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PRESENCE OF CAFFEINE IN THE RUDAWA RIVER AND ITS TRIBUTARIES

ZAWARTOŚĆ KOFEINY W RZECE RUDAWIE I JEJ DOPŁYWACH

Abstract: 1,3,7-trimethylxanthine (caffeine) is an ingredient of coffee, tea, energy drinks, drugs and cosmetics. Generally, it is the most consumed pharmaceutical substance all over the world. Although it is easily metabolized, caffeine is present in wastewaters generated by households. Therefore, its detection in streams and rivers shows that untreated wastewaters are discharged into environment. Determination of caffeine in waterways could be an indicator of their anthropogenic pollution. Rudawa is the river flowing through southern Poland, with the river basin area about 318 km^2. It is a left tributary of the Vistula River, with the river mouth located in the Krakow city. Rudawa is one of the drinking water supplies for the city. It provides about 40000 m^3 of water per year. Water used as a source of drinking water must be the highest quality. Therefore the river on which drinking water intakes are located is the subject of the special monitoring. Water quality monitoring has always been important on Rudawa river and it continues to be monitored today. The aim of this study has been to check whether the caffeine is present in Rudawa waters, to determine its concentration and localization of potential sources of pollution. Samples taken from the river in twelve selected locations along the Rudawa River and its tributaries have been analyzed. Solid phase extraction combined with gas chromatography-mass spectrometry (GC-MS) has been used. Caffeine isotope 13-C3 in methanol, Sigma Aldrich, has been used as an internal standard. The concentration of caffeine in samples has ranged from 40 to 380 ng/dm^3.

Keywords: watercourse, caffeine, water pollution

Introduction

1,3,7-trimethylxanthine (caffeine) is an ingredient of coffee, tea, energy drinks, drugs and cosmetics. Generally, it is the most consumed pharmaceutical substance all over the world. Although it is easily metabolized, caffeine is present in wastewaters generated by households. Therefore, its detection in streams and rivers shows that untreated wastewaters are discharged into environment. Determination of caffeine in waterways could be an indicator of their anthropogenic pollution [1, 2].

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Experimental

Water from the Rudawa River basin was analyzed. The coordinates and description of the sampling points can be found in Table 1 and on Figure 1. Samples were gathered at 26 June 2011. On the day the samples were collected temperature was around 20ºC. There was no rain, but the day was cloudy, the sun started shining only at the afternoon. 2.7 dm^3 amber glass bottles were used to contain the samples.

Table 1

Water sampling spots

Creek	Sampling spot	Geographic coordinates	
		Latitude	Longitude
Krzeszowka	P1	50° 8'28.63"N	19°37'59.67"E
Filipowka	P2	50° 7'53.30"N	19°37'7.65"E
Dulowka	P3	50° 7'40.05"N	19°37'10.20"E
Krzeszowka	P4	50° 7'28.47"N	19°40'56.17"E
Rudawka	P5	50° 7'21.39"N	19°42'30.91"E
Bedkowka	P6	50° 8'19.74"N	19°44'42.11"E
Kobylanka	P7	50° 7'50.57"N	19°47'42.57"E
Kluczwoda	P8	50° 7'17.63"N	19°49'22.85"E
Rudawa	P9	50° 6'49.54"N	19°43'57.80"E
Rudawa	P10	50° 6'31.93"N	19°49'3.16"E
Rudawa	P11	50° 5'11.86"N	19°48'59.44"E
Rudawa	P12	50° 3'10.25"N	19°54'56.55"E

As soon as the samples were transported to the laboratory an internal standard (Caffeine isotope 13C3 in methanol, Sigma Aldrich) was added to the sample and the samples were put to the refrigerator. During the next few days samples were taken out and warmed to room temperature. The solutions' pH was elevated to 9 pH by adding a concentrated solution of sodium hydroxide (POCH). The solution was divided into three parts proportionally. Solid phase extraction was done by a VISIPRED 24TM DL (Supelco) set with 6 cm^3 cartridges containing 500 mg of C18 sorbent (J.T. Baker). The mixture of solvents ethyl acetate: acetone 1:1 (v/v) (POCH) was used as an eluent. The samples were concentrated in a vacuum concentrator (Concentrator 5301, Eppendorf) until the solvent was completely evaporated. Afterwards methanol (POCH) was added and methanol solutions were analyzed using gas chromatography and mass spectroscopy.

The GC/MS analyses were carried out on a Clarus 500 gas chromatograph (PerkinElmer)/ Clarus 500 mass spectrometer (PerkinElmer). A 30 m x 0.25 mm ID x 0.25 μm film Rtx®-200MS fused silica capillary column (Restek) was used. The GC oven temperature was programmed as follows: initial temperature of 70ºC was held for 120 s, and then raised at 0.2ºC/s to 250ºC with a hold time for 120 s. The 1 mm^3 injection volume was carried out in a splitless mode at temperature of 250ºC. The carrier gas was helium at a flow of 0.025 cm^3/s. The mass spectrometer was working in:

scan mode from 70 to 230 amu with scan time of 40 ms, sir mode m/z =194 amu of 100 ms and sir mode m/z = 197 amu of 100 ms.

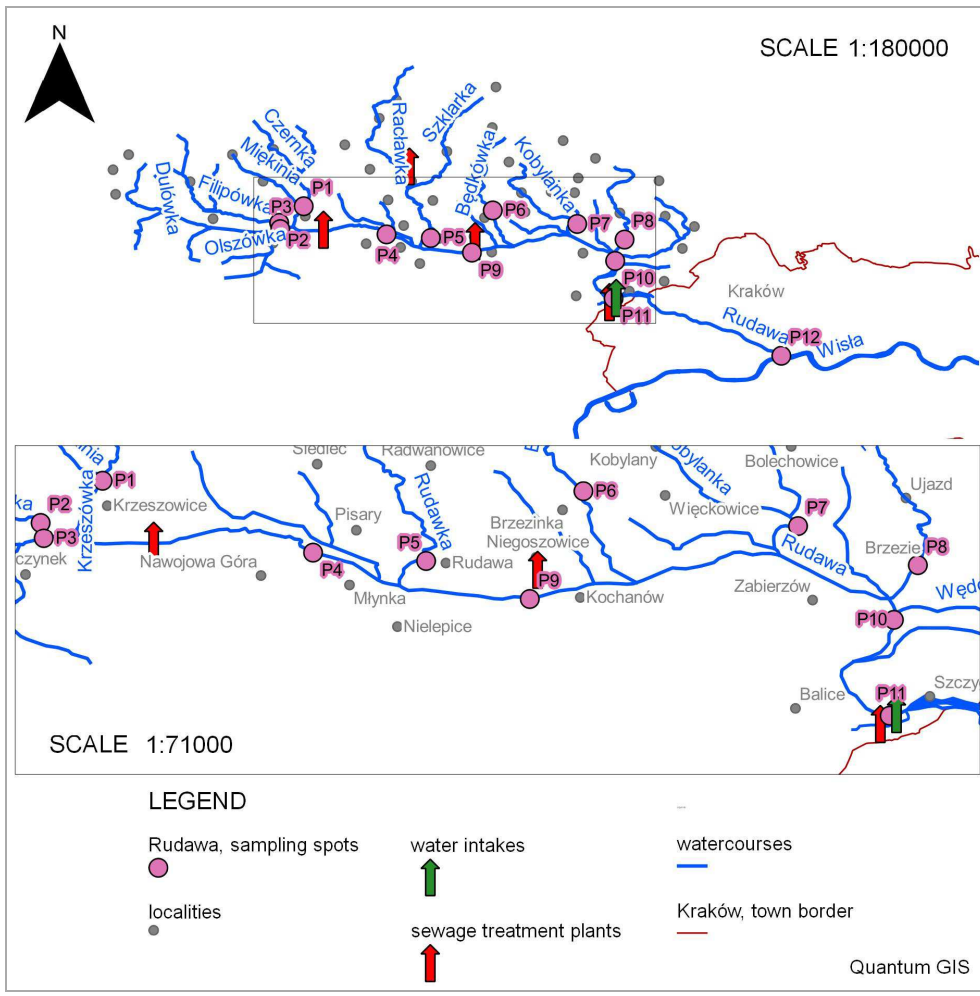

Fig. 1. Maps with system of surface water and samples locations points

Results and discussion

Table 2 contains the results of determination of caffeine concentration in the water collected from different sampling spots. Caffeine was detected in all studied samples. The concentration level ranged from 40 to 380 ng/dm^3. The lowest concentration was found in sample spot P6, and the highest one in sample spot P1.

Recovery of the internal standard for a single trial ranged between 35 and 170% and average recovery for all trials was 98%. The value of the average recovery of internal standard above one hundred percent could be caused at the stage of re-dissolution samples in methanol. Methanol can partly evaporate during dissolution of sludge because it is very volatile and thus concentrate samples. Maximum relative standard deviation is about sixteen percent shows the good precision of developed method.

Table 2

Caffeine concentration in water samples

Sampling spot	Number of samples	Average recovery of standard [%]	Caffeine concentration in water samples [ng/dm^3]	Relative standard deviation [%]
P1	3	118	380.1	9.0
P2	2	108	306.4	7.6
P3	3	106	163.2	8.2
P4	3	110	271.7	4.6
P5	3	66	67.5	8.9
P6	3	79	40.1	16.4
P7	3	45	116.1	16.1
P8	3	52	114.2	1.4
P9	3	83	180.4	10.8
P10	3	106	273.6	2.3
P11	3	116	288.2	3.7
P12	3	147	202.4	5.7

Conclusions

The determination of caffeine concentration in creeks of the Rudawa River basin was done. Caffeine is an anthropogenic waste and its presence in the surface water confirms that untreated sewage is discharged into watercourses. This is unsafe because water from Rudawa is used as source of drinking water. The water samples were collected only once at the measuring points. It is necessary to repeat the analysis in the future. This will eliminate the influence of weather conditions.

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ZAWARTOŚĆ KOFEINY W RZECE RUDAWIE I JEJ DOPŁYWACH

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Abstrakt: 1,3,7-trimetyloksantyna (kofeina) jest składnikiem kawy, herbaty, napoi energetyzujących, leków i kosmetyków. Jest najpowszechniej spożywanym farmaceutykiem na całym świecie. Chociaż jest łatwo metabolizowana, kofeina jest obecna w ściekach powstających w gospodarstwach domowych. Wykrycie kofeiny w wodach powierzchniowych dowodzi, że ścieki są bez oczyszczenia odprowadzane do środowiska. Oznaczenie zawartości kofeiny w ciekach może być uznane za wskaźnik ich antropogennego zanieczyszczenia. Rudawa to rzeka płynąca w południowej Polsce o powierzchni zlewni około 318 km^2, jest lewostronnym dopływem Wisły, do której uchodzi na terenie miasta Krakowa. Rudawa jest jednym ze źródeł zaopatrzenia mieszkańców miasta w wodę. Dostarcza około 40 000 m^3 wody rocznie. Woda wykorzystywana jako źródło wody pitnej powinna być najwyższej jakości. Dlatego jakość wody rzeki, na której zlokalizowane jest ujęcie wody pitnej, powinna być pod szczególnym nadzorem. Monitorowanie jakości wody z rzeki Rudawy zawsze było prowadzone i jest nadal. Celem badania było sprawdzenie, czy kofeina występuje w wodach Rudawy, określenie jej stężenia i lokalizacji potencjalnych źródeł zanieczyszczeń. Pobrano dwanaście próbek wody z Rudawy i jej dopływów oraz przeprowadzono ich analizy metodą ekstrakcji do fazy stałej połączonej z chromatografią gazową ze spektrometrią mas (GC-MS). Zastosowano izotop 13-C3 kofeiny w metanolu (Sigma Aldrich) jako wzorzec wewnętrzny. Stężenie kofeiny w próbkach wahało się od 40 do 380 ng/dm^3.

Słowa kluczowe: ciek, kofeina, zanieczyszczenie wody