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ASSESSMENT OF POLLUTION BY HEAVY METALS AND POLYCYCLIC AROMATIC HYDROCARBONS OF SURFACE WATER IN KAMPINOS NATIONAL PARK

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OCENA ZANIECZYSZCZENIA METALAMI CIĘŻKIMI ORAZ WIELOPIERŚCIENIOWYMI WĘGLOWODORAMI AROMATYCZNYMI WÓD POWIERZCHNIOWYCH W KAMPINOSKIM PARKU NARODOWYM

W latach 2000-2002 badano niektóre naturalne i antropogenne właściwości wód powierzchniowych Kampinoskiego Parku Narodowego. Uzyskane wartości średnie omówiono w porównaniu do odpowiednich norm. Analizy większości próbek wykazały, że odpowiadają one I klasie czystości. Benzo(a)pirenu nie wykryto. Jednak w dwóch przypadkach zaobserwowano wysokie stężenie żelaza i manganu. Próbki pobrane w listopadzie zawierały więcej manganu. W jednym przypadku oznaczono wysokie stężenie azotanów. Większość próbek pobranych w Aleksandrowie odpowiadała II klasie czystości ze względu na zawartość fosforanów.

Summary

Some natural and anthropogenic properties of surface water were investigated in National Park of Kampinos in years 2000-2002. Obtained results were compared with corresponding standards. Analyses of samples of water revealed most of them to be adequate to the I class of purity. Benzo(a)pyrene was not detected. However, in two cases high concentration of iron and manganese was observed. As a rule, the samples collected in November exhibited higher concentration of manganese. In one case high concentration of nitrates was determined. Most of samples collected in Aleksandrów met the requirement for the II class of purity because of phosphate concentration.

INTRODUCTION

Magnitude of Kampinos National Park (38 500 ha, the second national park in Poland regarding the largeness of area) as well as its location (neighborhood of Warsaw and big water node) give ground for many year numerous scientific investigations [10]. The Park contains terrain of flood plain of the Vistula and consists of different bands: marshy zones parallel to the Vistula course are divided by dune landscapes. Some areas spreading to the

south of the riverbed can be marked out: flood terraces (lower and higher), northern band of dunes, northern marshy band (which is a valley of Łasica canal), southern band of dunes, scarp of Vistula valley and Błońska Upland. Much attention was paid to hydrological and hydrogeological conditions, especially to the seasonal level variation of surface and underground water as well as to the chemical properties of water [3, 12, 15].

Fig. 1. Location of sample points

However, the examinations were carried out rather at random. Among other parameters, variability of pH values was investigated. It was established, that canals flowing through southern part of the Park (more agriculturally exploited than northern part) exhibited higher pH values (up to 8.0). Canals flowing out from the marshes exhibited low pH values, especially in periods of plant vegetation. Similar regularity can be observed concerning calcium content and water hardness. In southern tributaries of the Łasica the highest concentrations of sulphates(VI), phosphates and chlorides were reported, perhaps due to the presence of waste dumps and uncontrolled sewage discharge. In the case of phosphates the influence of fertilizers used in agriculture should be considered. Nitrates(V) found in significant amounts in downstream are descended in part of fertilizers, in part are products of oxidation of ammonia (which is produced in marsh). A total content of iron(II and III) is higher in

waterlogged zones and in the period of plant vegetation (up to 2 mg/dm^3), while in winter it is reduced to > 0.6 mg/dm^3. Common for majority of investigated impurities were considerable seasonal variability and tendency to reduction of impurity concentration in downstream, showing activity of self-purification process [2, 11].

This investigation was performed in order to evaluate the content of heavy metals and polycyclic aromatic hydrocarbons in surface water in Kampinos National Park. These impurities were not determined in this area. Determination of concentration of biogenic ions: nitrates (V) and phosphates and ions of calcium and magnesium were carried out, too. The samples were collected in central stream of the Łasica, Zaborowski Canal and Canal Łasica 9.

METHODS

Samples of water were collected from Zaborowski Canal near Roztoka, from Łasica Canal near Aleksandrów and from Canal Łasica 9 near Wędziszew in November 2000, April and July 2001 and May and November 2002. The samples were stored in bottles made from dark glass in order to prevent photochemical decomposition of PAHs. Directly after collecting chloroform (3 cm^3/dm^3) was added. Before determination of PAHs, hyamine (12 μg/dm^3 of water) was added, the sample precisely mixed and passed through an extraction column C18 (flow rate 3-4 drops per second). Then, inert gas (nitrogen) was passed through the column for 10 minutes. PAHs were eluted from dried column using dichloromethane (8 cm^3). To the filtrate acetonitrile (2 cm^3) was added, the solution was carefully mixed and then mildly concentrated in the stream of nitrogen at the temperature of 37°C, to the volume 0.5 cm^3. After supplementing the volume with water to 1 cm^3, the solution was mixed and subjected to high performance liquid chromatography (HPLC), in the presence of 16 standard PAH compounds (some of them considered by US EPA to be carcinogenic and mutagenic [1, 8, 14].

Determination of metals was carried out by means of atomic absorption spectrometry (AAS) using atomization of samples in acetylene flame or electrothermic atomization (in the cases of cadmium and lead). The samples of water were filtered directly after collecting and eight-time concentrated with simultaneous mineralization by adding nitric acid of special purity. In order to prove determination correctness, attested reference material, i.e. samples of water SPS-SW1, were analyzed parallel with examined samples. The obtained results were in agreement with the certificate. Parameters of quality of used AAS method were in accordance with their characteristics described in the literature [4, 5, 7]. Determination of nitrates and phosphates were performed up to the Polish standards: PN-82/C-04576/08 and PN-89/C-04537/02.

RESULTS OF INVESTIGATION

Our aim in this paper was among others to examine concentration of 16 PAHs: naphthalene (N), acenaphthene (Af), fluorene (F), anthracene (A), fluoranthene (Flt), pyrene (P), benzo(a)anthracene (B[a]A), chrysene (CH), benzo(b)fluoranthene (B[b]F), benzo(a)pyrene (B[a]P), dibenzo(a,h)anthracene (B[ah]A), benzo(g,h,i)perylene (B[ghi]P), indeno(1,2,3-c,d)pyrene (I[cd]P) in samples of surface water from Kampinos National Park. The results of determinations are shown in Table 1.

Table 1. The concentration of PAHs [mg/dm^3] in investigated samples of water of Kampinos National Park

Sampling place (date)	N	Afy	Af	F	Ft	A	Flt	P	B[a]A	CH	B[b]F	B[k]F	B[a]P	B[a,h]A	B[g,h,i]P	I[c,d]P
Roztoka																
XI 00	$1.1x10^{-2}$	$2.0x10^{-3}$	–	$1.1x10^{-2}$	–	$2.1x10^{-4}$	–	–	–	$1.1x10^{-3}$	$1.3x10^{-3}$	$2.0x10^{-4}$	–	$1.6x10^{-4}$	–	–
IV 01	$9.6x10^{-3}$	$1.7x10^{-4}$	$1.4x10^{-2}$	$7.8x10^{-3}$	$1.8x10^{-3}$	$4.2x10^{-4}$	–	–	–	–	–	–	–	–	–	–
VII 01	$3.1x10^{-6}$	–	$2.3x10^{-6}$	–	$2.0x10^{-6}$	–	–	–		–	–	–	–	–	–	–
V 02	$4.4x10^{-5}$	$1.2x10^{-5}$	$3.3x10^{-5}$	$1.1x10^{-6}$	–	–	–	–	–	–	–	–	–	–	–	–
XI 02	$2.9x10^{-4}$	$5.2x10^{-5}$	–	–	$7.3x10^{-6}$	–	–	–	–	–	–	–	–	–	–	–
Aleksandrów																
XI 00	$1.2x10^{-2}$	$1.3x10^{-2}$	$7.3x10^{-3}$	$1.6x10^{-3}$	–	$1.4x10^{-3}$	$1.2x10^{-3}$	–	–	$2.6x10^{-3}$	$2.8x10^{-4}$	$5.1x10^{-4}$	–	–	$1.2x10^{-3}$	–
IV 01	$1.8x10^{-2}$	$2.6x10^{-3}$	$1.5x10^{-3}$	$3.1x10^{-3}$	–	$3.0x10^{-4}$	$2.1x10^{-3}$	$1.1x10^{-4}$	–	–	–	–	–	–	–	–
VII 01	$8.6x10^{-6}$	$8.1x10^{-6}$	$6.4x10^{-6}$	$7.0x10^{-6}$	$3.9x10^{-6}$	$1.0x10^{-5}$	$1.2x10^{-6}$	$6.5x10^{-6}$	$1.2x10^{-6}$	–	–	–	–	–	–	–
V 02	$7.7x10^{-5}$	$2.9x10^{-5}$	$4.3x10^{-6}$	$2.1x10^{-5}$	$1.1x10^{-7}$	$5.4x10^{-6}$	$2.7x10^{-7}$	–	–	–	–	–	–	–	–	–
XI 02	$1.5x10^{-4}$	$4.6x10^{-4}$	$1.1x10^{-3}$	$2.1x10^{-5}$	–	–	–	–	–	–	–	–	–	–	–	–
Wędziszew																
XI 00	$2.1x10^{-2}$	$1.9x10^{-2}$	–	$5.4x10^{-3}$	–	–	–	–	–	–	–	–	–	–	–	–
IV 01	$7.8x10^{-3}$	$7.6x10^{-3}$	$7.2x10^{-3}$	$5.8x10^{-3}$	$2.8x10^{-4}$	–	–	–	–	–	–	–	–	–	–	–
VII 01	$3.3x10^{-6}$	–	–	–	$2.5x10^{-7}$	–	–	–	–	–	–	–	–	–	–	–
V 02	$4.2x10^{-6}$	–	–	$2.2x10^{-6}$	–	–	–	–	–	–	–	–	–	–	–	–
XI 02	$2.9x10^{-4}$	$4.8x10^{-4}$	$1.1x10^{-3}$	–	–	–	–	–	$2.8x10^{-5}$	–	–	–	–	–	–	–

Similarly, results of determination of heavy metals (cadmium, copper, iron, lead, manganese, zinc) are shown in Table 2.

Table 2. The concentration of heavy metals [mg/dm^3] in surface water of Kampinos National Park

Place sample/date	Pb	Cd	Zn	Fe	Mn	Cu
Roztoka XI 2000	0.005	0.0001	0.003	0.92	0.05	0.005
IV 2001	0.002	–	0.005	0.39	0.05	0.012
VII 2001	0.003	–	0.080	0.76	0.02	0.001
XI 2001	0.002	–	0.010	0.39	0.14	0.010
V 2002	0.002	0.0001	0.003	0.18	0.01	0.000
XI 2002	0.002	0.0001	0.003	0.10	0.13	0.001
Aleksandrów XI 2000	0.001	0.0000	0.000	0.58	0.28	0.006
IV 2001	0.001	–	0.011	0.77	0.16	0.040
VII 2001	0.003	–	0.050	0.76	0.02	0.001
XI 2001	0.003	–	0.070	0.79	0.24	0.010
V 2002	0.001	0.0001	0.005	0.33	0.00	0.001
XI 2002	0.001	0.0004	0.000	0.01	0.00	0.000
Wędziszew XI 2000	0.003	0.0000	0.003	1.70	0.90	0.006
IV 2001	0.002	–	0.000	0.51	0.18	0.003
VII 2001	0.003	–	0.080	11.5	6.85	0.005
XI 2001	0.004	–	0.010	0.38	0.04	0.010
V 2002	0.001	0.0001	0.030	0.27	0.01	0.001
XI 2002	0.001	0.0001	0.002	0.03	0.00	0.000
Admissible content [6]:						
I class purity	0.05	0.005	0.2	1	0.1	0.05
II class purity	0.05	0.03	0.2	1.5	0.3	0.05
III class purity	0.05	0.1	0.2	2.0	0.8	0.05

The results of determinations of nitrates, phosphates, calcium and magnesium are shown in Table 3.

Table 3. The concentration of nitrates, phosphates, magnesium and calcium [mg/dm^3] in surface water of Kampinos National Park

Sampling place	Nitrates	Phosphates	Magnesium	Calcium
Roztoka – average	3.44	0.10	12.7	97.0
range min – max	1.14 – 8.53	0.06 – 0.14	12.4 – 13.1	86.0 – 116
Aleksandrów average	0.70	0.25	5.3	69.0
range min – max	0.21 – 1.34	0.14 – 0.36	5.0 – 5.5	65.0 – 72.0
Wędziszew average	1.35	0.14	5.6	102
range min – max	0.82 – 1.86	0.04 – 0.24	4.6 – 6.3	90.9 – 115
Admissible content [6]:				
I class purity	5	0.2	–	–
II class purity	7	0.6	–	–
III class purity	15	1.0	–	–

DISCUSSION

The results, obtained as averages, calculated from two parallel analyses, served to evaluate medium concentrations of individual hydrocarbons and total concentrations in consecutive seasons and years. The most carcinogenic compound, i.e. benzo(a)pyrene, was been detected. The second hydrocarbon, regarding carcinogenic activity, was found only in two samples in November 2000 (Roztoka, 1.3×10^{-3} mg/dm^3 and Aleksandrów, 2.8×10^{-4} mg/dm^3). Indeno(1,2,3-c,d)perylene was been detected. Some hydrocarbons were found in single analyses, e.g. benzo(a)anthracene (Roztoka, July 2001, 1.2×10^{-6} mg/dm^3), dibenzo(a,h)anthracene (Roztoka, November 2000, 1.6×10^{-4} mg/dm^3) and benzo(g,h,i)perylene (Aleksandrów, November 2000, 1.2×10^{-3} mg/dm^3). The highest concentrations of PAHs were determined in November 2000 (e.g. naphthalene at about 10^{-2} mg/dm^3). Further analyses exhibited still lower values of PAHs, up to at about 10^{-5} mg/dm^3. Total concentrations of PAHs in individual points in 2002 were in interval 1.9×10^{-3} mg/dm^3 in Wędziszew and 3.5×10^{-4} mg/dm^3 in Roztoka. These values are lower than values acceptable in Poland according to the decree of adequate Ministry [6]. The scatter of results can be explained by biodegradation depending on climate conditions.

The concentrations of cadmium, copper, lead and zinc in water were very low, on the limits of detection of AAS method. They did not exceed concentrations acceptable for surface water of I grade of purity: cadmium between 0.0000 and 0.0004, copper between 0.000 and 0.04, lead between 0.001 and 0.005, zinc between 0.000 and 0.08 mg/dm^3. For concentrations of iron and manganese a bigger scatter of results was observed: iron between 0.03 and 1.70 mg/dm^3, manganese between 0.00 and 0.90 mg/dm^3. However, in July 2000, in Wędziszew the concentration of iron was 11.5 mg/dm^3 and concentration of manganese was 6.85 mg/dm^3. For the reason of manganese content, six examined samples can be classified as

II grade of water purity, two samples as water out of classification (per total number of samples: 18). Higher concentration of manganese is characteristic for water supplied by marshes [9]. Concentrations of calcium and magnesium are not diversified. They are characteristic for medium hardness of water, the highest degree of mineralization exhibited samples collected in Roztoka, whereas the samples collected in Aleksandrów exhibited the lowest. The concentrations of other anions were different, depending on place and time of sample collecting: the average nitrates concentrations were between 0.70 and 3.44 mg/dm^3, in one sample a value acceptable for I grade of purity was exceeded. The concentration of phosphates exceeded the limit in two samples. On the basis of average concentrations the samples collected in Aleksandrów (0.25 mg/dm^3) should be classified as II grade of purity, however, the infringement was not very big.

A comparison of our results with investigations of professor J. Siepak is team [13] concerning Wielkopolski National Park showed that despite numerous differences between two national parks (e.g. geological structure, population density) some conclusions are similar the concentrations of polycyclic aromatic hydrocarbons and heavy metals are low. In both areas phosphates should be considered as a most serious anthropogenic polutants.

CONCLUSIONS

On the basis of three year investigations concerning occurrence of polycyclic aromatic hydrocarbons and heavy metals in Kampinos National Park the following conclusions can be formulated:

- the most carcinogenic hydrocarbon i.e. benzo(a)pyrene was nor found;
- the presence of benzo(b)fluoranthene was confirmed only in two samples in November 2000 (1.3×10^{-3} mg/dm^3 in Roztoka and 2.8×10^{-4} mg/dm^3 in Aleksandrów);
- total average content of polycyclic aromatic hydrocarbons in individual points did not exceed 2.5×10^{-3} mg/dm^3 and was lower than the acceptable value for surface water in Poland [6];
- concentrations of cadmium, copper, lead and zinc were very low, in any case close to the limits for I grade of water purity;
- surface water of Kampinos National Park can be qualified as water of II or III grade because of increased concentration of manganese, but the reasons seems to be not of anthropogenic kind;
- average concentrations of nitrates (V) were very low (between 0.70 and 3.44 mg/dm^3), on the other hand the concentrations of phosphates were close to the limit for II grade of purity (between 0.10 and 0.14 mg/dm^3) or even slightly exceeded the acceptable level (i.e. 0.20 mg/dm^3);
- some of above formulated conclusions are in accordance with results of investigations carried out by professor J. Siepak is team concerning Wielkopolski National Park [13].

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