Oceanological and Hydrobiological Studies

International Journal of Oceanography and Hydrobiology

Volume 45, Issue 2, June 2016
pages (172-181)

ISSN 1730-413X
eISSN 1897-3191

Partition of pentachlorophenol (PCP) into particulate and dissolved phases in the waters of the Vistula River mouth at the Gulf of Gdańsk

by

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DOI: **10.1515/ohs-2016-0016**
Category: **Original research paper**
Received: **August 28, 2015**
Accepted: **September 28, 2015**

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Abstract

The Vistula River plays an important role in the supply of autochthonous and allochthonous material to the Gulf of Gdańsk. The suspended particulate matter (SPM) of fluvial origin is considered to constitute a specific sorbent for halogenated organic compounds due to their lipophilic characteristics and relative solubility. Because there are many factors affecting the input of SPM into the estuarine environment of the Gulf of Gdańsk, e.g. hydrological characteristics of the Vistula River, it became necessary to verify whether the same processes may affect a discharge of organic contaminants. The study presents an approach to the assessment of temporal trends in SPM concentration in the Vistula River discharged into the Gulf of Gdańsk as well as the analysis of pentachlorophenol (PCP), a commonly used agricultural biocide, a precursor of dioxins in either dissolved or particulate phases in the river (the Vistula River) and sea waters (the Gulf of Gdańsk). The study revealed that the hydrological characteristics appear to influence a load of SPM. However, the discharge of PCP is additionally related to the environmental conditions, physicochemical properties of the compound and the sorbent, affecting the partitioning of PCP into dissolved and particulate phases.

Key words: suspended particulate matter (SPM), chlorophenols, pollution load, the Vistula River, the Baltic Sea

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Introduction

Suspended particulate matter (SPM) plays many important roles in aquatic systems (Håkanson & Boulion 2002). It is considered that SPM regulates two major transport pathways of materials and contaminants, i.e. the dissolved pelagic route and the particulate sedimentation (or benthic) route. SPM in the riverine and estuarine ecosystems is characterized by high variability in time (seasonal cycles, increased water discharge) and by patchiness. Many factors are known to influence the SPM concentrations such as autochthonous production, related to climate factors, e.g. temperature, radiation and depth of the euphotic zone (Wallin et al. 1992; Wulff et al. 2001), as well as the inflow of allochthonous matter (especially important in estuarine systems). SPM concentrations remain higher in the riverine environment and its content is related to the water discharge rate (Q, $m^3 s^{-1}$). Suspended particulate matter discharged into the sea water undergoes the flocculation process due to increased salinity and enhances the sedimentation of suspended particulate matter causing a decrease in the SPM content in the seawater (Håkanson et al. 2004).

The quality of the Gulf of Gdańsk is under the influence of the largest Polish river – the Vistula River, which is one of the most important suppliers of fresh water and terrigenous matter to the marine environment of the southern Baltic Sea. The contamination discharge is related to hydrological characteristics of the river such as the water flow rate as well as properties of the Gulf of Gdańsk, e.g. reduced dynamics and water exchange, regions of the depositional basin bottom, a high content of organic carbon and insufficient oxygen saturation. For this reason, a wide range of pollutants, including the most hazardous halogenated organic compounds such as pentachlorophenol (PCP) – a precursor of dioxins, a commonly used biocide in agriculture, are transported while adsorbed on suspended particles via riverine transport with the Vistula River and deposited in the Gulf of Gdańsk. Unlimited use of the PCP technical solvent, which contained about 14% of other, so-called microcontaminants, including polychlorinated dibenzo-p-dioxins and dibenzo-furans (PCDD/F), polychlorinated biphenyls (PCBs) and hexachlorobenzene (HCB), has resulted in an increased supply of PCP to agricultural lands, and hence its discharge into the Baltic Sea. Despite the restrictions on its use, high concentrations of this compound are continuously recorded in the marine environment (Kobusińska et al. 2014; Lewandowski et al. 2014). The previous research revealed that the highest concentration of PCP wasobserved in the surface layer of bottom sediments from the Gdańsk Basin, suggesting a continuous inflow of this contaminant by the Vistula River and its sedimentation (Kobusińska et al. 2014). The distribution of this compound in aqueous media (sea, river) is associated with its chemical properties. The hydroxyl group present in the PCP molecule is responsible for a relative solubility in water. Hydrophobicity, relatively low vapor pressure and recalcitrant to biodegradation result in its preferred sorption on suspended particulate matter (SPM), depending on environmental conditions (Guerrero et al. 2001; Wu et al. 2005; Ingerslev & Nyholm 2000). Its presence in either dissolved or particulate phase is considered to be directly related to the concentration of SPM in the water (Håkanson et al. 2004). Partition of pentachlorophenol in the marine environment, particle-water interactions are known to be one of the most important mechanisms controlling the distribution and movement of hydrophobic organic chemicals, hence such an approach is necessary for an accurate prediction of its transport and fate (Zhou et al. 1999).

The aim of the presented study was to examine:

a) long-term SPM concentration changes in the Vistula River and the influence of hydrological factors such as the water flow rate (Q) on the load of SPM to the Gulf of Gdańsk,

b) determination of PCP in the river and sea water, including the particle-water phase approach to the assessment of an empirical discharge of this pollutant with the Vistula River into the Gulf of Gdańsk and the influence of environmental conditions on its occurrence,

c) assessment of the environmental risk based on limits proposed by the European Water Framework Directive.

Materials and methods

Study area

The research was carried out at the Kiezmark (Tczew) station, the Vistula River mouth cross-section, the Swibno station – the Vistula River mouth and in the coastal zone of the Gulf of Gdańsk, within the seaside resorts – Gdynia, Sopot, Gdańsk (Fig. 1). The Vistula River is the longest river in the Baltic catchment area (1022 km long) with the mean water discharge equal to 1080 $m^3 s^{-1}$ (Niemirycz 2008). Eighty seven perecent of its drainage area is located in Poland (Niemirycz 2008, 2011). The river sections close to its mouth reflect the pollution caused by discharges from the river drainage area of 194 400 km^2 (Niemirycz 2008).

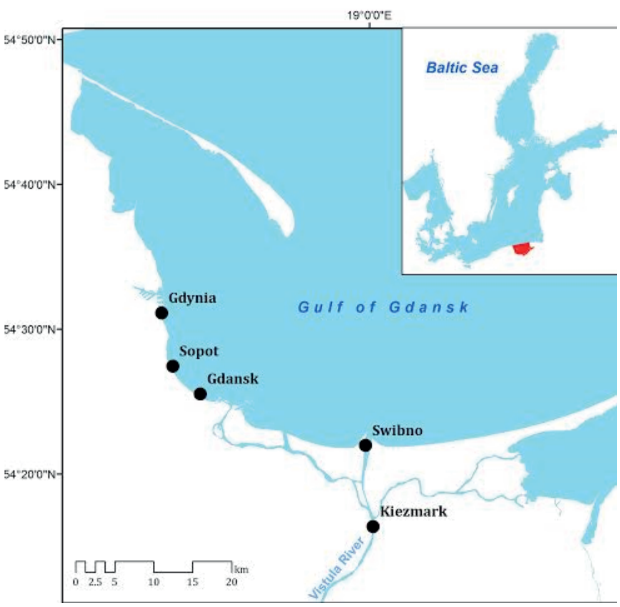

Figure 1

Sampling sites of sea water (sea-side resorts – Gdynia, Sopot, Gdańsk), estuarine water (Swibno – the Vistula River mouth) and river water (Kiezmark – the Vistula River mouth cross-section)

SPM- river water

Samples of SPM from the Kiezmark station (the Vistula River mouth cross-section), used for the determination of long-term temporal fluctuactions, were collected in 2002-2006 in seasonal cycles (twice per month).

Surface river water (0-5 m) was collected (1 dm^3) and filtered through the Whatman GF/F 0.45 μm membranes (47 mm filter diameter). Prior to use in the analysis, membranes were combusted at 550°C in a furnace to eliminate any traces of organic contamination. SPM concentration was calulated gravimetrically.

PCP- river, sea water

River (Kiezmark) and sea water (Gdańsk, Sopot, Gdynia, Swibno) was collected from March to December 2014 with the Niskin bottle from the surface layer (0-5 m). The sample collected in March form the Kiezmark station had to be excluded due to the damage during transportation.

The 2 dm^3 volume of a sample was divided into two replicates to determine the concentration of SPM in a sample and PCP in either dissolved (PCP_{diss}) or particulate phase (PCP_{spm}), after filtration, GF/F 0.45 μm. The dissolved fraction was analyzed within 24 h, while filters with SPM were deep-frozen at 28°C, then freez-dried and analyzed after 48 h. Concentration of SPM was measured gravimetrically.

Basic parameters such as salinity, temperature, oxygen saturation and pH were determined in the whole sample using a multifunctional measurement device (EC410 ExStik II Conductivity/TDS/Salinity Kit). Chemical parameters: nitrates (NO_3^-) and ortho-phosphates (PO_4^{3-}) were determined using spectrophotometric methods in order to examine a possible impact of primary production on PCP dissociation or adsorption on SPM.

Data (daily mean) on the water flow rate (Q) from the Kiezmark station from 2002-2006 and 2014, used as an additional parameter, were obtained from the Institute of Meteorology and Water Management in Warsaw, Poland.

Number of samples and characteristics of the collected environmental material are given in the Table 1.

Chemical analysis

Analysis of PCP in sea and river water

Pentachlorophenol was extracted from samples using solid fraction extraction C18 SPE columns. After the purification, extracted analytes were eluted from the solid fraction with a solution of 1% acetic acid in methanol and concentrated to a volume of 1.5 cm^3.

Analysis of PCP in suspended particulate matter (SPM)

Whatman filters with SPM were dried to a constant weight and subjected to further steps

Table 1

Environmental material collected and analyzed within the present study

Station	Water type	Year	Samples (N)	Analysis
Kiezmark (the Vistula River mouth cross-section)	riverine	2002-2006	120	SPM
Kiezmark (the Vistula River)	riverine	2014 (April-December)	9 9	SPM, PCP_{spm} PCP_{diss}
Swibno (the Vistula River mouth)	estuarine	2014 (March-December)	10 10	SPM, PCP_{spm} PCP_{diss}
Gdańsk (the Gulf of Gdańsk)	marine	2014 (March-December)	10 10	SPM, PCP_{spm} PCP_{diss}
Sopot (the Gulf of Gdańsk)	marine	2014 (March-December)	10 10	SPM, PCP_{spm} PCP_{diss}
Gdynia (the Gulf of Gdańsk)	marine	2014 (March-December)	10 10	SPM, PCP_{spm} PCP_{diss}
			Total	SPM= 170 PCP_{spm}= 50 PCP_{diss}= 50

of chemical analysis. PCP was extracted from filters with a solution of triethylamine (TEA) in methanol: water (4:1) in a Soxhlet apparatus for 24h. After concentration, extracts were purified on C18 SPE. Analytes were eluted with 1% acetic acid in methanol. The purified extract was evaporated on a rotary evaporator to a volume of 1.5 cm^3.

The weight of SPM was calculated gravimetrically and expressed in mg dm^{-3}. The concentration of PCP was calculated using a volume of water filtered, the weight of SPM and expressed in µg g^{-1} d.w.

Chromatographic conditions

Pentachlorophenol was analyzed using a High Performance Liquid Chromatograph (DIONEX) with a UV-VIS detector at a wavelength of λ = 300 nm. The chromatographic column Hypersil GOLD PFP GOLD (150 mm × 2.1 mm × 5 mm) was thermostated at 60°C. The following mobile fraction mixtures were used: A: water + 0.1% acetic acid, and B: methanol + 0.1% acetic acid (gradient: 5% B for 1.5 min, then to 95% B at 19.5 min, maintained for 1.5 min, flow rate of 0.6 ml min^{-1}).

Quality assurance/quality control (QA/QC)

The quality of the results was assured based on the use of external and internal standards. Accuracy was expressed as a recovery of pentachlorophenol and equal to 87%. Precision of the analysis was expressed by the relative standard deviation (RSD) – 8.4%. The limit of quantitation (LOQ), calculated as 10 times the signal-to-noise ratio (S/N), was 10 ng dm^{-3}. The correlation coefficient of the regression equation of the calibration curve was 0.9867.

Results and discussion

Concentration of SPM-temporal trends and affecting factors

In order to determine long-term changes (annual, seasonal) in the concentration of SPM in the Vistula River, the collected data were related to a mean value of the water flow rate (Q) [m^3 s^{-1}]. Based on the collected data, seasonal differences in the water flow rate and the SPM concentration were confirmed by the statistical ANOVA Kruskall-Walis (K-W) test ($p<0.05$). No statistical differences were observed during the study period (2002-2006, 2014) regardless of the season.

For further interpretation of the collected data, the load of SPM discharged into the Gulf of Gdańsk by the Vistula River was calculated according to the equation presented below (Niemirycz 2008).

$$L_y = \frac{m}{n} \sum_{i=1}^{n} C_i \times Q_i$$

where:

- L_y – Q_i load (kg year^{-1})
- m – a unit coefficient
- n – the number of measurements
- C_i – instantaneous concentration (g m^{-3})
- Q_i – instantaneous water flow (per second corresponding to the concentration C_i (m^3 s^{-1})

The estimated SPM load significantly correlated with the mean water flow rate (Q) in the Vistula River, resulting in the following regression equation with the satisfactory and statistically significant correlation coefficient ($r=0.7982$, $p<0.05$), (Fig. 2). This fact confirms the thesis on the relationship between the SPM load and the water discharge rate observed by others (Jansson 1982; Walling & Amos 1999; Walling 2000). However, this phenomenon may differ in rivers depending on the catchment soil type, climate conditions, the existence of upstream lakes, which would act as sediment traps, land-use, vegetation, etc. (Håkanson et al. 2004).

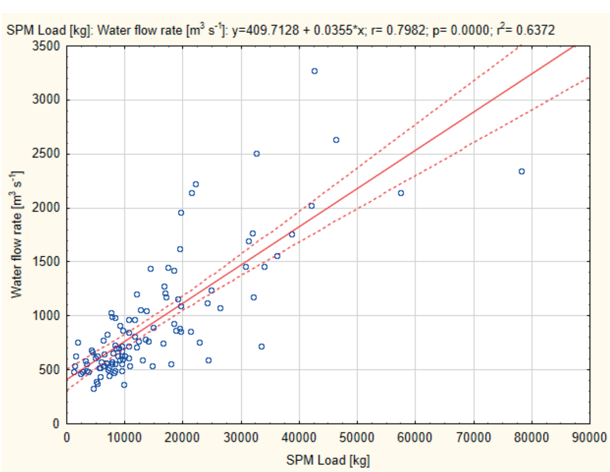

Figure 2

Relationship between the SPM load (kg) and the mean water flow rate (m^3 s^{-1}) in the Vistula River at the Kiezmark station (river mouth cross-section) during the period of 2002-2006 and 2014

PCP-partition between dissolved and particulate phases (PCP_{spm}, PCP_{diss})

Pentachlorophenol was identified in all SPM samples collected in 2014. The Predicted No-Effect Concentration (PNEC) value established for PCP adsorbed on SPM was exceeded in all samples by more than an order of magnitude (Muir & Eduljee 1999).

Values of PCP concentrations in both fraction in river (Kiezmark), estuarine (Swibno) and sea (Gdynia, Sopot, Gdańsk) water are presented below (Table 2).

Additionally, statistics on river (Kiezmark), estuarine (Swibno) and sea (Gdynia, Sopot, Gdańsk) water parameters were presented, as well as SPM concentration, which was measured in order to interpret the results.

Table 2

Statistical parameters describing the data on PCP concentration (PCP_{diss}, PCP_{spm}) in river, estuarine and sea water

	Unit	N	Median	Minimum	Maximum
RIVERINE					
PCP_{diss}	ng dm^{-3}	9	53.13	15.67	120.45
PCP_{spm}	µg g^{-1} d.w.	9	12.85	3.20	27.01
ESTUARINE					
PCP_{diss}	ng dm^{-3}	10	55.09	23.43	94.21
PCP_{spm}	µg g^{-1}d.w.	10	16.40	13.52	25.61
MARINE					
PCP_{diss}	ng dm^{-3}	30	28.98	12.85	62.36
PCP_{spm}	µg g^{-1}d.w.	30	17.35	8.58	37.76

PCP- the Vistula River (Kiezmark station – river mouth cross-section)

The analysis of PCP_{spm} from the Kiezmark station revealed that the concentration of PCP adsorbed on SPM is not correlated with the sorbent (SPM) measured at this station, but the statistically significant and negative relationship ($r=-0.616667$) was observed for the particulate phase of PCP (PCP_{spm}) and the mean water flow rate (Q) at the same station in 2014 (Fig. 3, Table 3). This fact may indicate that the hydrological characteristics, dynamics of the Vistula River

Table 3

Spearman rank correlation test for verification of correlation between the particulate phase of PCP (PCP_{spm}) and the mean water flow rate in the Vistula River in 2014

	Unit	PCP_{spm} (µg g^{-1} d. w.)	Water flow rate (Q) (m^3 s^{-1})
PCP_{spm}	µg g^{-1} d. w.	1.000000	-0.616667
Water flow rate (Q)	m^3 s^{-1}	-0.616667	1.000000

appear to significantly affect the partitioning of PCP into dissolved and particulate phases (Fig. 3). Since the analysis of the SPM concentration (mg dm^{-3}) and the mean water flow rate (Q) revealed a significant positive, strong correlation, the concentration of PCP does not appear to be related to the SPM concentration. However, the Spearman rank correlation test revealed a significant ($p<0.05$) negative correlation between PCP_{spm} and the mean water flow rate (Q), thus the lowest values of this form at the Kiezmark station were observed during the period of the highest water flow rate (April). This phenomenon may indicate that there are different processes or factors affecting the sorption of PCP on SPM in the water of the Vistula River.

PCP_{diss}/PCP_{spm} – river, sea water

The ANOVA Kruskal-Wallis (K-W) test revealed significant ($p<0.05$) differences between the concentrations of PCP_{diss} at selected stations during 2014. No significant differences were reported in PCP in the particulate fraction (PCP_{spm}) applying the same statistical test.

Given that the sampling stations and the material collected (riverine, estuarine and marine) may have different properties, the U-Mann-Whitney test was carried to verify the statistical differences between the mean values of PCP_{diss}

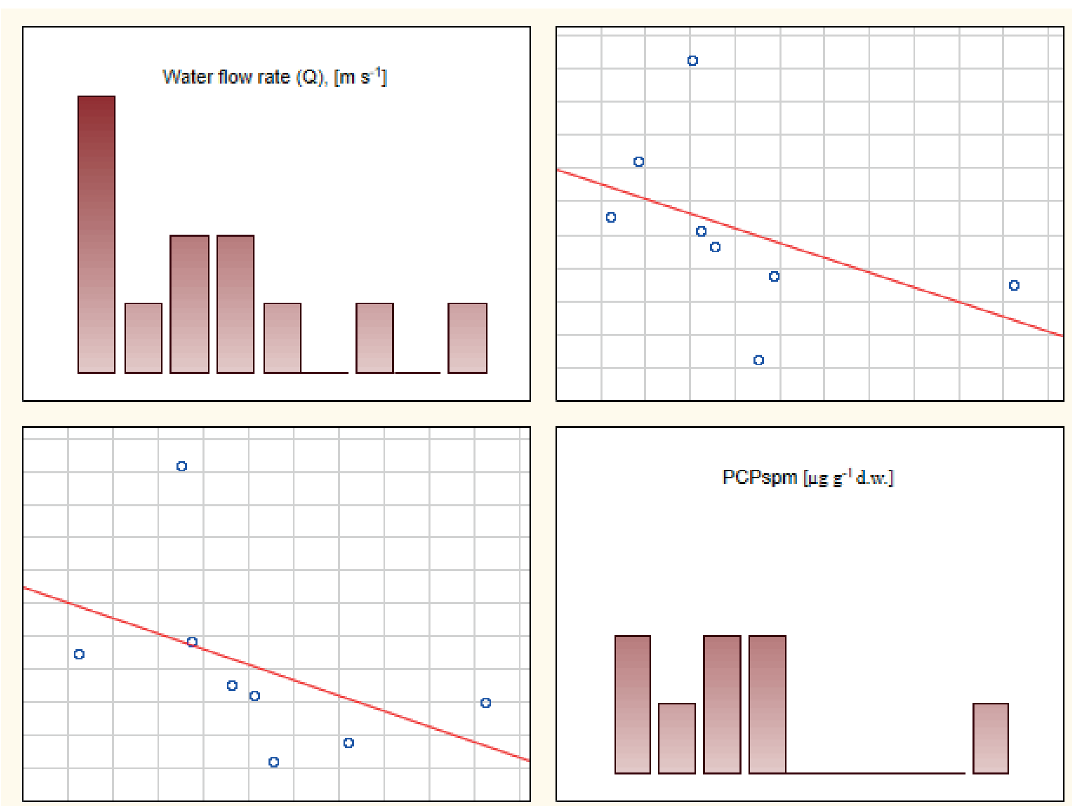

Figure 3

Relationship between PCP_{spm} (µg g^{-1} d.w.) and the mean water flow rate (Q), (m^3 s^{-1}) in the Vistula River at the Kiezmark station (river mouth cross-section) in 2014 and PCP_{spm} in all water types. The test proved significant differences between the analyzed water types ($p<0.05$).

Statistically significant seasonal differences in the occurrence of pentachlorophenol, also in the dissolved phase were observed. These fluctuations could possibly be related to the unstable form of PCP in the dissolved phase due to its varying solubility in water depending on temperature and redox conditions (Andersen et al. 2005). The distribution of PCP between both phases in water is apparently controlled by the complex physicochemical properties of the compound, such as solubility, vapor pressure and hydrophobicity. Due to the fact that hydrophobicity expressed by the K_{ow} (octanol-water) coefficient increases with a decrease in pH, the redox conditions may be responsible for the reactions of PCP sorption on SPM and fluctuations in partitioning of this chemical.

Concentrations of PCP_{spm} tend to increase during summer months until September to decrease in the autumn (Fig. 4), which could possibly be explained by the increase in the total suspended particulate matter concentration, observed during summer months in the Gulf of Gdańsk (Krężel & Cyberski 1983). However, no significant correlation between these two parameters was observed to confirm this thesis.

The episode with the highest PCP_{diss} concentration was recorded in the Vistula River (Kiezmark) and in Swibno in September (120.45 ng dm^{-3}, 94.21 ng dm^{-3}, respectively), the highest concentration of PCP_{spm} was observed in the sea water station-Gdynia in April. In order to verify the potential cause of this fact, a hypothesis proposed by Schwarzenbach et al. (1993) was tested, which assumes that fluctuations in salinity affect the partitioning of hydrophobic substances into particulate and dissolved forms.

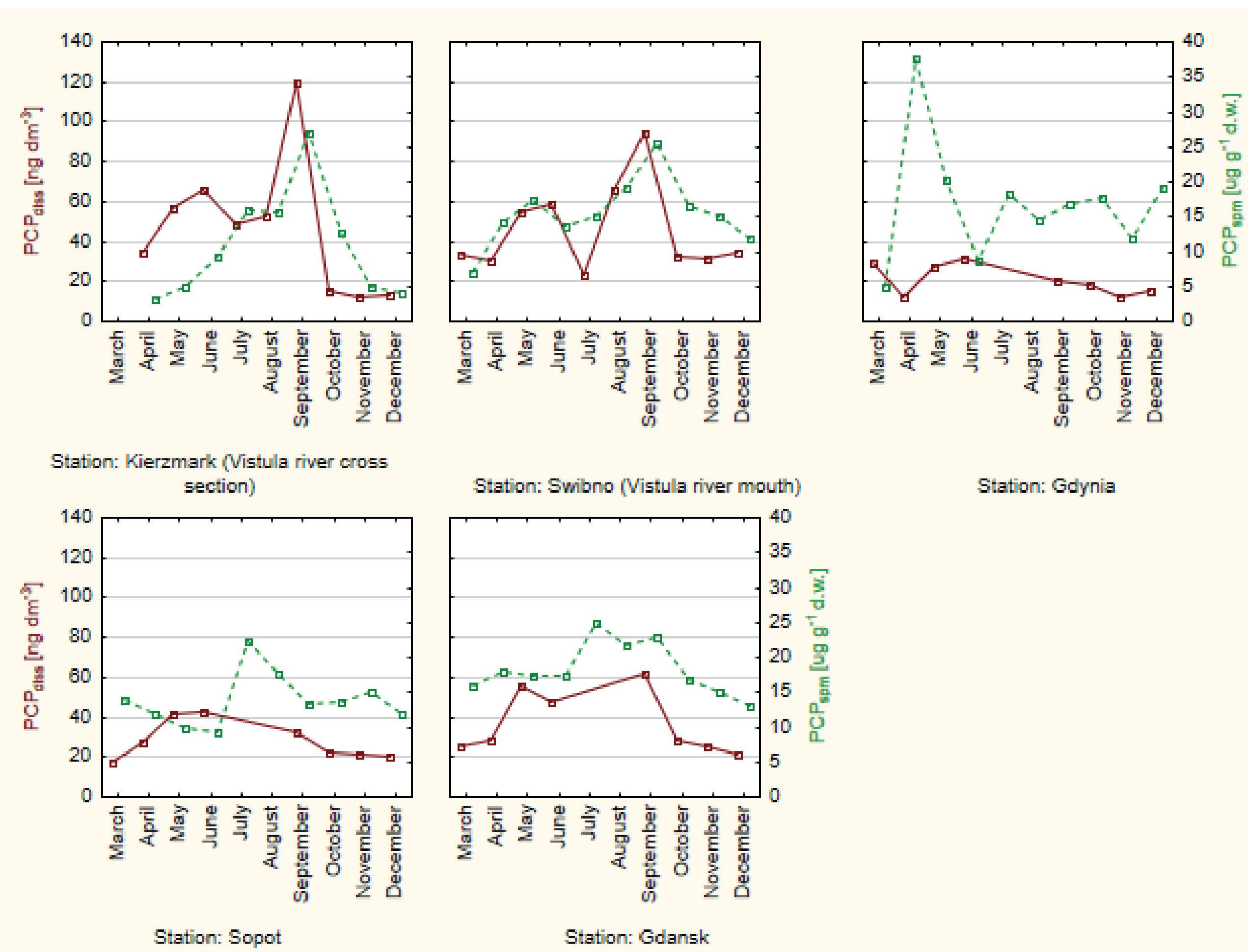

Figure 4

Seasonal variability in PCP_{spm} and PCP_{diss} concentrations at selected sampling stations in 2014

Partitioning is expected to increase with salinity, primarily due to the fact that solubility of organic substances decreases with increased salinity. The significant negative correlation between PCP_{diss} and salinity determined in this study confirms the presented hypothesis (Table 4). The correlation between PCP_{spm} and salinity revealed a contrasting (positive) trend which is likely to be related to the increased association of pollutants with suspended solids in the transition from the river to marine environment (Zhou et al. 1999). Additionally, a significant correlation between PCP in both phases and pH of the collected water was observed, confirming that the solubility of PCP increases with pH of water and sorption of PCP on SPM is enhanced while the hydrophobicity of the compound is intensified by a reduction in this parameter (Table 4).

The studies also demonstrated that approximately 80% of PCP is associated with the particulate fraction in water and only about 10% of PCP dissolved in water. There were no changes in this distribution during the year.

Analysis of two PCP forms independently (PCP_{diss}, PCP_{spm}) does not give a complete picture of seasonal variations of this substance, contrary to the analysis of both forms together. This suggests the probability of an unstable PCP molecule bound to SPM, and thereby the continuous reaction of sorption and desorption (Czaplicka 2004), related to various environmental conditions.

Based on the obtained results, the statistical Spearman's rank correlation test ($p<0.05$) was carried out for the variables. The test showed significant correlations for PCP_{diss} (NO_3^-, PO_4^{3-}, pH, T). This may suggest a relationship between PCP and the parameters of the water, while in the case of the particulate form, its sorption is more likely related to the properties of the sorbent (SPM) such as the content of organic matter, nitrogen, phosphorus or the presence of various functional groups (Pu & Cutright 2006; Luo et al. 2011).

Table 4

Spearman rank correlation test for the assessment of selected parameters and their effect on the partition of PCP into dissolved and particulate phases (statistically significant p<0.05 marked in red)

Parameter	PCP_{diss} (ng dm^{-3})	PCP_{spm} (µg g^{-1} d.w.)	S (PSU)	pH
PCP_{diss} (ng dm^{-3})	1.000000	0.127301	-0.478481	0.575308
PCP_{spm} (µg g^{-1} d.w.)	0.127301	1.000000	0.185959	0.099283
S (PSU)	0.575308	0.185959	1.000000	-0.492416
pH	-0.492416	0.099283	0.147645	1.000000

Environmental risk assessment – a dilution factor (DF)

In order to identify the substances that could represent a relevant risk to the environment, an environmental risk evaluation was carried out using two different approaches: first of all (PCP_{diss} + PCP_{spm}), the concentrations were compared with the Environmental Quality Standards (EQS). The purpose of this comparison was to present the threat to the aquatic environment caused by the release of contaminants. This approach was applied to substances having an EQS established by the European Commission in the Directive 2008/105/EC (EC 2001), referring to the concentration in the whole water sample (at 0.45 µm).

In accordance with the objective of the study, the analyses were performed on both the dissolved and particulate phases to assess the partition of contaminants. As there are no available EQS for both fractions, PCP_{diss} + PCP_{spm} concentrations were compared to EQS. This approach gives an indicative rate of dilution necessary in the environment to prevent any pollution impact. The dilution factor (DF) was therefore calculated as follows:

$$DF = \frac{PCP_{diss} + PCP_{spm}}{EQS}$$

However, this method needs to be considered with some caution when one of the PCP fraction values is below LOQ. The dilution factor established for PCP within the Water Frame Directive in the rangeof DF < 0 ≤ 1 and the EQS value included in the groudwater and surface water assessment criteria is 100 ng dm^{-3}.

The table below presents the data, including mean values of the total PCP in both fractions, the EQS value established by the EU Commission for PCP in surface waters and the calculated DF. The calculated values of DF exceed the required level of PCP dilution in water which would prevent any environmental risk and it remains similar in both water types (Table 5).

Table 5

Calculated values of the dilution factor (DF) for PCP in the sampled surface waters with respect to the EC (2001) environmental quality standard (EQS) for the assessment of environmental risk

Water type	$\Sigma PCP_{diss}/PCP_{spm}$	EQS value	DF
riverine	336.69	100	3.37
marine	237.46	100	2.37

PCP concentrations in water and suspended particulate matter (SPM) worldwide

The results on PCP in sea (the Gulf of Gdańsk), estuarine (Swibno-the Vistula River mouth) and river water (Kiezmark - the Vistula River cross section) obtained during this study are similar to those obtained, respectively, in the surface waters of the Gulf of Gdańsk (Kot-Wasik et al. 2004), the Elbe estuary, Germany (Penta Task Force 1997), the north-east coast of England (Muir & Eduljee 1999). The maximum concentration of PCP_{diss} determined in the estuarine water from the mouth of the Vistula (Swibno) is almost four times lower than the maximum concentration of this substance in the mouth of the Elbe River (410 ng dm^{-3}), but almost two times higher than the level indicated in the water of the Rhine River (Germany), where the maximum concentration does not exceed 50 ng dm^{-3} (ICRP 1991).

Estimation of an annual load of PCP with the Vistula River into the Gulf of Gdańsk

The average annual load of PCP delivered to the Gulf of Gdańsk by the Vistula River in 2014 was estimated using the results of PCP determined in the water on the basis of the equation (Equation 1) approved by HELCOM and proposed by Niemirycz (2008). The calculated load of PCP_{diss} and PCP_{spm} is equal to 64 kg and 131 kg, respectively, which is similar to loads estimated by Niemirycz (2008) for other organic pollutants (ΣDDT-230 kg $year^{-1}$, ΣPCBs - 260 kg $year^{-1}$, γ-HCH-380 kg $year^{-1}$), discharged into the Gulf of Gdańsk by the Vistula River.

Conclusions

The results obtained during the conducted research led to the following conclusions:

- Seasonal differences were confirmed for the SPM concentration and the water flow rate in the Vistula River in the study period, but no annual variability was observed regardless of the season.
- The load of SPM discharged into the Gulf of Gdańsk by the Vistula River remains related to the hydrological characteristics of the river, such as the water flow rate.
- PCP is preferably sorbed on SPM particles than dissociated in the water resulting in 80% of PCP_{spm} contribution in the total concentration. The chemical structure of the sorbent is considered to be of major importance in the sorption-desorption reaction of PCP. The type of water (marine, riverine) seems to affect the contribution of selected phases of PCP, due to the fluctuation of solubility with a varying salinity range as well as redox condition.
- Hydrological characteristics and dynamics of the Vistula River as well as physicochemical properties of the compound appear to affect the partitioning of PCP between the dissolved and particulate phases.
- The calculated dilution factor for PCP in the Gulf of Gdańsk and the Vistula River exceeds the acceptable level of dilution estimated for this compound within the European Water Frame Directive.
- The estimated, annual loads of PCP discharged by the Vistula River remain similar to the outflow of other organic contaminants into the Gulf of Gdańsk.

Acknowledgments

The Institute of Meteorology and Water Management in Warsaw is greatly acknowledged for providing the data on the Vistula River water flow at the Kiezmark station in 2014.

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