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CHANGES IN MERCURY CONTENT IN WATERS OF THE NAREW RIVER AND SOME OF ITS TRIBUTARIES

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Abstract

Although some small amounts of mercury in surface water come from natural environment, much higher quantities originate from anthropogenic sources, including industry and agriculture. Mercury readily accumulates in bottom sediments, from which it can return to water, which can be a serious cause of mercury pollution even after other mercury sources are removed from a river's drainage basin. Concentration of mercury was examined in river waters flowing from basins characterised by different land use and population density. Samples of water were collected from two right tributaries of the Narew River, called the Pisa and the Biebrza, and at six sites in the middle section of the main river. The areas drained by these three rivers lie within the ecosystem known as the Green Lungs of Poland. It was found that the average mercury concentration in the waters of the Narew and its tributaries ranged between 0.3 and 0.9 μg dm^{-3}, being only slightly higher than the concentrations typical of unpolluted territories. The highest mercury content occurred in spring and in the waters from agricultural-forested basins with large towns. Changes in the mercury outflow were associated with accumulation of household pollutants downstream, atmospheric conditions as well as the content of organic matter and suspended solids in the river waters. Low concentration of mineral suspension and organic substance carried by the Pisa River significantly depressed the mercury content in the water of this river. In the Biebrza River, the concentration of both organic and mineral substance was directly proportional to the content of mercury.

Key words: agricultural basin, river water, mercury, concentration, load.

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ZMIANY ZAWARTOŚCI RTĘCI W WODACH NARWI I WYBRANYCH JEJ DOPŁYWÓW

Abstrakt

Niewielkie ilości rtęci w wodach powierzchniowych pochodzą ze źródeł przyrodniczych. Wielokrotnie więcej tego metalu pochodzi ze źródeł antropogenicznych, w tym z przemysłu i rolnictwa. Rtęć łatwo gromadzi się w osadach, skąd może powracać do wód, co może stać się istotnym jej źródłem po usunięciu zagrożeń w zlewni. Badano zawartość rtęci w wodach rzecznych odpływających ze zlewni o zróżnicowanym użytkowaniu i zaludnieniu. Próbki wody pobrano z dwóch prawostronnych dopływów Narwi, tj.: Pisy i Biebrzy, oraz w sześciu punktach środkowego odcinka rzeki głównej. Tereny odwadniane przez badane cieki położone są w zasięgu ekosystemu „zielonych płuc" Polski. Stwierdzono, że średnie stężenie rtęci w wodach Narwi i jej dopływów mieściło się w granicach od 0,3 do 0,9 µg dm^{-3} i były niewiele wyższe od stężeń charakterystycznych dla obszarów niezanieczyszczonych. Najwyższe stężenie rtęci wykazano wiosną w wodach ze zlewni rolniczo-leśnych z dużymi ośrodkami miejskimi. Średni roczny odpływ rtęci wyniósł 0,3–3,3 g z 1 ha, średnio ok. 1 g z 1 ha zlewni. Na różnice w odpływie rtęci miały wpływ kumulacja zanieczyszczeń bytowych z biegiem rzeki, warunki atmosferyczne oraz zawartość materii organicznej i zawiesin w wodach rzecznych. Niska zawartość zawiesiny mineralnej i substancji organicznej w wodach Narwi nie wpływała istotnie na stężenia Hg. Stwierdzono, że mineralna część substancji niesionych wodami Pisy miała istotny wpływ na obniżenie stężenia rtęci w wodzie tej rzeki. W wodach Biebrzy zarówno stężenia substancji organicznych, jak i mineralnych wykazywały wprost proporcjonalną zależność w stosunku do zawartości rtęci.

Słowa kluczowe: agricultural basins, river water, mercury, concentrations, load.

INTRODUCTION

Regular environmental monitoring is a basic measure which enables us to determine the causes and their quantitative and qualitative contribution to pollution. As a result, it can imply possible preventive actions to stop degradation of natural resources. Water ecosystems largely contribute to influx of pollutants. Content of harmful substances in river ecosystems is shaped, either directly or indirectly, under the effect of natural conditions and man-made factors (HERMANOWICZ et al. 1999). Dispersion of elements in a river channel depends on hydrodynamic processes, the river's hydrological regime as well as physical and chemical parameters, which, on a global scale, are differentiated primarily by climatic conditions (GRABIŃSKA et al. 2005a, JAIN et al. 2005). Other than natural factors contributing to pollution of surface waters with heavy metals are intensive farming practice, increasing urbanisation and growth of industry (ADAMIEC, HELIOS-RYBICKA 2002).

The content of mercury in the waters of the Narew could be conditioned by the agricultural use of its basin (surface influx) and atmospheric depositions. Mercury compounds are found in minerals fertilisers, pesticides and waste products used in agriculture (FALENICKA-JABŁOŃSKA 1991). The quality of water in the Narew River is also affected by household sewage and wastewater from larger human settlements (Białystok, Bielsk

Podlaski, Łapy, Łomża, Ostrołęka, Różan) as well as wastewater from agricultural, food processing, construction material industries and power plants located in the river's catchment basin (SKORBIŁOWICZ 2005).

This article deals with concentrations of mercury in river waters depending on the atmospheric conditions and land use. The analysis of Hg content fluctuations is a preliminary step towards studying changes in the Hg concentration in bottom sediments. Negative effect of mercury accumulated in sediments on living organisms can occur also when the Hg concentration in the water above is within the water purity standards. Elements retained in bottom sediments can be a secondary source of pollution, which threatens not only a given water ecosystem but also the nearby land ecosystems (BOJAKOWSKA 2001). By knowing the volume of Hg outflow, we should be able to predict the ecological state of the whole ecosystem, which belongs to the extraglacial lowland belt and the Green Lungs of Poland. This knowledge can also help to plan and implement a sustainable development concept for the whole basin of the Narew River. Mercury, like cadmium and lead, is useless and often harmful to water plants and animals. In man, mercury causes neurological disorders (HERMANOWICZ et al. 1999). Another reason why our study seemed worthwhile was the fact that waters from the Narew River are used by Warsaw agglomeration (Zegrzyński reservoir).

MATERIAL AND METHODS

The results presented in this paper comprise seven years (1997–2003). The study involved the middle part of the Narew at six gauging sections, with one site, in Strękowa Góra (262 km from the river mouth) being treated as a representative point for the partial catchment basin of the Narew. The sampling site in Różan (117 km from the river mouth) served as a closing point for the area distinguished for the research project. Comparative analysis was performed for the two main tributary rivers of the Narew, the Pisa and the Biebrza, at the mouth profiles.

The natural conditions and varied effects of man's economic activities within the drainage basin of the three rivers have been discussed in the paper published by GRABIŃSKA et al. (2005b). Detailed description of field work (hydrometric measurements) and data processing (statistical processing and graphic presentation of the results) can be found in GRABINSKA et al. (2006).

The results concerning the mercury content in river waters are part of the physicochemical determinations performed on samples of water collected in the basin. Water samples were obtained four times a year: in spring (April), summer (July), autumn (October) and winter (January) from the river current. Water sampling and mercury determinations relied on the methods presented by HERMANOWICZ et al. (1999).

RESULTS

The literature claims that the migration rate of trace elements from water solution to sediments in a river channel depends on physicochemical properties of river waters, proportion between the suspension mass and mass of water as well as presence of fine-grain deposits (clay and silt), which are highly sorptive (MILLER 1997). The results of our analyses suggest that the Narew and its two tributary rivers, compared to other Polish rivers (the Vistula and the Bug) carried very small amounts of suspended solids (an annual average of 37.8 thousand tonnes). GRADZIŃSKI et al. (2000) emphasise that the load in the Narew River is dominated by sandy material (medium and coarse-grain), the river waters are rich in organic suspension, and the amount of mineral suspension (i.e. silt and clay) is small. Increasing quantities of heavy metals transported by the Narew can be attributed to small amounts of clastic material (small sorptive properties) carried by the river waters and the presence of organic matter. Humus compounds, common in soils, marshes, peatbogs and wetlands, and such types of land are present in the Biebrza River valley and the upper Narew drainage basin, shape the distribution of heavy metals in water environment in the form of dissolved organic complexes (HERMANOWICZ et al. 1999).

The highest concentration of mercury was determined in the waters of the Biebrza and Pisa (Table 1). The ranges of mercury concentration in the Biebrza and Pisa remained on approximately the same level, but were wider in the Narew (the longitudinal profile).

As regards the land use, less mercury was determined in waters flowing from the forested- agricultural basin (the upper Narew), which, in terms of mercury content, were classified as water purity class I (very good) than from the agricultural-forested basins, where the waters belonged to water purity class II (good).

According to the seasons of the year (Table 2), the highest average Hg concentration occurred in summer (0.7 $\mu g \cdot dm^{-3}$) and the lowest one – in winter (0.4 $\mu g \cdot dm^{-3}$). Particularly high levels of mercury (3-fold higher) in summer were determined in the Biebrza compared to the other two rivers. Elevated concentrations of mercury in summer could be attributed to the surface influx of pollutants (e.g. plant protection chemicals) caused by rains. The content of mercury in each season of the year in the waters of the Narew was much more variable than in the waters of the Biebrza and Pisa, which is due to the contribution of different sources of pollution.

Table 1
Tabela 1

Effect of land use in the drainage are on average mercury concentration in waters of the three rivers (μg·dm^{-3})
Wpływ zagospodarowania zlewni na średnie stężenia rtęci w wodach badanych rzek (μg·dm^{-3})

Land use Użytkowanie zlewni	Basin/gauging point in a longitudinal profile of the Narew Zlewnia/ punkt pomiarowy w profilu podłużnym Narwi	Year – Rok							Average Średnia
		1997	1998	1999	2000	2001	2002	2003	
Agricultural and forested Rolniczo-leśne	Biebrza/mouth Biebrzy/ujście	0.3	0.4	1.5	0.9	0.4	0.5	0.5	0.7
	Pisa/mouth Pisy/ujście	0.3	0.4	1.5	0.8	0.4	0.5	0.6	0.7
Forested and agricultural Leśno-rolnicze	upper Narew górnej Narwi (262 km rzeki)	0.3	0.5	0.5	0.4	0.3	0.5	0.6	0.4
Agricultural and forested Rolniczo-leśne	Narwi/Wizna (246 km rzeki)	0.8	0.5	0.8	0.4	0.3	0.5	0.8	0.5
	Narwi/Piątnica (204 km rzeki)	0.3	0.3	0.9	0.3	0.3	0.5	0.7	0.5
	Narwi/Nowogród (181 km rzeki)	0.4	0.5	0.6	0.4	0.3	0.5	0.5	0.5
	Narwi/Ostrołęka (147 km rzeki)	0.5	0.6	0.9	0.7	0.4	0.4	0.9	0.6
	Narwi/Różan (117 km rzeki)	0.5	0.6	1.0	0.6	0.6	0.3	0.9	0.7
Average – Średnia		0.4	0.5	1.0	0.6	0.4	0.5	0.7	

Different loads of mercury transported by the Narew in its longitudinal profile (Fig. 1) could prove that the source of this element is anthropogenic. Our study showed that the highest levels of mercury were in the waters of the Narew collected at the last gauging section (in Rózan). This could have been a result of the increasing accumulation of mercury in the river water downstream, caused by the influx of household sewage and wastewater from treatment plants in the towns located on the Narew (i.e. Łomża, Nowogrów, Ostrołęka and Rózan) and from some smaller towns and villages, situated in the river valley, which lack proper wastewater management systems.

Table 2
Tabela 2

Comparison of seasonal concentrations of mercury in waters of the three rivers (μg·dm^{-3})
Porównanie sezonowych stężeń rtęci w wodach badanych rzek (μg·dm^{-3})

Land use Użytkowanie zlewni	Basin/gauging point in a longitudinal profile of the Narew Zlewnia/ punkt pomiarowy w profilu podłużnym Narwi	Spring Wiosna	Summer Lato	Autumn Jesień	Winter Zima	Average Średnia
Agricultural and forested Rolniczo-leśne	Biebrza/mouth Biebrzy/ujście	0.4	1.5	0.4	0.3	0.7
	Pisy/ujście	0.6	0.4	1.0	0.5	0.6
Forested and agricultural Leśno-rolnicze	upper Narew górnej Narwi (262 km rzeki)	0.4	0.4	0.5	0.4	0.4
Agricultural and forested Rolniczo-leśne	Narwi/Wizna (246 km rzeki)	0.7	0.5	0.6	0.3	0.5
	Narwi/Piątnica (204 km rzeki)	0.6	0.5	0.4	0.3	0.4
	Narwi/Nowogród (181 km rzeki)	0.5	0.4	0.5	0.4	0.4
	Narwi/Ostrołęka (147 km rzeki)	0.5	0.5	0.6	0.6	0.6
	Narwi/Różan (117 km rzeki)	0.6	0.6	0.6	0.7	0.6
Average – Ś rednia		0.5	0.7	0.6	0.4	

The mean outflow of mercury (Table 3) in the upper Narew (Strękowa Góra) was 0.7 g·ha^{-1}, rising to 1.0 g·ha^{-1} in Różan. The average annual load of mercury transported by the water of the Biebrza was slightly higher than that determined for the Pisa. The fact that loads of mercury transported by the Biebrza and Pisa were similar could be explained by similarities in the land use between both drainage areas.

The distribution of Hg concentrations (Table 1) and outflow (Table 3) was not uniform in the years, as it depended on the volume of flow, which was a product of time-related variability in atmospheric precipitation, on the basis of which unit outflows were computed (GRABIŃSKA et al. 2005b). In 1999, which was a wet year (KACZOROWSKA 1962), the outflow was 17% higher than the average unit outflow for the whole time period (1997–2003), Increased concentrations of mercury in the waters of all the three rivers in this wet year exceeded those in years characterised by typical

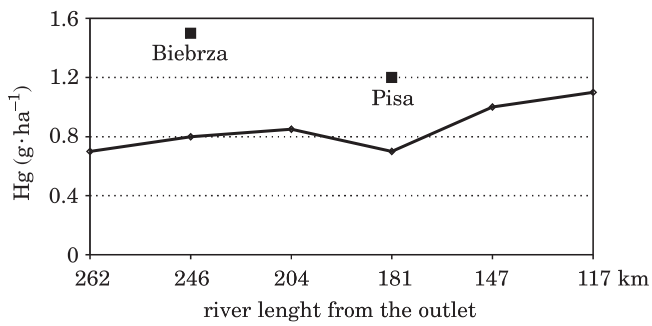

Fig. 1. Changes in the mean annual load of mercury in a longitudinal profile of the Narew river (g·ha^{-1}). The tributary river Biebrza – 248.5 km of the Narew's course; the Pisa – 181 km

Rys. 1. Zmiany średniego rocznego ładunku rtęci w profilu podłużnym rzeki Narwi (g·ha^{-1}). Dopływ Biebrzy – 248,5 km biegu Narwi; Pisy – 181 km

Table 3
Tabela 3

Effect of land use in the drainage basin on the outflow of mercury with waters of the three rivers (g·ha^{-3})
Wpływ zagospodarowania zlewni na odpływ rtęci z wodami badanych rzek (g·ha^{-3})

Land use Użytkowanie zlewni	Basin Zlewnia	Year – Rok							Average Średnia
		1997	1998	1999	2000	2001	2002	2003	
Agricultural and forested Rolniczo-leśne	Biebrza/mouth Biebrzy/ujście	0.3	0.6	3.3	1.2	0.5	1.1	1.0	1.5
	Pisy/ujście	0.4	0.7	2.9	1.3	0.5	0.9	1.0	1.2
Forested and agricultural Leśno-rolnicze	upper Narew górnej Narwi (262 km rzeki)	0.4	0.7	1.1	0.5	0.4	0.7	0.9	0.7
Agricultural and forested Rolniczo-leśne	Narwi/Wizna	1.1	0.6	1.1	0.5	0.4	0.7	1.1	0.8
	Narwi/Piątnica	0.5	0.5	1.4	0.5	0.5	0.8	1.0	0.8
	Narwi/Nowogród	0.6	0.8	0.9	0.7	0.5	0.8	0.8	0.7
	Narwi/Ostrołęka	0.8	1.0	1.4	1.1	0.6	0.6	1.4	1.0
	Narwi/Różan	0.8	1.0	1.6	1.0	0.9	0.5	1.4	1.1
Average – Średnia		0.6	0.7	2.0	0.9	0.5	0.8	1.1	

rainfalls, and the average Hg load computed for 1999 was 50% higher relative the value obtained for the whole experiment.

No elevated Hg concentrations or outflows were observed in the upper Narew, where the largest urban settlement (Białystok) in the whole basin is located.

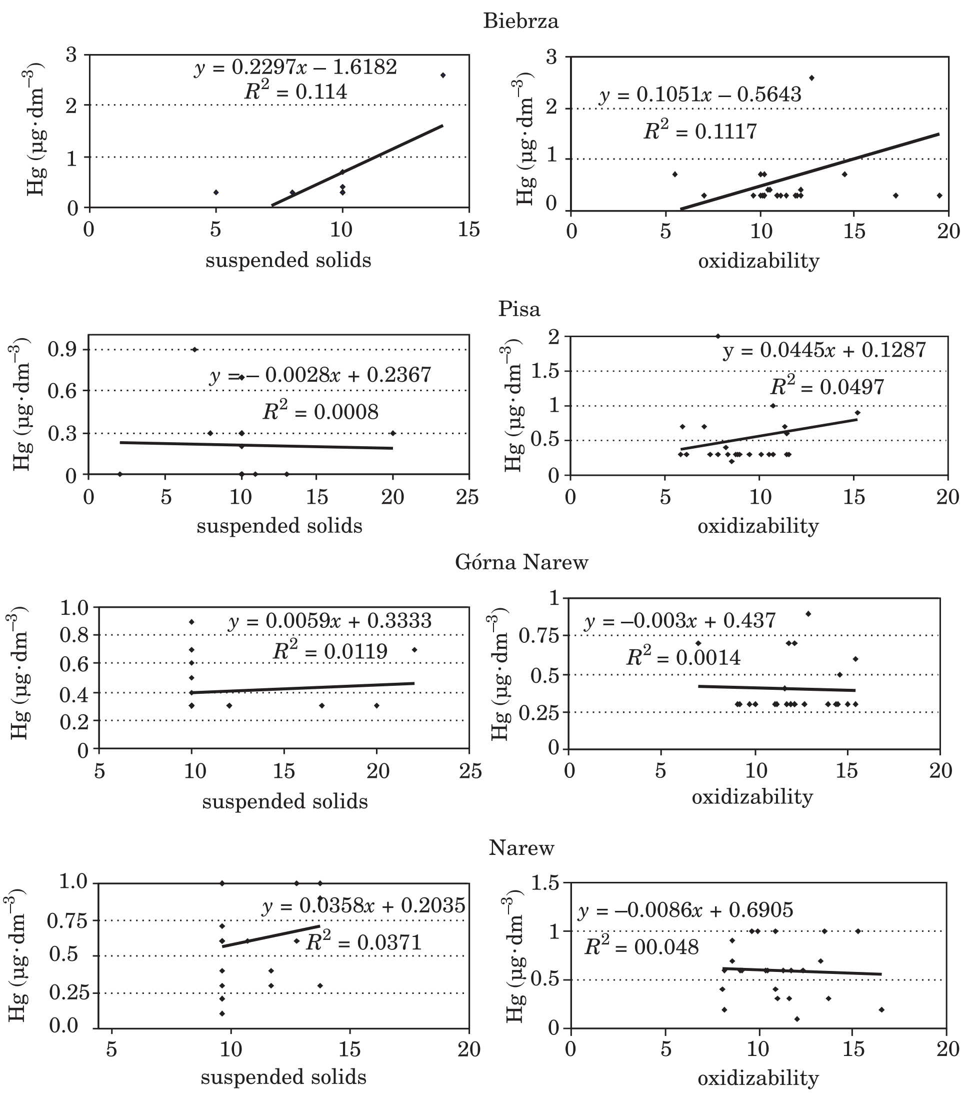

Fig. 2. Correlation between the content of suspended solids and oxidizability ($\mu g \cdot dm^{-3}$) and concentrations of mercury in waters of the three rivers

Rys. 2. Zależność między zawartością zawiesin i utlenialności ($\mu g \cdot dm^{-3}$) a stężeniami rtęci w badanych wodach rzecznych

Changes in the content of total suspended solids and organic matter versus Hg concentrations in the river waters are shown in Figure 2. Concentrations of the heavy metals in the Biebrza waters turned out to be directionally proportional in terms to oxidizability. In the waters of the Narew, Hg concentrations showed no correlation with the content of organic matter, whereas in the Pisa River they were directly proportionally correlated with the oxidizability value (concentration of easily decomposable substances). Reversely proportional correlation occurred between concentrations of mercury and contribution of matter suspended in the waters of the Pisa. Likewise, the concentrations of Hg were directly proportionally correlated with the amount of organic matter in the waters of the Biebrza River, which were classified as belonging to the poorest water quality class among the three rivers (GRABIŃSKA et al. 2005b). The analyses suggest that the mineral part of the substances transported by the Narew River did not have any influence on retaining mercury in the river. The suspended and organic material carried by the Biebrza River seemed to produce a much stronger effect.

In the waters of the tributary rivers, increase in the concentration of mercury corresponded to a highly significant (α<0.01) increase in the value of expected cadmium concentrations (Table 4). Negative, highly significant correlation was found between Hg and Ni in the Biebrza River. Positive, significant correlations were determined for Hg and Cu, Cd, Pb and Ni in the waters of the Narew. As regards the remaining elements, increased concentrations of mercury were accompanied by significant decrease in expected concentrations of sulphates.

The results indicate that the waters of the Narew and its two tributary rivers contained small quantities of mercury compared to other major Polish rivers (ŚWIDERSKA-BRÓZ 1987). However, the Hg concentrations

Table 4
Tabela 4

Coefficients of linear correlation (r) between mercury concentrations and chosen properties of water in investigated river
Współczynniki korelacji prostej (r) między stężeniami rtęci oraz niektórymi cechami badanych wód rzecznych

Basin Zlewnia	Zn	Cu	Cd	Pb	Ni	SO_4^{-2}	PO_4^{-3}	Ca
Biebrza	-0.080	-0.043	0.408*	0.005	-0.992***	-0.447*	0.256	0.185
Pisa	-0.038	-0.086	0.802***	-0.198	-0.066	0.197	-0.086	0.132
Górna Narew	-0.117	-0.164	-0.191	-0.158	-0.131	-0.224	-0.236	-0.294
Narew	-0.117	0.328*	0.391*	0.492**	0.415*	-0.185	-0.043	0.010

*r – significant at level α=0.05; **α=0.01; ***α=0.001;
n=24; sample size

determined in the course of the study were slightly higher than the value regarded as natural in river waters (KABATA-PENDIAS, PENDIAS 1993). The statistical analyses confirmed that the presence of towns or large villages and, in consequence, influx of household sewage and wastewater, results in increased loads of mercury transported in a river down its flow. The distribution of mercury loads in river waters was affected by particular meteorological and hydrological conditions prevailing in the years and seasons of the year during our experiment. The concentration of mercury in the Narew River did not depend significantly on its content of organic matter and mineral substances. This dependence was stronger in the case of the Biebrza and Pisa.

CONCLUSIONS

1. Waters transported down the Narew River and two of its tributaries contained slightly higher mercury concentrations than typical of unpolluted environment. Differences in the hg content were conditions by atmospheric factors and accumulation of household pollutants downstream.

2. In a wet year (1999), the unit outflow of water increased by 17% and the load of mercury went up by 50% compared to an average water outflow and mercury concentration in 1997-2003.

3. Waters drained from a forested-agricultural catchment area (the upper Narew) contained 57% less mercury than those flowing from agricultural-forested drainage areas (the Biebrza and the Pisa). The mean annual load of mercury carried away with the waters of the Narew River was increasing down the river stream, as a result of increasing loads of household pollutants from point sources of pollution (wastewater treatment plants) and surface flows from farmland.

4. Concentration of organic matter and mineral suspension in the waters of the Narew did not affect significantly the concentration of mercury. Stronger dependence between these two factors was found in the case of the Biebrza River.

5. Statistical analyses revealed highly significant positive correlation between mercury concentrations and expected concentrations of cadmium as well as highly significant but negative correlation between nickel concentrations in the waters of the Biebrza and Pisa. In the waters of the Narew, increased Hg concentrations corresponded to a significant increase in the values of expected concentrations of Cu, Cd, Pb and Ni, which may confirm the fact that all these metals originate from a similar source and circulate in a similar way. On the other hand, increased concentrations of sulphates were accompanied by significantly depressed levels of mercury.

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