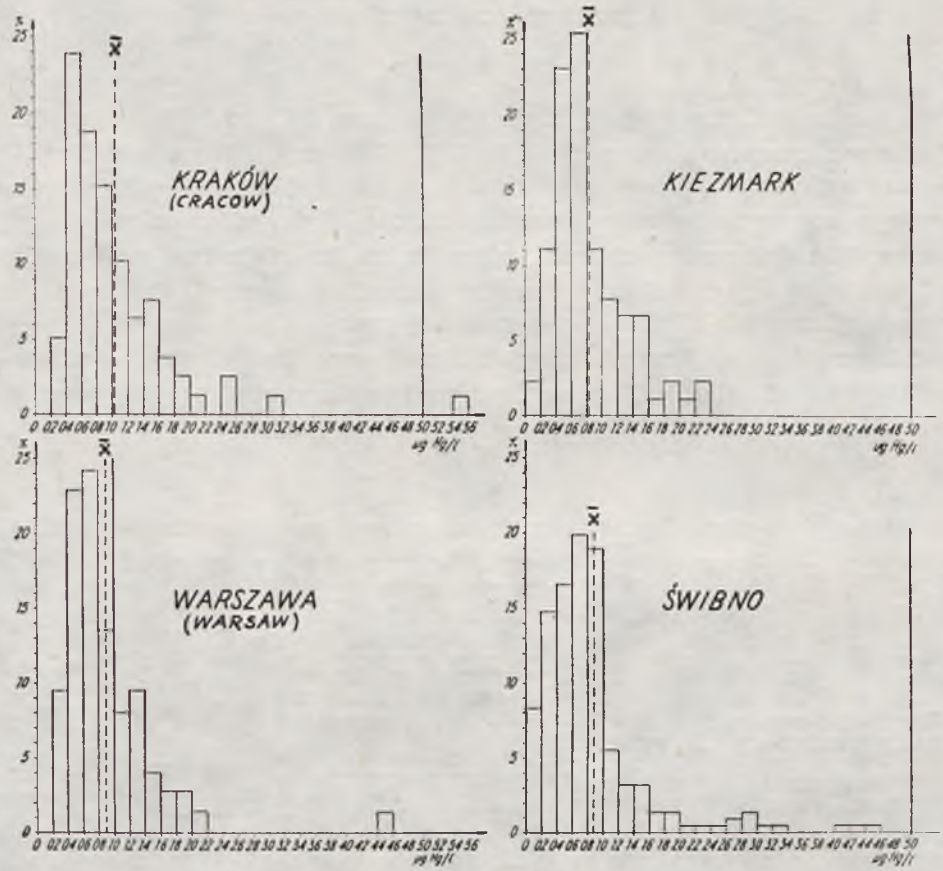

Fig. 1. Histograms of total mercury concentration in the Vistula in the years 1974 through 1976 (the broken line denotes the weighted mean, the solid line — the permissible concentration along the given river section)

Ryc. 1. Histogram stężeń rtęci całkowitej w Wiśle w latach 1974—1976 (linią przerywaną zaznaczono wartość średnią, linią ciągłą — stężenie dopuszczalne na danym odcinku rzeki)

sections studied (Fig. 1). The predominant concentrations were seven to ten times lower than the quantities accepted by Polish standards *. The mean concentration of total mercury in the Vistula River at Warszawa (Warsaw) was slightly lower than that permissible for the class I waters, that this section belongs to. The most frequent concentrations were lower than the permissible by a factor of almost two.

High mercury concentrations, of up to 5 μg per litre, have been noted in the Vistula River occasionally. They were mostly due to organic compounds in the upper and middle Vistula while the ionic form prevailed

* Rozp. Rady Min. of 29th November 1975, Dziennik Ustaw 41 of 13th December 1975, par. 214 and Zarz. Prez. CUGW of 15th February 1972, Monitor Polski 15/1972.

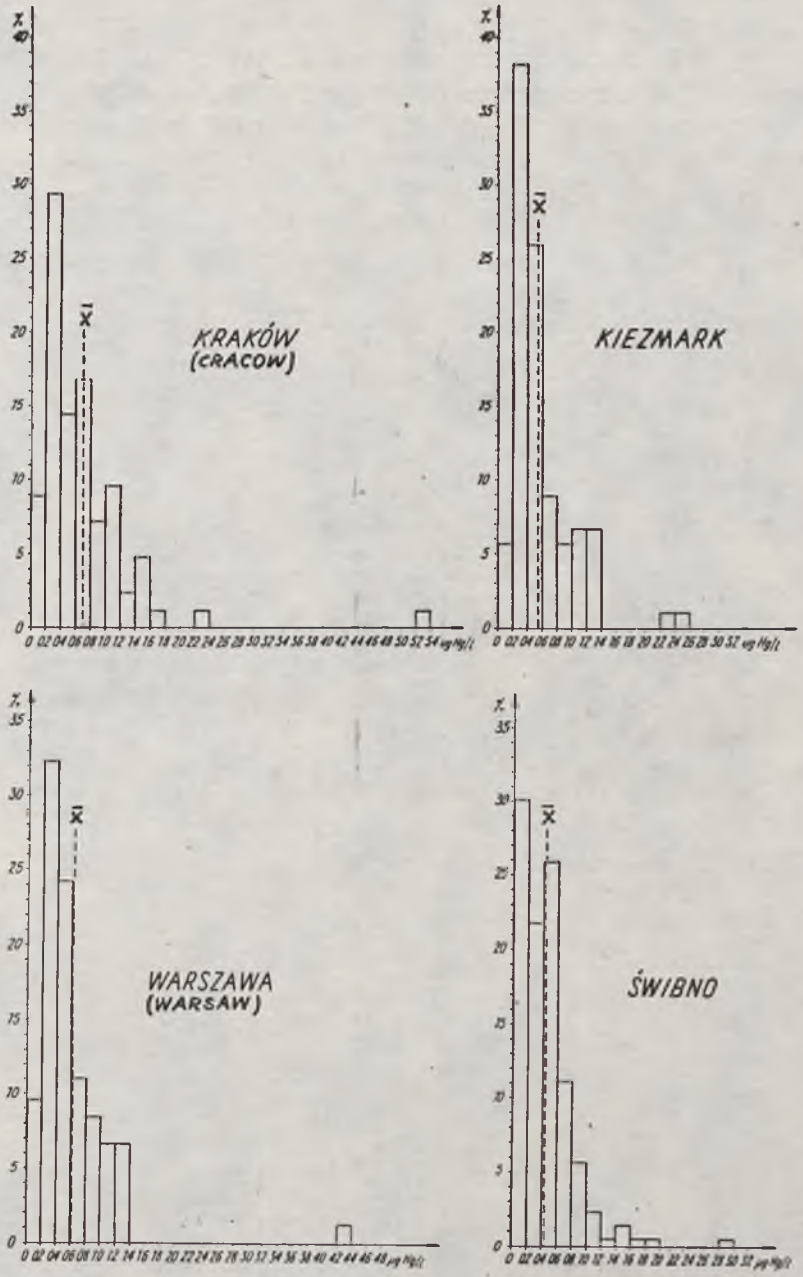

Fig. 2. Histograms of organic mercury concentration in the Vistula in the years 1974 through 1976 (the broken line denotes the weighted mean)

Rys. 2. Histogram stężeń organicznych związków rtęci w Wiśle w latach 1974—1076 (linią przerywaną zaznaczono wartość średnią)

in the estuary (Figs 2 and 3). These outbreaks were short-lasting and their instantaneous character can be observed in measurment results carried out daily at the Świbno cross-section (Fig. 4). It should be taken into account that mercury was determined in water samples containing suspended matter. From bibliographical sources [18] and our studies [9] on

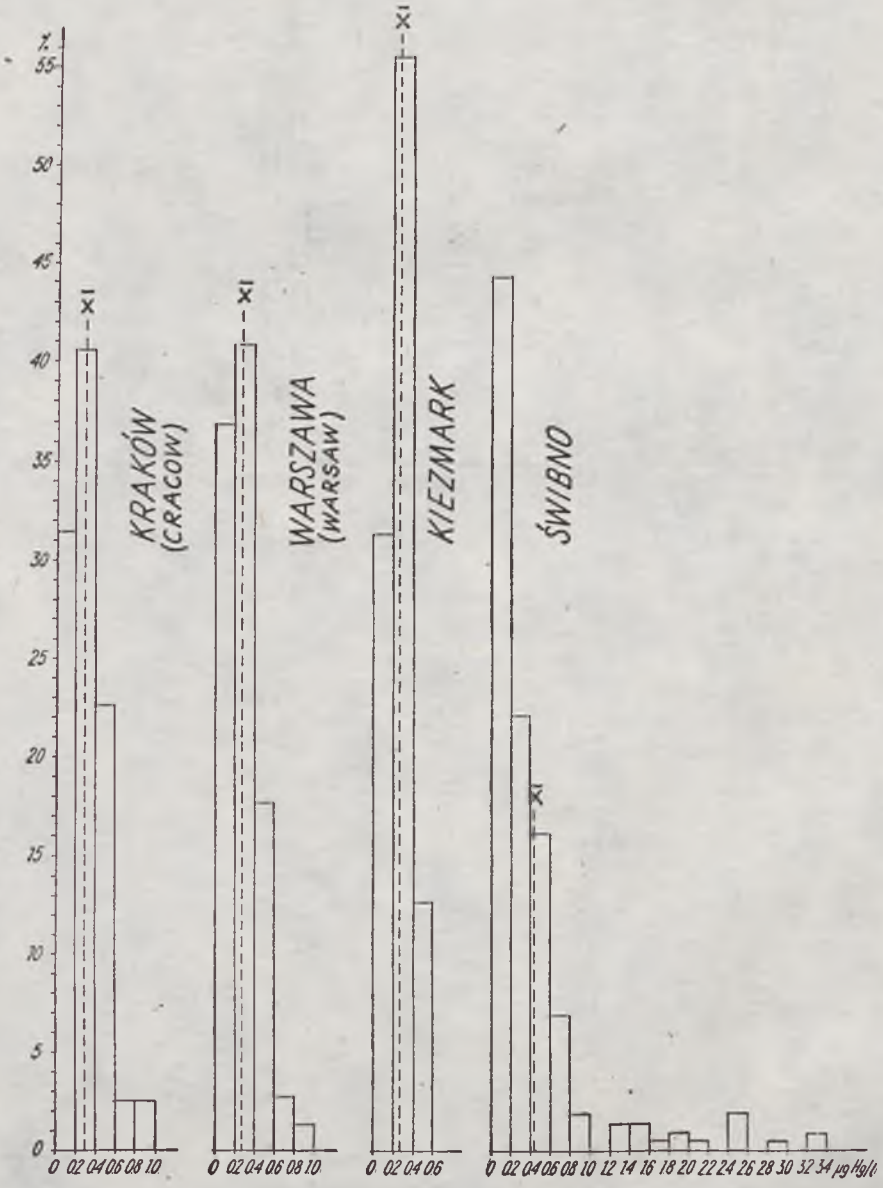

Fig. 3. Histograms of inorganic mercury concentration in the Vistula in the years 1974 through 1976 (the broken line denotes the weighted mean)

Ryc. 3. Histogram stężeń nieorganicznych form rtęci w Wiśle w latach 1974—1976 (linią przerywaną zaznaczono wartość średnią)

the mercury contents in estuarine waters it follows that the quantities absorbed on the suspended matter can vary from several to about forty per cent.

The present average level of mercury in the Vistula River does not seem to endanger the aquatic ecosystems. However, the two-year research does not enable long-term trends to be defined, so that continuous monitoring of mercury contents in the Vistula is necessary, especially along the sections which constitute sources of water supply for human consumption.

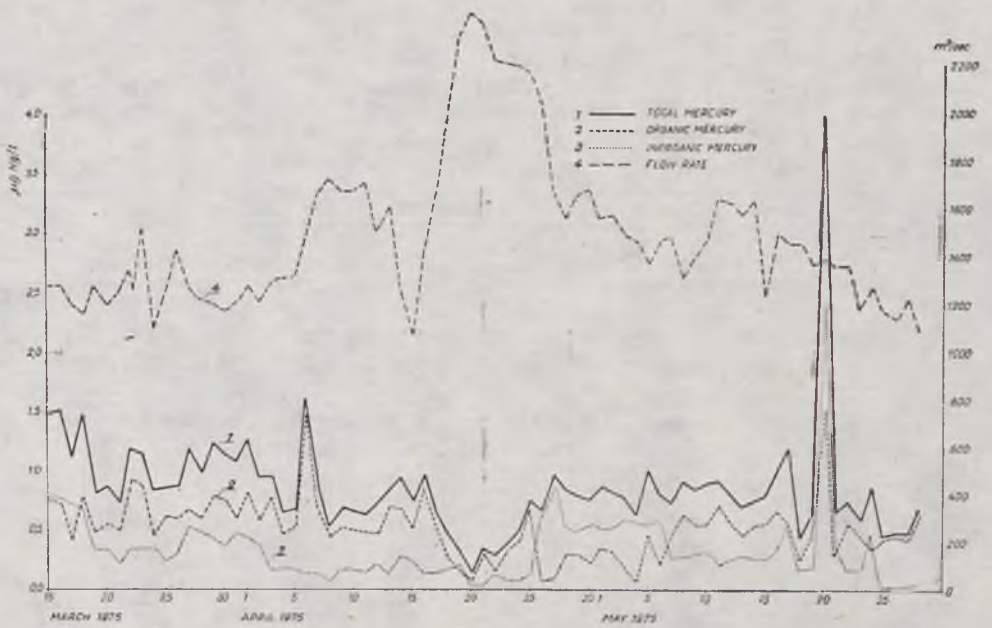

Fig. 4. Daily fluctuations in mercury concentration and flow rate at the Vistula mouth during the period 15th March through 31st May, 1975

Ryc. 4. Codzienne zmiany stężenia związków rtęci w wodach ujściowych Wisły w okresie od 15 marca do 31 maja 1975

The average amount of organic mercury compounds was about 70 per cent of the total mercury in all river sections, except the estuarine section, where a decrease to about 55 per cent was found (Table 2). The measurements conducted simultaneously in the Gulf of Gdańsk [9] showed that the ratio of organic-to-inorganic mercury was about 1 : 1. A systematic decrease of mean organic mercury concentrations towards the mouth of the river was also noted (Table 1, Fig. 2).

From the analysis of mean loads of total mercury transported into the sea daily (Table 2) one is unable to find a regular relationship with flow rate and time of year, this feature being characteristic for micro-components of river runoff particularly for those which depend strongly

Table 2

Tabela 2

Mean concentrations and daily loads of mercury compounds in the Vistula

Średnie stężenie i ładunki dobowe związków rtęci w Wiśle

Year and month Rok i miesiąc	Total mercury µgHg/l Rtęć całkowita µgHg/l	Inorganic mercury µgHg/l Rtęć nieorganiczna µgHg/l	Organic mercury % Rtęć organiczna %	Flow rate m³/s Przepływ m³/s	Total * mercury load kg/day Ładunek * rtęci całkowitej kg/doba	Total mercury µgHg/l Rtęć całkowita µgHg/l	Inorganic mercury µgHg/l Rtęć nieorganiczna µgHg/l	Organic mercury % Rtęć organiczna %	Flow rate m³/s Przepływ m³/s	Total * mercury load kg/day Ładunek * rtęci całkowitej kg/doba
1	2	3	4	5	6	7	8	9	10	11
	Kraków (Cracow)					Warszawa (Warsaw)				
1974										
09.74	0.94	0.28	70.2	54	4.2	1.22	0.25	79.5	407	41.5
10	0.88	0.26	70.5	220	17.5	0.65	0.09	86.2	1778	101.2
11	0.73	0.22	69.9	97	5.9					
12	1.08	0.17	84.3	136	12.0	0.75	0.15	80.0	1068	71.3
1975										
01.75	2.87	0.51	82.2	172	37.3	2.41	0.53	78.0	1241	283.0
02	1.54	0.47	69.5	61	8.0	1.36	0.41	69.9	588	66.8
03	1.19	0.49	58.8	68	6.3	1.15	0.43	62.6	546	53.8
04	1.43	0.34	76.2	179	15.3	0.81	0.26	67.9	1037	81.5
05	1.81	0.58	67.9	79	12.2	0.72	0.29	59.7	650	42.5
06	0.55	0.17	69.1	126	5.7	0.94	0.31	67.0	781	64.9
07	0.85	0.57	32.9	135	6.9	0.69	0.26	62.3	837	47.2
08	0.59	0.17	71.2	115	6.3	0.65	0.23	64.6	784	44.5
09	0.65	0.31	52.3	74	4.2	0.68	0.33	51.5	463	28.5
10	0.55	0.26	52.7	79	9.7	0.47	0.23	51.1	594	25.8
11	0.40	0.18	55.0	72	2.6	0.38	0.18	52.6	449	14.8
12	0.58	0.22	62.1	97	5.6	0.45	0.20	55.6	420	17.5
1976										
01.76	0.68	0.32	52.9	299	17.6	0.59	0.23	61.0	859	24.7
02	1.52	0.47	69.1	92	12.1	1.54	0.35	77.3	543	72.1
03	1.49	0.34	77.2	106	13.5	1.58	0.46	70.9	610	83.2
04	1.39	0.47	66.2	136	16.4	1.33	0.46	65.4	1470	168.4
05	1.42	0.45	68.3	107	12.1	0.83	0.38	54.2	610	43.4
06	0.76	0.39	48.7	52	6.3	0.77	0.42	45.6	835	58.3
07	0.56	0.22	60.7	50	2.4	0.66	0.42	36.4	385	16.8
08	0.85	0.40	52.9	76	5.7	0.75	0.41	45.3	302	19.4
whole period	1.01	0.30	70.3	103	9.5	0.89	0.28	68.5	739	59.4

1	2	3	4	5	6	7	8	9	10	11
	Kiezmark					Świbno				
1974										
10.74	0.51	0.10	80.4	2208	83.9					
11	0.51	0.08	84.3	3420	143.4					
12	0.63	0.16	58.7	2837	125.3					
1975										
01.74	1.95	0.49	74.9	2730	372.4					
02	1.38	0.46	66.7	1615	192.6					
03	0.84	0.46	45.2	1343	96.6	1.10	0.46	58.8	1265	120.5
04	0.66	0.24	63.6	1668	113.9	0.73	0.24	66.2	1690	99.7
05	1.01	0.43	57.4	1404	120.7	0.76	0.31	61.1	1398	88.9
06	0.70	0.10	85.7	1270	78.7					
07	0.64	0.21	82.8	1919	78.3	0.70	0.66	5.5	1087	62.9
08	0.66	0.28	57.6	1406	76.4	0.77	0.39	40.0	1289	82.0
09	0.65	0.34	47.7	766	42.5	1.05	0.62	42.2	809	72.1
10	0.46	0.19	58.7	720	29.2	2.40	1.86	22.5	687	150.8
11	0.37	0.24	35.1	803	26.0	0.64	0.25	62.8	805	44.8
12	0.34	0.24	29.4	735	26.7	2.12	1.25	43.3	790	143.0
1976										
01.76	0.56	0.27	51.8	1435	67.6	0.35	0.15	54.7	1499	46.8
02	0.94	0.28	70.2	1012	63.1	0.78	0.44	47.1	959	55.3
03	1.49	0.37	75.2	1285	165.7	0.19	0.08	60.8	1298	21.6
04	1.35	0.31	77.0	2419	275.8	0.39	0.09	62.7	2218	68.4
05	1.14	0.35	69.3	1112	113.0	0.57	0.11	79.8	1111	53.1
06	0.88	0.37	58.0	1119	81.4	0.47	0.07	80.6	1177	44.0
07	0.62	0.18	71.0	530	27.9					
08	0.66	0.29	56.1	525	29.6					
whole period	0.83	0.27	67.4	1444	105.3	0.85	0.43	54.5	1201	80.8

* The average daily loads were computed using the flow rates measured on the days of water sampling.

Średnie ładunki dobowe obliczono na podstawie przepływów w dniach pomiarów.

on human activities. The monthly mean daily load varied greatly from 22 to 372 kg of mercury. The maximum values were rarely recorded, usually in the winter months, accompanied by extreme high water levels.

Based on measurements carried out in the period from March 1975 until the end of June 1976 at Kiezmark and Świbno, the total annual input of mercury (dissolved and particulate) into the Gulf of Gdańsk by the Vistula waters was 29.6 and 32.9 tons respectively. For comparison, the annual mercury discharge of the Rhine is assessed as 100 tons [17]. The mean annual runoff of the Rhine is 2.5 times that of the Vistula, although the drainage area of the Raine is only 14 per cent greater.

Table 3
Tabela 3

Mercury contents in Vistula fish
Zawartość rtęci w ciele ryb z Wisły

Date caught Data połowu	Fish species Gatunek ryby	Total length of fish, cm Całkowita dł. ryby, cm	Mercury contents mg/kg, wet weight Zawartość rtęci mg/kg mokrej masy
2.09.74	pike: *Esox lucius*	30	0.955
	bream: *Abramis brama*	20	0.304
	roach: *Rutilus rutilus*	22	0.202
26.09.74	roach	13	0.446
	roach	19	0.270
	Eur. whitefish: *Coregonus albula*	20	0.363
	Eur. whitefish	18	0.370
	Eur. whitefish	18	0.376
	lamprey: *Petromyzon fluviatilis*	38	0.650
	Vimba vimba	31	2.866
	Vimba vimba	32	2.133
17.10.74	carp: *Cyprinus carpio*	18	0.506
	bream	22	0.420
4.11.74	bream	21.5	0.473
	bream	23.5	0.423
18.11.74	eel: Anguilla anguilla	52	0.443
2.12.74	bream	19	0.413
9.12.74	roach	24	0.305
11.08.75	roach	24	0.175
	bream	19	0.483
	bream	25	0.676
18.08.75	roach	24	0.215
	bream	32	0.393
1.09.75	*Vimba vimba*	32.5	1.600

The data on mercury in fish indicate that the level depends on the fish species, the quantity increasing with the age of the fish within the same species (Table 3). The highest mercury level, of 2.8 mg per kg, was found in *Vimba vimba,* which feeds on the benthic fauna. The direct source of mercury can thus be attributed to bottom sediments. For other fish species (bream, roach, European whitefish, lamprey, eel and pike) the mercury contents varied from 0.18 to 0.96 mg per kg and was 0.42 mg per kg on average. The mercury levels in fish caught in the lowest section of the Vistula were found to agree with those given in world data [6, 12, 15], although they sometimes exceeded the concentrations generally accepted as critical for consumption standards. It should be pointed out that our analyses of the Vistula fish were random; much more on this

matter was done by Nabrzyski and Gajewska [14]. They found among other things that the flesh of the fish caught in the lower Vistula early in the spring of 1972 contained relatively high amounts of mercury, namely 0.48, 0.58 and 0.38 mg per kg for pike, bream, and *Cyprinidae*, respectively.

Chodyniecki et al. [5] found that the mercury levels of various fish species caught in the Gulf of Pomerania and the lower sections of the Oder were lower and varied from 0.00 to 0.37 mg per kg. Herring and cod displayed a tendency to accumulate mercury in the liver, while pike — both in the liver and in the tissue. The highest contents were noted in eel and pike.

The results of studies hitherto point to the necessity for systematic monitoring of mercury contents in the environment and fish of our rivers, particularly the Vistula.

ACKNOWLEDGEMENT

This study was performed at the Institute of Meteorology and Water Management, Marine Branch, Gdynia, and partially supported by the U.S. Environmental Protection Agency under the Project No PR.05·532-13.

ANNA BRZEZIŃSKA
TERESA BOGACKA
REGINA TAYLOR
ANNA TRZOSIŃSKA

Instytut Meteorologii i Gospodarki Wodnej
Oddział Morski — Gdynia

SPŁYW ZWIĄZKÓW RTĘCI Z WODAMI WISŁY

STRESZCZENIE

W pracy przedstawiono wyniki dwuletnich (1974—1976) systematycznych badań nad zawartością związków rtęci w Wiśle, na 69., 509., 926. i 941. km biegu rzeki. Oznaczenia zostały wykonane w dwóch różnych lobaratoriach techniką absorpcyjnej spektrofotometrii atomowej metodą zimnych par, w niesączonych próbkach wody. Dodatkowo uwzględniono ryby wyłowione w dolnej Wiśle, analizując średnią próbkę z całego ciała osobnika.

Stężenie rtęci całkowitej w wodzie wynosiło średnio: 1.01 μg/l w Krakowie, 0,89 μg/l w Warszawie, 0,83 μg/l w Kiezmarku i 0,85 μg/l w Świbnie. Przeciętna zawartość organicznych związków rtęci stanowiła około 70% całkowitej ilości tego metalu we wszystkich przekrojach rzeki, z wyjątkiem odcinka przyujściowego, gdzie wystąpił spadek do 55%. Nie stwierdzono regularnych zmian poziomu rtęci w Wiśle w zależności od sezonu i wielkości przepływu. Na podstawie pomiarów wykonanych na wysokości Kiezmarka i Świbna ocenia się, że ilość rtęci całkowitej, wnoszonej rocznie do Zatoki Gdańskiej, jest rzędu 30 ton.

Wyniki oznaczania rtęci całkowitej w rybach wskazują na zależność między ilością zakumulowanego metalu a gatunkiem i wiekiem osobników. Najwięcej rtęci zawierały certy, które odżywiają się fauną bentosową. W innych gatunkach (leszcz, płoć, sielawa, minoga, węgorz i szczupak) zawartość rtęci mieściła się w granicach od 0,18 do 0,96 mg/kg.

Wyniki pracy wskazują na konieczność wprowadzenia kontroli nad zawartością rtęci w Wiśle.

REFERENCES

LITERATURA

1. Branderberger H., Bader H., *The determination of nanogram levels of mercury in solution by a flameless atomic absorption technique*, Atomic Absorption Newsletter, 1967, 6, s. 101—103.
2. Branderberger H., Bader H., *The determination of mercury by flameless atomic absorption*, II: *A static vapor method*, Atomic Absorption Newsletter, 1968, 7, s. 53—56.

3. Brzezińska A., Trzosińska A., *Oznaczanie związków rtęci w Morzu Bałtyckim metodą bezpłomieniowej spektrofotometrii atomowo-absorpcyjnej*, Studia i Mat. Oceanol., 1976, 14, s. 65—82.
4. Brzozowska K., Podfigurna H., Kosek M., *Badania nad zawartością rtęci w wodach ujścia Wisły*, Ann. Acad. Med. Gedan., 1973, 3, s. 17—27.
5. Chodyniecki A., Protasowicki M., Ociepa A., Juran J., *Badania nad stopniem zanieczyszczenia rtęcią ryb Zatoki Pomorskiej i Dolnej Odry*, Studia i Mat. Oceanol., 1976, 15, s. 33—45.
6. Estes G.O., Knoop W.E., Houghton F.D., *Soil-plant responses to surface-applied mercury*, J. Environ. Qual., 1973, 2, 4, s. 451.
7. Feldman C., *Preservation of dilute mercury solutions*, Anal. Chem., 46, 1974, 1, s. 99—102.
8. Friberg L., Nordberg G., Piscator M., Kjellsbrom T., Vostal J., *Mercury in the environment*, Karolińska Institute, Stockholm, Prepared for US EPA, 1973.
9. *Hydrological, chemical and physical processes in the Gdańsk Basin, Final Report, Project No PR 05.532-13*, IMGW, Gdynia 1977.
10. Januszkiewicz T., *Problem rtęci w środowisku naturalnym i zmienionym przez człowieka*, Wiad. Ekolog., 20, 1974, 3, s. 264—285.
11. Jeffus M.T., Ellins J.S., Kenner C.T., *Determination of mercury in biological materials*, J. Assoc. Off. Anal. Chem., 1970, 53, s. 1172—1175.
12. Johnels A.G., Olsson M., Westermark T., *Esox lucius and some other organisms as indicators of mercury contamination in Swedish lakes and rivers*, Bull. of. int. Epiz., 69, 1968, 9—10, s. 1439—1452.
13. Kečkeš S., Miettinen J.K., *Mercury as a marine pollutant.* Marine Pollution and Sea Life. Fishing News (Books) Ltd. London 1972, s. 276—289.
14. Nabrzyski M., Gajewska R., *Badania nad zanieczyszczeniem rtęcią niektórych ryb słodkowodnych i bałtyckich poławianych głównie w latach 1971—1973*, Studia i Mat. Oceanol., 1976, 15, s. 47—68.
15. Richins R.T., Risser A.C. Jr., *Total mercury in water, sediment and selected aquatic organisms Carson River, Nevada — 1972*, Pest. Mon. J., 9, 1975, 1, s. 44.
16. *U. S. Geological Survey. USGS completes nationwide reconnaissance of metals in streams*, Wat. Sewage Works, 1971, 118, s. 174—195.
17. Weichart G., *Pollution of the North Sea*, Ambio, 2, 1973, 4, s. 99—106.
18. Windom H.L., *Heavy metal fluxes through salt-marsh estuaries*, Estuarine Research, Vol. 1, Asademic Press, 1975, s. 137—152.