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*Original Research*

# Magnitude of Nitrogen and Phosphorus Delivered to Baltic Sea via Polish Rivers

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## Abstract

The purpose of the presented paper is to recognize the impact of the Baltic Sea drainage basin, located on Polish territory, on nitrogen and phosphorus riverrine exports to sea. Yearly figures from 1990 to 2011 in Statistical Yearbooks were used. Figures comprising data before were not presented. Load of substance transferred was significantly correlated with water inflow to sea. No trend to increase the load of total and nitrate and total nitrogen was observed, though significant trends to decrease the loads of ammonia nitrogen and phosphate phosphorus were ascertained. Nitrogen and phosphorus loads in wastewater discharged after its purification were significant. The greatest future risk to the Baltic Sea environment is the huge amount of phosphorus application in agriculture in the drainage basin.

**Keywords:** Baltic Sea, water pollution, nitro gen load, phosphorus load, impact of agriculture

## Introduction

Environmental conditions in the waters around the coasts of the Baltic Sea are presently the focus of research, monitoring, and international measures. Major remediation efforts are expected in the drainage area to comply with international agreements. Eutrophication can be regarded as the major environmental problem of the Baltic Sea. The pollution of the Baltic Sea with phosphorus and nitrogen is recognized as a main problem to be solved. A decisive reduction of these nutrient emissions is needed in order to restore the Baltic Sea to a sound balance. Nutrients and other contaminants enter the Baltic Sea in rivers, in runoff from coastal areas, through exchange of water with the North Sea, through atmospheric deposition, and due to human activities at sea [1]. The sources of pollution around an entire sea were made subject to the first convention, signed in 1974 by the then seven Baltic coastal states. In the light of political changes a new convention was signed in 1992 by all the states bordering the Baltic, and the European Community. The governing body of the Convention is the Helsinki Commission – the Baltic Marine Environment Protection Commission (also known as HELCOM). The present contracting parties declared to take appropriate action [2]. Proper operations were taken to mitigate the inflow of nutrients originating from wastewater and measures were elaborated to abate the non-point water pollution from agricultural sources.

Nutrients – especially nitrogen and phosphorus – are vital for marine life. But the presence of excessive nutrients can seriously disturb the functioning of marine ecosystems. Agricultural activities and municipal wastewater are supposed to be the main causes of pollution with these nutrients as well as with some organic substances. Pollutant flow dimension on the spot needs to be distinguished, a rather complex demand. Assessed relations among the changes of multi-parameter concentrations in river water showed that the inflow nitrate nitrogen and total nitrogen followed the dispersed source pattern, and phosphorus the point source pattern [3].

The aim of the presented paper is the use of multi-parameter concentration changes to distinguish the origins of nitrogen and phosphorus delivered with rivers from Poland into the Baltic.

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## The Baltic Sea

The Baltic Sea is almost totally enclosed by land, and only connected to the North Sea by narrow and shallow straits around Denmark and Sweden. This limits the exchange of water with the open sea. It typically takes about 25-30 years for all the water in the Baltic Sea to be replaced. More than 200 large rivers bring fresh water into the Baltic, making it the world's biggest brackish sea. Fourteen countries lie within the catchment area of the Baltic, which covers 415,266 km$^2$ with a total drainage area of about 2,150,000 km$^2$ (Fig. 1). In Denmark, Germany, and Poland as much as 60-70% of the Baltic's catchment area consists of farmland. Forests, wetlands, and lakes make up between 65% and 90% of the catchment area in Finland, Russia, Sweden, and Estonia. Nine countries share the Baltic Sea coastline: Sweden, Finland, Russia, Estonia, Latvia, Lithuania, Poland, Germany, and Denmark. The drainage area also includes parts of Belarus, Norway, Ukraine, the Czech Republic, and the Slovak Republic. Nearly 85 million people live in the Baltic catchment area: 26% of them in large metropolitan areas, 45% in smaller urban areas, and 29% in rural areas. Population densities vary from over 500 inhabitants per km$^2$ in urbanized regions of Poland, Germany, and Denmark to fewer than 10 inhabitants per km$^2$ in northern parts of Finland and Sweden. Almost 15 million people live within 10 km$^2$ of the coast. Contaminants and nutrients enter the Baltic Sea in rivers, in runoff from coastal areas, through exchange of water with the North Sea, through atmospheric deposition, and due to human activities at sea. It takes about 25-30 years for all the water in the Baltic Sea to be renewed, so persistent pollutants can remain in the Baltic for a long time [1].

## Nutrient Sources

Baltic Sea water is supplied with phosphorus from two sources, from atmospheric deposition and river input, and nitrogen from microbial activity. Wasmund et al. [8] have estimated annual nutrient input from different sources into Baltic Sea (Table 2).

Atmospheric deposition is an important input source of nitrogen to the Baltic. Nitrogen atmospheric deposit was increased 2.5 times in 1970-95; the rise was not so intensive in following years. Average deposition of inorganic nitrogen to the Gulf of Finland was 6.8, and to the Baltic proper 8.3 kg $N \cdot ha^{-1} \cdot y^{-1}$ [4]. Nitrogen in precipitation was composed of 10% of organic N and approximately equal amounts of ammonium and nitrate [5]. Bartnicki et al. [6], using the EMEP Unified model, calculated the total deposition of nitrogen to the Baltic. This deposit comprises wet and dry deposition of oxidized and reduced nitrogen species. Its depositions reached 202 kt N in 2007.

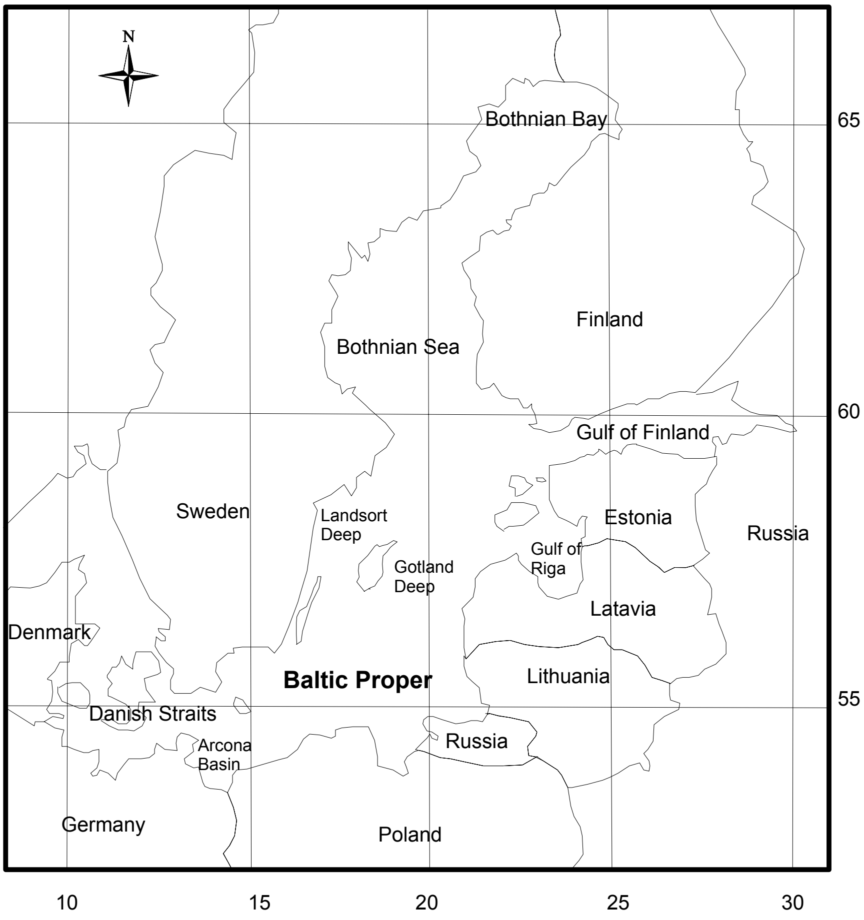


Fig. 1. Map of Baltic Sea.

Table 1. Total riverrine loads of nitrogen and phosphorus flowing to the Baltic Sea from adjusted countries in 2006 [2].

| Country | $N_{tot}$ (tonnes $t \cdot y^{-1}$) | $P_{tot}$ (tonnes $a^{-1} \cdot t \cdot y^{-1}$) | Population mln |
|---|---|---|---|
| Denmark | 53.0 | 1.520 | 5.5 |
| Estonia | 20.4 | 790 | 1.3 |
| Finland | 79.0 | 3.490 | 5.1 |
| Germany | 16.9 | 490 | 82.129 |
| Latvia | 59.5 | 2.800 | 2.3 |
| Lithuania | 28.0 | 1.240 | 3.4 |
| Poland | 152.6 | 10.240 | 38.1 |
| Russia | 107.6 | 4.070 | 132.1 |
| Sweden | 121.0 | 3.730 | 9.2 |
| Total | 638.0 | 28.370 | - |

The greatest deposition, above 10 kg $N \cdot ha^{-1} \cdot y^{-1}$, was observed on the southern part of the sea, and was decreasing gradually to the north down to 1 kg near the North Pole. The main emission countries contributing to total nitrogen deposition are: Germany 18-22%, Poland 11-13%, and Denmark 8-11%. There is also a significant contribution from distant sources like the United Kingdom (6-9%), as well as from international shiping traffic on the Baltic (4-5%) [6].

Diazotrophic cyanobacteria in marine environments represent an important instantaneous source of new nitrogen in marine environments for bacteria and higher trophic levels. Some species of cyanobacteria contribute to the nutrient input by their ability for nitrogen fixation, an enzymatic process that converts binitrogen ($N_2$) into organic nitrogen. Total fixation in the Baltic Sea proper, a part of the sea (Fig. 1), was estimated for 180-430 kt $N \cdot y^{-1}$. In the central Baltic Sea an average fixation was 24.2 kg $N \cdot y^{-1}$, which exceeds five times the annual atmospheric deposition of dissolved inorganic nitrogen (DIN) equal to 5.2 kg $N \cdot y^{-1}$ [7]. The Baltic proper is the marine region with the most intensive nitrogen fixation of the global oceanic nitrogen fixation, which can reach 640 kt $N \cdot y^{-1}$. Though its area covers only 0.06% of the world's oceans it accounts for 0.3 to 0.6% of the global oceanic nitrogen fixation [8].

The main amount of nitrogen is entering the Baltic via rivers, and this part of input is faithfully monitored. Riverrine load of nitrogen are divided among the countries in the Baltic watershed (Table 1). The greatest load originates from Poland because Poland has the highest population.

One way to remove nitrogen from the sea is the denitrification process, which efficiency varies between 426-652 kt $N \cdot y^{-1}$, which is around 48-73% of the external N inputs supplied via rivers, coastal point sources, and atmospheric deposition [9].

The estimated total load of phosphorus on the Baltic in 2000 was 34,600 tons P. Assumed atmospheric deposition is less than 5% of the total load, but is the greatest from Poland [2]. The most recent estimates of atmospheric phosphorus deposition to Baltic are those reported by Knulst [10], who found annual deposition rates of 0.508, 0.230, and 1.16 kg total $P \cdot ha^{-2} \cdot yr^{-1}$ at sites of three Swedish inland [10]. 20% of phosphorus in deposit was in organic form. There is observed a worldwide tendency to a bigger phosphorus deposition on lakes of greater area [11].

## Materials and Methods

Water flowing from Polish territory to the Baltic Sea in 98.9 percent originates from the Polish drainage area. Records of precipitation, water inflow into sea, and substance loads carrying with rivers, nitrogenous gases emissions, pollutant loads in municipal wastewater discharged after treatment, and mineral fertilizer consumption covering 1990-2011 are collected from statistical year books [12]. In a recent edition (2011) some 2010 casings are omitted. The above facts regarding Poland before 1989 are not plainly obtainable from the official national statistical data.

## Results

The trend in precipitation changes was insignificant. A period with higher precipitation occurred from 1994 to 2002, and next an opposite period, with lower precipitation happened from 2003 to 2009. Average water input with precipitation on total Polish territory was 201.7 $km^{-3} \cdot y^{-1}$, with 21% standard deviation, water outflow into the Baltic Sea was respectively 52.3 $km^{-3} \cdot y^{-1}$, with 11% standard deviation. Likewise, the riverine water inflow to the Baltic was changing with agreement to high precipitation (Fig. 2); correlation coefficients between these two elements were significant, though of low values (0.62** – Pearson, 0.59** – Spearman).

This results in an apparent relationship of substance load from water inflow in each case. Average yearly inflow of total nitrogen was low, but was evidently greater in years when floods occurred (Fig. 3). No changes of total nitrogen load in years were observed, and the trend was insignificant with $R^2$ equal 0.001. Similaly, no significant trend was found in the case of nitrate nitrogen (Table 3). The load of

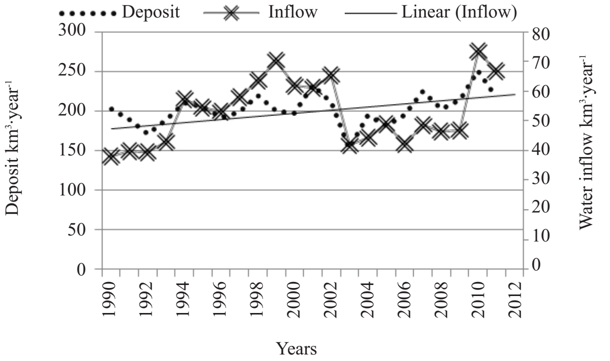


Fig. 2. Annual riverine water inflow to the Baltic Sea from Polish territory vs. precipitation.

Table 2. Estimated total annual nutrient input into the Baltic Sea [8].

| Pathway | Nitrogen (kt·a$^{-1}$) | Phosphorus (kt·a$^{-1}$) |
|---|---|---|
| Riverine load | 638 | 41,000 |
| Atmospheric deposition | 202 | 5,500 |
| N$_2$ fixation | 426–652 | |
| All pathways combined | 1,400 | 45,500 |

nitrate-nitrogen was half of the total nitrogen load; however, both were significantly correlated with water inflow to the sea. Ammonia-nitrogen loads showed a decreasing trend from 2000, with R$^2$ equal to 0.424*, but was not significant (Table 3). Ammonia-nitrogen shares only 7% of total nitrogen inflow. The nitrogen load depended on the nitrogen budget on Polish territory, which includes consumption of nitrogen mineral fertilizers, emissions of nitrogenous gases, and amount of nitrogen discharged with wastewater to surface waters. The average nitrogen fertilizer consumption reached 688 kt·N·a$^{-1}$, and was doubled since the beginning of the study, but on average only 27% of nitrogen applied with mineral fertilizer reached the sea (Fig. 4). The load of nitrogen in riverine was merely 27% of 15 Mg t N in fertilizers applied in Polish agriculture during study time. The average total of nitrogen emitted with gaseous nitrogenous compounds (NH$_3$ and NO$_x$) reached 595 Kt N·y$^{-1}$, and this portion of nitrogen was equivalent to only 31% of total nitrogen load in inflow to sea (Fig. 5). However, the difference in methods of data collection should be considered in these comparisons. The figures of substance load inflow to the sea are facts experimentally measured, whereas emissions data are simulated by use of chosen models. The load of nitrogen discharged with treated wastewater to surface waters decreased significantly and was plainly halved since the 1990s (Fig. 6).

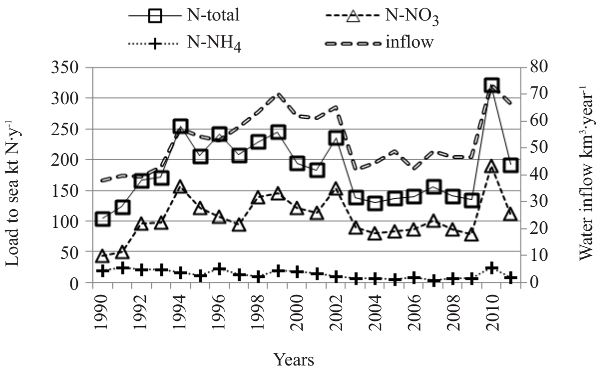


Fig. 3. Annual riverine inflow of nitrogen species from Polish territory to the Baltic Sea.

The load of total phosphorus was also dependent on water inflow to the sea. It was low, though increased up to 16 Kt P·y$^{-1}$ when floods occurred (Fig. 7). No trend of

Table 3. Annual loads of substances delivered with rirverine water from Polish territory into the Baltic Sea and significance of trends of its changes in 1990-2011 [12].

| Cause | Mean | Total 1990-2011 | Variation coefficient % | Trend significance R$^2$ |
|---|---|---|---|---|
| Precipitation (km$^{-3}$·a$^{-1}$) | 202.4 | 4,452 | 10.3 | 0.132 |
| Water inflow to Sea (km$^{-3}$·a$^{-1}$) | 53.0 | 1,165 | 20.5 | 0.096 |
| Load of N$_{tot}$ (G·a$^{-1}$) | 184.2 | 4,053 | 29.5 | 0.001 |
| Load of N-NO$_3$ (G·a$^{-1}$) | 106.5 | 2,344 | 32.9 | 0.044 |
| Load of N-NH$_4$ (G·a$^{-1}$) | 13.6 | 299 | 50.8 | 0.424 |
| Load of P$_{tot}$ (G·a$^{-1}$) | 11.6 | 255 | 21.4 | 0.015 |
| Load of P-PO$_4$ (G·a$^{-1}$) | 4.9 | 108 | 36.6 | 0.588* |
| Load of Mg (G·a$^{-1}$) | 585 | 12,864 | 16.1 | 0.015 |
| Load of Ca (G·a$^{-1}$) | 4332 | 95,296 | 22.5 | 0.093 |
| Load of Cl (G·a$^{-1}$) | 5322 | 117,077 | 11.8 | 0.096 |
| Load of S-SO$_4$ (G·a$^{-1}$) | 2,106 | 46,343 | 19.4 | 0.064 |
| Load of BOD$_5$ (G·a$^{-1}$) | 206 | 4,543 | 19.4 | 0.211 |
| Load of dissolved substances (G·a$^{-1}$) | 23,723 | 521,910 | 16.5 | 0.044 |
| Load of suspension (G·a$^{-1}$) | 898 | 16,168 | 24.4 | 0.072 |
| N-NH$_3$ emissions (G·a$^{-1}$) | 293 | 6,445 | 20.2 | |
| N-NO$_x$ emissions (G·a$^{-1}$) | 302 | 5,740 | 14.1 | |
| N fertlization (G·a$^{-1}$) | 688 | 15,142 | 17.3 | |

*Trend significant at 0.54

changes was observed ($R^2 = 0.015$). Load of phosphate phosphorus was 42% of total, although in opposition to total phosphorus showed a significant trend to decrease ($R^2$=0·588), especially since 2003. Consumption of phosphorus fertilizer was really high, but was halved since 1990. No relationship between fertilization and phosphorus inflow to the sea was found (Fig. 8). The load of phosphorus introduced with discharged treated wastewater was 60.4 kt t P·y$^{-1}$, that is 24% of total load in riverine water. Amounts of phosphorus in this discharge were significantly decreasing down to 1.2 from 6.9 kt t P·y$^{-1}$ (Fig. 9).

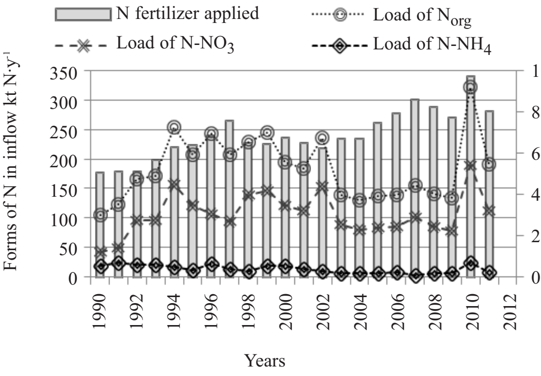


Fig. 4. Agricultural use of nitrogenous mineral fertilizer vs. nitrogen species load in riverine inflow to the Baltic Sea from Polish territory.

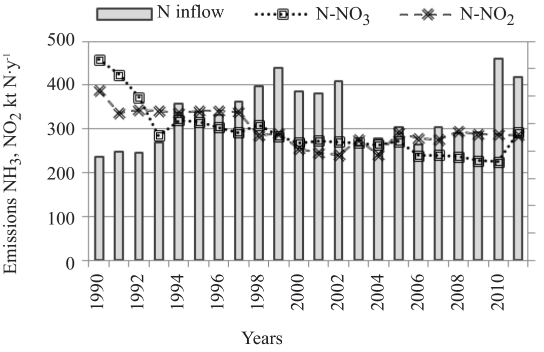


Fig. 5. Relationship between emissions of nitrogen gaseous species from Poland and riverrine nitrogen inflow to the Baltic Sea.

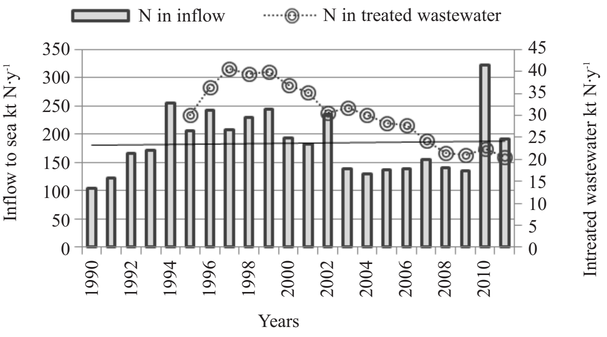


Fig. 6. Annual treated wastewater discharged to surface waters on background of inflows of total nitrogen load with riverine water.

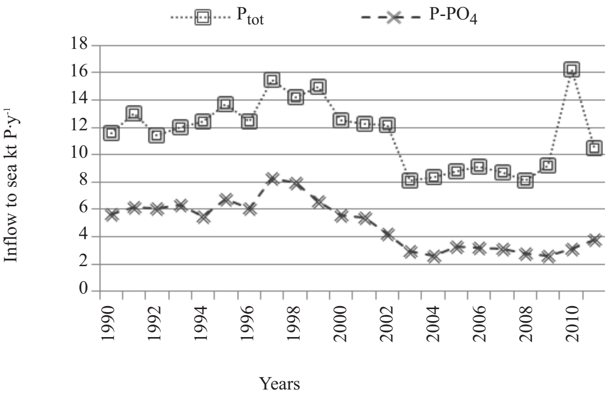
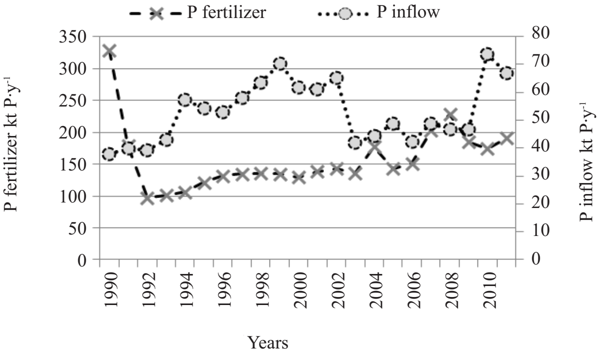


Fig. 7. Annual riverine inflow of phosphorus species from Polish territory to the Baltic Sea.



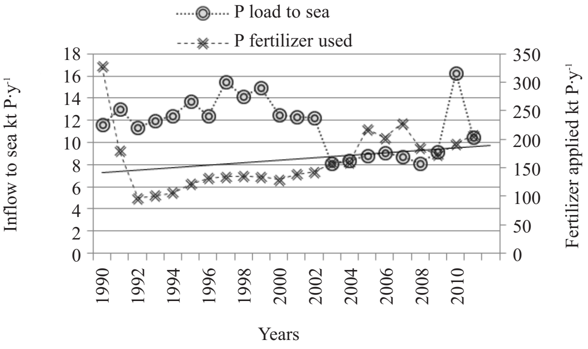


Fig. 8. Annual riverine inflows of total phosphorus from Poland vs. phosphorus fertilizer consumption.

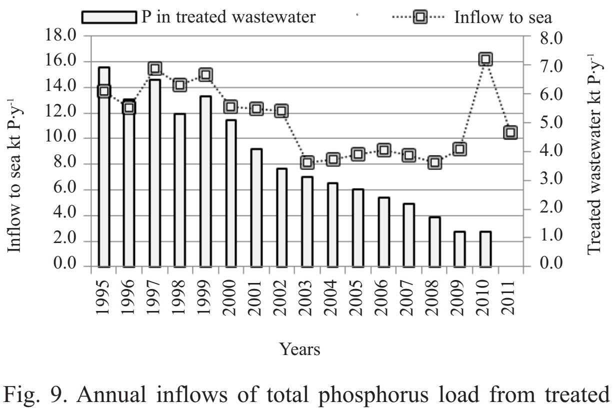


Fig. 9. Annual inflows of total phosphorus load from treated wastewater discharged to surface waters on background nitrogen inflow to the sea.

## Other Substances

The lack of significant trends in load changes also regards substances such as salt components, namely magnesium (Fig. 10), calcium (Fig. 11), Cl and S-$SO_4$ (Fig. 12), dissolved substances (Fig. 13), and biological and chemical oxygen demand (Fig. 14). Loads of these substances were dependent on water inflow to the sea.

## Discussion

Presented studies comprise facts since 1990. At that time deep political and economic changes were ongoing in Poland. Unfortunately no data from years of the previous political system are available for study. This makes any long-term conclusion or forecast difficult or impossible. Though, some facts were gathered, the most important clue is that no significant increase of Baltic Sea water pollution with reactive nitrogen occurred in the last 22 years, and this positive process is ongoing up to now. The main cause is that no significant trends in changing the water inflow to the sea were witnessed. Nitrogen losses to the Baltic originate from natural and anthropogenic sources in drainage basis; the main problem is to distinguish among them.

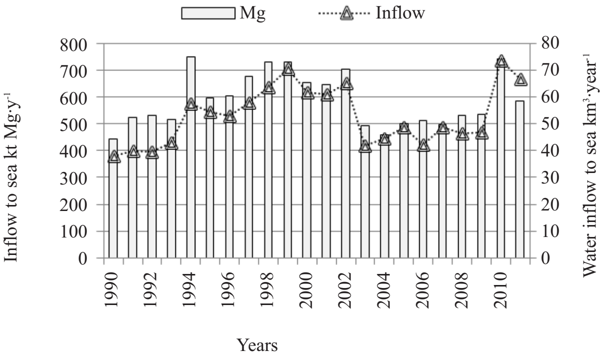


Fig. 10. Annual riverine inflow of magnesium from Poland to the Baltic Sea.

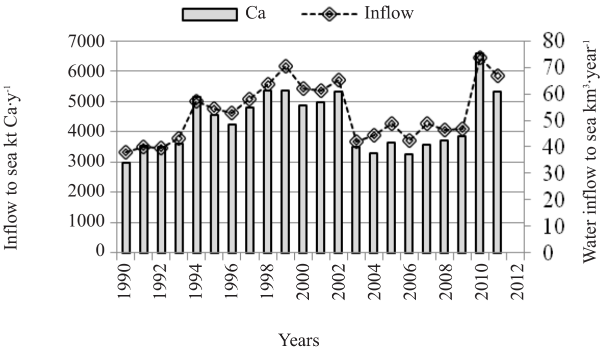


Fig. 11. Annual riverne inflow of calcium from Poland to the Baltic Sea.

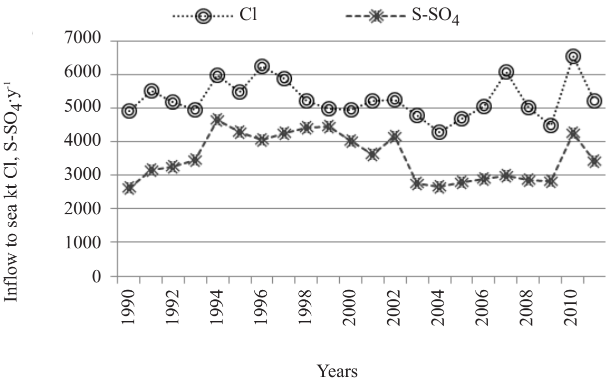


Fig. 12. Annual riverine inflow of chloride and sulfate from Poland to the Baltic Sea.

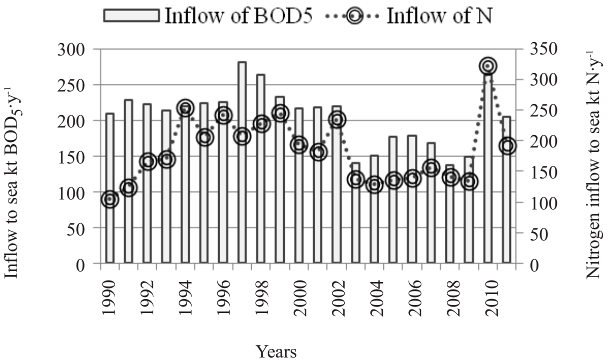


Fig. 13 Annual riverine inflow of biological oxygen demand ($BOD_5$) from Poland to the Baltic Sea on the background of nitrogen load.

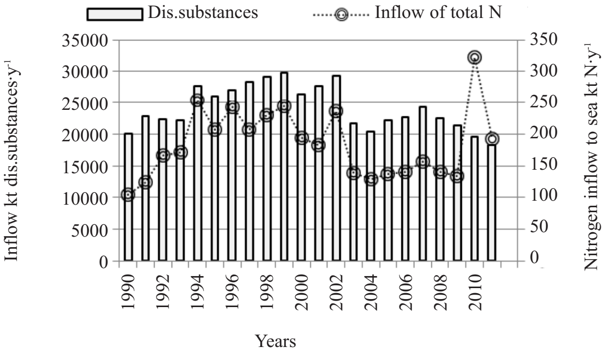


Fig. 14. Annual riverine inflow of dissolved substances from Poland to the Baltic Sea.

Mean annual inflow of total nitrogen load into the sea does not change much in years and trends of any changes are insignificant (Table 4, Fig. 3). There are some external agents, which are expected to have some impacts on these nutrient losses. The use of nitrogen fertilizers in Polish agriculture has increased (Fig. 4). On the other hand, the emissions of nitrogenous gases – $NH_3$ and $NO_x$ have significantly decreased (Fig. 5). Furthermore, the load of total nitrogen in treated wastewater discharged to surface waters was also two times decreased (Fig. 6). These effects are in opposition to fertilization processes and result in maintaining equilibrium of nitrogen potential in the environment, and losses of this nutrient remain at a steady level. Ammonia nitrogen load is only 7% of total nitrogen load, though the significant trend to reduce its load has no greater impact on total load flowing to the sea,

Table 4. Regression coefficient for correlation between deposition water inflow to sea and load of select substances'.

| | Deposit | Inflow | $N_{tot}$ | $P_{tot}$ | Mg | Cl |
|---|---|---|---|---|---|---|
| Inflow | 0.63** | | | | | |
| $N_{tot}$ | 0.51* | 0.84** | | | | |
| $P_{tot}$ | 0.39 | 0.61** | 0.74** | | | |
| Mg | 0.39 | 0.81** | 0.80** | 0.69** | | |
| Cl | 0.42 | 0.44 | 0.54* | 0.38 | 0.36 | |
| $BOD_5$ | 0.34 | 0.55* | 0.67** | 0.95** | 0.60** | 0.47* |

*significant at 0.05, **significant at 0.01

but provides information that the oxygen potential in water is improving. But no trend to decrease the biological oxygen demand was ascertained (Fig. 13).

Changes in phosphorus load are governed by its other behavior and cycling as nitrogen. The trend to reduce the load of total phosphorus was insignificant in spite of its apparent mitigation observed since 2000 (Fig. 7). A significant trend to reduce the load of phosphate phosphorus enforces the discovery that some changes in phosphorus riverrine input to the Baltic Sea from the Polish drainage basin were initiated. The reason for this reduction could not be in agricultural sources, because the phosphorus fertilizer application in Poland was doubled in the last 20 years (Fig. 8). A vast improvement was made in wastewater management systems and the load of phosphorus discharged with treated wastewater has been reduced several times (Fig. 9). Reduced phosphorus load in discharged wastewater was gone together with a decrease of ammonia and biological oxygen demand load in river waters (Figs. 3 and 13). The advances at this mitigation result from ongoing positive changes in the wastewater management system. Though this optimistic conclusion is weakened by the fact that current phosphorus fertilizer use is 13.6 times greater than this nutrient output from the drainage basin. Phosphorus sorption capacity of terrestrial environment is limited, and due to advanced saturation the sorption strength will be weaker and more and more phosphorus will be released to the sea.

Observed reduction of both nutrient loads does not result from any positive changes in fertilizer management, especially phosphorus fertilizers. In most cases the application of commercial fertilizer increases the environmental risk, and the difference between the amount of nutrient applied and its amount in products is a measure of this risk. The last could be adapted to drainage basin. In the case of nitrogen its amount in fertilizers is an input, and the amount in emitted nitrogenous gases and wastewater the output and difference is 91 kt $N \cdot y^{-1}$. More nitrogen was dispersed than applied, because the input of nitrogen from emitted nitric oxide and microbiological fixation were not calculated. The phosphorus budget is much more considerable. The annual input of phosphorus with fertilizer is 158 kt $P \cdot y^{-1}$, whereas the load leaving the Polish drainage basin is only 11.6 kt $P \cdot y^{-1}$. The difference of 146 kt is remaining in the basin each year. Capacity of the basin to fix such a huge amount of phosphorus is limited. This fact is well known [3], but not followed with sound decisions to drasticly reduce phosphorus application in agriculture to the scientific based levels.

## Conclusions

1. Riverine water inflow to the Baltic Sea was significantly correlated with water outflow from the drainage basin; as a consequence the loads of substances inflowing to the Baltic Sea were also correlated with this water inflow.
2. No increase of total nitrogen input to the Baltic Sea was determined during 22 years. Average annual nitrogen load of 184 kt $N \cdot y^{-1}$ was only 27% of nutrient applied with mineral fertilizer. The risk of sea water pollution with reactive nitrogen is moderate.
3. A trend to decrease the phosphorus input to Baltic Sea has been observed. The main cause of this reduction was improvements in wastewater management systems, but the applied phosphorus fertilization in the studied drainage basin was 13 times higher than nutrient inflow to the sea. That makes a severe risk of Baltic Sea eutrophication in the future.
4. The fact that nitrogen loads from Poland did not increase and phosphorus load showed a trend to decrease could be optimistic, if only that were the result of controlled actions, as in the case of phosphorus from point sources.

## Acknowledgements

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