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Original Research

Transformation of Pollutants in the Stormwater Treatment Process

Andrzej Wałęga[1]*, Agnieszka Cupak[1], Jan Pawełek[1], Bogusław Michalec[2]

[1]Department of Sanitary Engineering and Water Management,
[2]Department of Water Engineering and Geotechnics,
University of Agriculture in Kraków,
Mickiewicza ave. 24/28, 30-059 Kraków, Poland

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Abstract

Our paper evaluates the effectiveness of pollutant removal from stormwater in a semi-natural treatment plant and develops stochastic models of their transformations in a soil bed. The examined wastewater treatment facilities consisted of reduction chambers and a retention-infiltration reservoir. The following indicators of pollution were subjected to analysis: BOD_5, COD, total suspended solids, and chlorides. It was shown that COD, total suspended solids, and chlorides are the indicators that have the greatest impact on stormwater quality. However, the possibility of removal of the analyzed pollutants from stormwater is affected by the sedimentation process occurring in the reduction chambers and in the retention-infiltration reservoir, as well as by the process of infiltration through the soil bed. The developed models of pollutant transformation during wastewater infiltration through the bed were presented as the regression equations, where the selected pollution indicators in the filtrate were the dependent variable, while the analyzed pollution indicators in water from the retention-infiltration reservoir, coefficients of constant reaction kinetics determined for each variable, and the time of infiltration of wastewater through the soil bed were adopted as independent variables.

Keywords: stormwater, retention, infiltration, transformation models

Introduction

Urban areas and industrial conurbations in particular are large clusters of sources of air, water, and soil pollution, as well as the pollution of streets, yards, roofs, and open spaces. Pollution flushed from streets or other sealed surfaces pose a serious threat to the soil and water environment during rainfalls or snowmelts [1, 2]. There may be the following sources of stormwater contamination [3]:

– motorization (hydrocarbons, carbon and nitrogen dioxide, lead, suspensions, zinc)
– pollution of the atmosphere by industry or heating of buildings (heavy metals, dust)
– snow and ice cover
– street pollution
– elution of putrid sediments from channels and settling tanks during torrential rains.

Runoff from transportation areas need to be classified as the most dangerous ones. Pollution they contain originates mainly from combustion gases, surface or tire abrasion products, vehicle component wear, improper material transport, and substances used to fight ice, and road construction. Road accidents may also cause a serious threat to water and soil environments. A particularly heavy load of pollutants is carried by runoff after a long-term period of dry weather due to the accumulation of pollutants on the road surface and by melting residual snow cover on the roadsides. According to [4], levels of heavy metals and total phosphorus in storm water were the highest at the site with the highest traffic density (7,000 vehicles/day).

*e-mail: a.walega@ur.krakow.pl

Table 1. The percentage efficiency of pollutants removal in natural systems [9].

Solution	Pollution indicators						
	Total suspended solids	Total phosphorus	Total nitrogen	Heavy metals	Bacteria	Organic carbon	Oils and fat
Dry detention reservoirs	51-75	0-25	26-51	26-51	26-51	0-25	51-75
Wet detention reservoirs	76-100	51-75	26-51	51-75	51-75	26-51	51-75
Wetlands	51-75	51-75	26-51	26-51	51-75	0-25	76-100
Bioretention systems	51-75	0-25	26-51	76-100	76-100	51-75	76-100
Infiltration devices	76-100	51-75	26-51	76-100	n.d	76-100	76-100
Swales	76-100	0-25	26-51	51-75	0-25	51-75	76-100

n.d. – no data

A characteristic feature that can be observed in the case of precipitation runoff is the occurrence of the wave of the most heavily contaminated runoff during the first 10-15 minutes of rainfall, followed by a significant reduction in the concentration of pollutants. This phenomenon is called "the first runoff wave" [5]. Stormwater that enters the sewerage system has an adverse effect on the operation of treatment plants. According to Kaczor and Bugajski [6], the share from 43 to 70% of stormwater in municipal wastewater in sewerage systems in the winter half-year reduces the daily average wastewater temperature by 2 to 3ºC. This in turn affects the wastewater treatment process in bioreactors and in particular slows down the nitrification process.

In order to remove pollutants from precipitation runoff, natural units are commonly used, such as retention reservoirs or basins, treatment wetlands, and bioretention systems, etc. [7, 8]. Studies have indicated that the quality of effluent is improved by incorporating plants within biofiltration systems compared with unvegetated soil media [9-11]. In addition to hydrological functions of enhancing water retention, such facilities contribute to the removal of different pollutants present in the runoff and are resistant to significant fluctuations in pollution load, which flows thereto. The effectiveness of these facilities is different and the exemplary values given by the U.S. Environmental Protection Agency are presented in Table. 1.

The objective of this research was to assess the effectiveness of pollutant removal from stormwater in a retention-infiltration reservoir and to describe the changes in the process of infiltration using statistical models.

Description of Research Object

The examined facility was located in the urban-industrial area of the city of Kraków, in the area of the Kraków-Bieżanów railway. The drained watershed is mostly urbanized, characterized by the presence of impermeable surfaces – these are asphalt roads, sidewalks, railway tracks and switches as well as areas underneath buildings. Permeable lands consist mainly of grasslands, overgrown wastelands, and vegetable cultivations. The analyzed area lacks a rainwater drainage system. The drained area is characterized by the presence of sub-watersheds with different surface runoff coefficients. The sub-watershed areas together with the surface runoff coefficients are given in Table 2.

Table 2. Areas of the sub-watersheds together with corresponding surface runoff coefficients [12].

Type of land	Area of the sub-watershed [km^2]	Surface runoff coefficient
Wastelands and vegetable plantations	0.387	0.15
Railway	0.058	0.30
Transportation (roadways, car parks, etc.)	0.00505	0.70
Total	0.45	0.175*

*the weight average surface runoff coefficient

Due to the occurrence of the water table under pressure, the operator of the wastewater treatment plant left 0.5 m (from the bottom of the reservoir) of cohesive soil layer with the filtration coefficient k_f = 0.0086 m·d^{-1} (9.90·10^{-8} m·s^{-1}), in order to balance the pressure of the groundwater column. The performed granulometric analysis of ground in the reservoir substrate confirmed earlier assumptions about soil permeability.

The aerometric analysis according to the modified method of Pruszyński showed the occurrence of cohesive soils with particle size corresponding to silty clay with sand in the bottom of the reservoir. The particle size of soils in the reservoir bottom is also affected by stormwater sediment.

The complex facilities for intake, transport, retention, and treatment of stormwater flowing from the watershed consist of:

– two concrete reduction chambers with settling tanks, located in roadside ditches by the railway viaduct along Półłanki street with pipelines connecting the chambers 3×400 mm

– 63 m long and 0.4 m wide at the bottom, open channel, with 2‰ slope, secured with precast concrete slabs, discharging water from reduction chambers to the reservoir, secured at the outlet with rip-rap in order to decrease energy of inflowing stormwater
– retention-infiltration reservoir with a bottom area of 1,605 m^2 and maximum capacity of 1951 m^3
– two piezometers

The reservoir has no drain or emergency spillway. In the situation of disastrous rains and subsequent runoff from catchment, the water surplus cannot be stored in reservoir floods in adjacent areas. These areas are wastelands, which are covered by grass and bushes, so it is potential ground for surface infiltration of precipitation.

The examined reservoir is a wedge-shaped earthen structure, narrower at the inlet (width B_1 = 15.0 m) in relation to the wider part (B_2 = 19.0 m). The reservoir's length from Złocieniowa Street is 78.8 m and from the railway embankment – 82.5 m. The slope of the embankment is 1:1.5, while at the entrance to the reservoir 1:3. Its average depth is equal to 1.50 m and the slope of the bottom is 2‰ toward the inlet to the reservoir.

Research Methodology

The material for the assessment of the effectiveness of stormwater treatment included physical and chemical analyses of the following pollution indicators: total suspended solids, BOD_5, COD_{Cr}, chlorides, copper, lead, zinc, chromium, and cadmium. Total suspension was marked with the use weighted method, BOD_5 by defining oxygen concentration using the Winkler method at the beginning of the measurement and after 5 days of incubation, COD using the spectrophotometric method with a Spectro3Photometer, chlorides using titration, and heavy metals using atomic spectrophotometric method ASA. In the case of spectrophotometric methods for the purpose marking of COD, tube tests were used and measurements were conducted using calibrated devices.

Samples for analysis were taken randomly during or after the occurrence of precipitation or snowmelt events. The analysis comprised the quality of stormwater in reduction chambers or retention-infiltration reservoir and the quality of groundwater in the piezometer. From reduction chambers and piezometers, samples of stormwater were taken with use a scoop of our own construction, which has a pressure click in the bottom, while from the reservoir also using a scoop with capacity of 1 dm^3 in distance about 2 m from the waterside. Samples of sewage form the reservoir were taken from the superficial area of water table.

Given the fact that the composition of stormwater depends on weather conditions, it was decided to determine the effect of season on the quality of runoff collected in reduction chamber 2 and in the retention-infiltration reservoir. The analysis was performed using t-Student's test, because of the small sample size (number of measurements below 30), earlier the hypothesis about normality of variables using Shapiro-Wilk's test was verified. In fact for each analyzed indicator there was no basis for rejection of hypothesis about the normality of the distribution in following analyses mentioned above t-Student test was taken. The whole study period was divided into months: March-July and August-February. Such a division of the year results from the following assumptions: the most polluted runoff occurs in the spring-summer period due to snowmelt (months: March, April) and heavy rainstorms (May-July) that cause flushing of pollutants accumulated on the surface of the watershed during the winter or dry period. In the period of August-February there is a tendency for smaller amounts of precipitation, particularly torrential ones, therefore the amount of stormwater is less and it is not overburdened by pollution. The analysis included only three indicators critical for stormwater pollution, including: total suspended solids, COD, and chlorides.

Stormwater that infiltrates through the aeration zone is subject to treatment trough mechanical, physical, and biochemical processes. In this paper, the time of infiltration was determined from the following formula [13]:

$$t_{\inf} = \frac{H_a}{0.5 \cdot k_f} \quad (1)$$

...where:
$t_{\inf}$ – time of infiltration, (d)
H_a – thickness of aeration zone (depth of groundwater table from the bottom of the reservoir), (m)
k_f – filtration coefficient of the unsaturated zone, ($m \cdot s^{-1}$).

The biochemical reduction of pollutants depends on the form in which they appear (dissolved or suspended) and on the speed of transformations [14]. Models describing the processes of pollutant decomposition in infiltrating stormwater were established for the given rate of reaction kinetics. A detailed methodology for determining the speed of pollutant transformations was described in the paper by Wałęga and Cupak [15]. Using the method of correlation, the factors most significantly affecting the transformations of the selected indicators of pollution (BOD_5, COD_{Cr}, total suspended solids) in the bed were established for the determined parameters. In this case BOD_5 was included, because this indicator can undergo biological and chemical transformation in the bed, opposite from chlorides. A "black box" model was applied, where the entry point was the concentration of the mentioned pollution indicators in water from the reservoir, and the output – their concentration in groundwater.

The selection of the set of optimal variables was based on the determination of interactions between independent variables and the dependent variable. The measure of this interaction is the multiple correlation coefficient R. The selection of variables was composed of several steps. In the first one, after examining all simple correlation coefficients between the dependent variable and independent variables, the highest one was selected. Then, its significance was determined and in the case of compliance it was adopted as the first variable of the optimal set. In next stages, the partial correlation coefficients were examined between the dependent variable and the other variables of the potential set, determining the relationship after considering the impact of variables adopted in the earlier stages of analysis. At each step the significance of the partial correlation coefficient was analyzed using t-test. The calculated values of the t-statistics were compared to the critical values given in tables and in the case when $t_{calc} \geq t_{cr}$ at the given level of significance and degrees of freedom, it was considered to be statistically significant. Those that were significant were adopted as next variables of the optimal set. After the procedure of the optimum variables selection was completed, transformations of a given pollution indicator during infiltration through the bed was described using a multiple regression equation.

Results and Discussion

As the character of stormwater is affected by a number of factors, the statistical analysis methods were applied in order to perform the objective analysis of results. Basic statistical characteristics of the analyzed physical and chemical indicators of stormwater pollution were presented in Table 3. The values given in Table 3 show high variability, mostly in the case of organic pollutants (BOD_5, COD), and total suspended solids and chlorides in the samples collected from the reduction chambers. The average value of BOD_5 in water of precipitation runoff in the reduction chamber 1 was 27.79 $mgO_2 \cdot dm^{-3}$. Values of this parameter vary from 1.80 to 104.65 $mgO_2 \cdot dm^{-3}$. Similarly, in the case of COD, a high variability is observed (range of values is 912.1 $mgO_2 \cdot dm^{-3}$) with the average of 305.32 $mgO_2 \cdot dm^{-3}$. The COD/BOD_5 ratio indicating the susceptibility of wastewater to biochemical decomposition processes in the samples collected from reduction chambers range from 10.98 to 11.69. This shows that the samples are dominated by hardly microbiologically-decomposable organic matter. The occurrence of some microbiological processes is evidenced by the increase of this ratio up to 14.17 in water from the reservoir.

The values of COD/BOD_5 ratio observed by Babelski [16] when studying precipitation runoff from the Warsaw Uprising Avenue in Rzeszów during outflow ranged from 2.7 in the final stage of runoff through the values 9.3, 12.8 up to 42.2, and 67.4. These results indicate low stability and unpredictability of the stormwater composition. Variability of pollution concentrations in stormwater depends not only on the type of surface, where the runoff occurs, but also on the intensity of the precipitation event [17]. Relatively low values of average total suspended solid concentrations in reduction chambers are particularly noteworthy. This is caused by the fact that during the sampling of stormwater the suspensions contained in them partially sedimented, sinking to the bottom of the chambers. On the other hand, high concentrations of chlorides are observed in reduction chamber 1 (average concentration equal to 786.05 $mg \cdot dm^{-3}$, with the range of 2,992.8 $mg \cdot dm^{-3}$) (Table 3). Maximum concentration of this indicator, observed during snowmelt, was 3,070.8 $mg \cdot dm^{-3}$.

According to [18], increased values of chlorides in water agglomerated in stormwater ponds could create a serious danger for the quality of the underground water. A significant decrease in the average values of the analyzed parameters as well as their variability is observed in the retention-infiltration reservoir. Lower values of the mentioned pollution indicators in the retention-infiltration reservoir as compared to the reduction chambers are caused by their sedimentation and mineralization involving plants growing on the slopes of the feeder and the reservoir. Sulej et al. [19] had similar observations regarding higher heavy metal concentrations in stormwater in the winter half-year studying runoffs from airports in Warsaw and Gdańsk. The highest heavy metal concentrations were observed in runoff from the pits and car parks.

The highest heavy metal concentrations were observed in samples collected from the reduction chambers. Similarly as in the case of other pollution parameters, the chambers are reached by the most heavily polluted batches of stormwater, hence the observed, highest concentration of this indicator. Polkowska et al. [20], based on the qualitative analyzes of precipitation runoff from highways, found that due to the significant level of pollutants, also toxic ones, that occur in these runoffs, it is necessary to monitor the stormwater outflows from roads with high traffic load in urban areas.

Much lower concentrations of heavy metals are observed in the reservoir and in groundwater, except for cadmium, where less effective reduction of its ions due to infiltration was the result of its occurrence in the dissolved form.

The reduction of heavy metal concentrations between chambers and the reservoir may be caused by the sedimentation of suspensions and thus heavy metals adsorbed on their surface. Other researchers also indicate the favorable role of infiltration in heavy metal retention. Nadler and Meiβner [21], when studying leachate from the experimental plots located near the communication path in Augsburg, applied the surface soaking through the area covered by plants growing on gravel substrate, soaking in mogul slopes, in which the subsoil and sand in different proportions were the filtration layer and soaking in ditches with similar composition of filtration layer as in the case of mogul slopes. The observed lead concentration in leachate did not exceed 0.010 $mg \cdot dm^{-3}$ (the lowest in the case of mogul slopes), copper < 0.048 $mg \cdot dm^{-3}$ (the lowest < 0.019 $mg \cdot dm^{-3}$ in the ditch overgrown with reeds), cadmium < 0.0004 $mg \cdot dm^{-3}$ (similar values in all solutions) and zinc < 0.120 $mg \cdot dm^{-3}$ (the highest in leachate from the gravel overgrown by grass). Similar values of reduction of suspension and heavy metals in result of sedimentation processes in ponds is described by Carpenter et al. [22] and Sebastian et al. [23]. It should be remembered that heavy metals could create a serious danger for conditions of health of water bodies, and fish, which are the last link in the trophy chain. This problem also affects reservoirs collecting precipitation runoff, because they are often settling by water bodies, which favors the reduction of contaminants. Although many metals are essential, all metals are

Table 3. Statistical characteristics of physical and chemical properties of stormwater.

Pollution indicator	Mean	Confidence interval of average at ±90%	Max.	Min.	Range	Standard deviation
Reduction chamber 1						
BOD_5 [$mgO_2 \cdot dm^{-3}$]	27.79	15.92-39.66	104.65	1.80	102.85	32.35
COD_{Cr} [$mgO_2 \cdot dm^{-3}$]	305.32	191.3-419.4	942.3	30.2	912.1	310.84
Total susp. sol. [$mg \cdot dm^{-3}$]	106.5	65.05-147.9	492.0	6.4	485.6	112.92
Chlorides [$mgCl \cdot dm^{-3}$]	786.05	514.6-1057.4	3070.8	78.01	2992.8	721.14
Cadmium [$mgCd \cdot dm^{-3}$]	0.0010	0.0001-0.002	0.0024	0.00029	0.0021	0.00095
Lead [$mgPb \cdot dm^{-3}$]	0.020	0.0-0.045	0.065	0.0033	0.062	0.026
Zinc [$mgZn \cdot dm^{-3}$]	0.225	0.031-0.419	0.46	0.05	0.41	0.203
Copper [$mgCu \cdot dm^{-3}$]	0.032	0.010-0.054	0.066	0.014	0.052	0.023
Chromium [$mgCr \cdot dm^{-3}$]	0.002	0.0-0.0042	0.0061	0.0010	0.0051	0.0023
Reduction chamber 2						
BOD_5 [$mgO_2 \cdot dm^{-3}$]	20.24	7.65-32.84	144.0	1.40	142.6	34.32
COD_{Cr} [$mgO_2 \cdot dm^{-3}$]	236.53	155.38-317.68	919.93	19.74	900.19	221.20
Total susp. sol. [$mg \cdot dm^{-3}$]	64.2	39.9-88.54	312.4	8.40	304.0	66.23
Chlorides [$mgCl \cdot dm^{-3}$]	461.13	274.46-647.8	2021.2	60.28	1960.9	495.97
Cadmium [$mgCd \cdot dm^{-3}$]	0.0010	0.00-0.0024	0.0036	0.00011	0.0035	0.0014
Lead [$mgPb \cdot dm^{-3}$]	0.026	0.00-0.063	0.095	0.0033	0.092	0.039
Zinc [$mgZn \cdot dm^{-3}$]	0.213	0.00-0.463	0.67	0.043	0.627	0.262
Copper [$mgCu \cdot dm^{-3}$]	0.035	0.00-0.071	0.102	0.010	0.092	0.038
Chromium [$mgCr \cdot dm^{-3}$]	0.0033	0.00-0.0073	0.0108	0.0010	0.0098	0.0043
Retention-infiltration reservoir						
BOD_5 [$mgO_2 \cdot dm^{-3}$]	8.72	5.57-11.87	36.0	1.20	34.80	9.41
COD_{Cr} [$mgO_2 \cdot dm^{-3}$]	112.45	69.38-155.51	452.52	16.34	136.18	94.6
Total susp. sol. [$mg \cdot dm^{-3}$]	58.95	34.99-82.91	165.6	6.8	158.8	49.72
Chlorides [$mgCl \cdot dm^{-3}$]	146.75	119.7-173.8	468.07	39.01	429.06	80.81
Cadmium [$mgCd \cdot dm^{-3}$]	0.00022	0.0-0.0006	0.0007	0.0000	0.0007	0.00032
Lead [$mgPb \cdot dm^{-3}$]	0.0043	0.001-0.007	0.007	2	0.0051	0.0027
Zinc [$mgZn \cdot dm^{-3}$]	0.043	0.009-0.076	0.08	0.0019	0.06	0.028
Copper [$mgCu \cdot dm^{-3}$]	0.018	0.003-0.033	0.036	0.02	0.029	0.013
Chromium [$mgCr \cdot dm^{-3}$]	0.0012	0.0007-0.002	0.0019	0.0010	0.0009	0.00046
Piezometer						
BOD_5 [$mgO_2 \cdot dm^{-3}$]	2.94	1.19-4.96	24.0	0.40	23.60	5.33
COD_{Cr} [$mgO_2 \cdot dm^{-3}$]	100.23	67.2-133.2	325.6	4.75	320.8	100.61
Total susp. sol. [$mg \cdot dm^{-3}$]	61.49	45.43-77.54	197.6	1.10	196.5	47.92
Chlorides [$mgCl \cdot dm^{-3}$]	129.10	115.8-142.4	187.9	53.2	134.74	40.53
Cadmium [$mgCd \cdot dm^{-3}$]	0.00013	0.00005-0.0002	0.0002	0.00002	0.0002	0.000084
Lead [$mgPb \cdot dm^{-3}$]	0.010	0.0047-0.016	0.021	0.0068	0.014	0.006
Zinc [$mgZn \cdot dm^{-3}$]	0.113	0.049-0.175	0.230	0.066	0.164	0.066
Copper [$mgCu \cdot dm^{-3}$]	0.014	0.010-0.018	0.019	0.0099	0.0091	0.0040
Chromium [$mgCr \cdot dm^{-3}$]	0.0010	–	0.0010	0.0010	0.00	0.00

Table 4. The significance of differences in the concentrations of the selected pollution indicators in different seasons of the year.

Indicator	Reduction chamber 2					Retention-infiltration reservoir				
	Mean [mg·dm^{-3}]		t	df	p*	Mean [mg·dm^{-3}]		t	df	p*
	III-VII	VIII-II				III-VII	VIII-II			
Suspensions	55.7	76.5	-0.72	20	0.482	53.1	129.7	-1.614	18	0.124
COD	241.5	229.3	0.124	20	0.902	120.6	101.6	0.447	19	0.600
Chlorides	**796.7**	**252.9**	**2.45**	**19**	**0.024**	**171.3**	**107.3**	**5.74**	**19**	**0.00002**

*differences are statistically significant at $p < 0.05$
Bold means indicator with statistically significant difference of the average concentration from the half-years periods

toxic at higher concentrations because they cause oxidative stress by the formation of free radicals. Aquatic organisms such as fish accumulate pollutants directly from contaminated water and indirectly via the food chain [24]. The accumulation of heavy metals in the tissues of organisms can result in chronic illness and cause potential damage to the population. Toxic effects of heavy metals on soil microorganisms in situ (near the roadside of the Vilnius-Kaunas-Klaipeda highway) were investigated by Jadhav et al. [25] and a negative influence of the test metals on actinomycetes, mineral nitrogen assimilating and oligonitrophilic bacteria was found.

The operation effectiveness of devices for infiltration of stormwater with respect to heavy metals may be increased by the enrichment of the bed with zeolites (e.g. aluminosilicates) [26, 27]. Among them, clinoptilolite is the most common component of protective barriers in systems for stormwater infiltration.

A significant influence of the year's season on the concentration of chlorides in the reservoir is indicated by the results of Student's t-test calculations (Table 4). This is affected by the supply of the reservoir by the direct watershed. In spring, those runoffs are loaded with a large amount of chlorides accumulated in snow as a result of procedures related to road maintenance in winter. Slightly lower concentrations of chlorides in wastewater from the reservoir in comparison to the samples collected from the reduction chamber may result from stormwater dilution by runoffs from undeveloped lands.

Another element of the study was to develop models for transformations of pollutants during infiltration. Determining the factors affecting pollutant transformations and a functional description of their course were based on the empirical data correlation analysis. The following indicators of pollution were adopted as dependent variables: BOD_5, COD_{Cr}, and total suspended solids. Independent variables that describe the modeled values were the pollution indicators in water of the retention-infiltration reservoir, constant reaction kinetics coefficients described in the paper by Wałęga and Cupak [15] for each variable, and the time of wastewater infiltration through the soil bed, determined based on formula (1). The analyses carried out in the above-mentioned paper indicated that the transformative reactions of COD and total suspended solids may be described by zero-order kinetics. This shows that the rate of elimination of these pollutants is independent of their concentration and that they occur mainly in dissolved form. Only in the case of BOD_5 values were their transformations in the ground described by the second-order reaction kinetics. Table 5 presents the simple correlation matrix between the dependent and independent variables.

As follows from Table 5, the BOD_5 values are significantly correlated (at the significance level $\alpha = 0.05$) only with the time of infiltration t_{inf} ($r_{calc} = 0.803 > r_{cr} = |0.423|$). According to formula 1, the time of infiltration is directly proportional to the thickness of aeration zone. Therefore, the larger the aeration zone, the longer the distance that infiltrating wastewater must follow and thus the longer is its contact with the soil air, which leads to biochemical oxidation of easily decomposed pollutants. This regularity is evidenced by the negative sign of the correlation coefficient. A negative sign by the correlation coefficient for the relationship between BOD_5 and rate constant of second-order kinetics k_2 proves that the higher its value, the more intense are the biochemical transformations and therefore the BOD_5 values are reduced. The correlation coefficient r=-0.15 is, however, statistically insignificant. This is due to the fact that this model is not the best one to describe the organic matter transformations in the soil. The amount of easily decomposable organic matter in stormwater is subject to considerable fluctuations depending on the character of precipitation event, hence the difficulty in the mathematical description of this process. In the case of COD values there is a statistically significant correlation with the water temperature at $\alpha = 0.05$. The obtained simple correlation coefficient r = 0.602 suggests the significant impact of thermal conditions on the organic matter transformations, expressed as COD. A positive value of correlation coefficient between COD and time of infiltration t_{inf} follows from the fact that organic matter may be eluted from the bed with increasing thickness of aeration zone resulting in an increase in this ratio.

The concentrations of total suspended solids in the filtrate are most significantly affected by zero-rate reaction constant (Table 5). The obtained result of simple correlation between these variables, equal to r = -0.642, is statistically significant at $\alpha = 0.05$ ($r_{calc} = -0.641 > r_{cr} = |0.412|$ at 15 degrees of freedom). Smaller values of reaction rate coefficient cause an increase in concentrations of total suspended solids in the filtrate. The reason for this may be elution of

Table 5. Matrix of simple correlation coefficients between dependent variables and a set of potential independent variables.

Dependent variables	Independent variables									
	k_0	k_2	t_{inf}	Stormwater temperature	pH	Total susp.	BOD_5	COD	Diss. oxygen.	Chlorides
BOD_5	-	-0.15	**-0.80**	0.171	0.047	-0.23	1.00	-	-0.08	-
COD	0.11	-	0.419	**0.602**	0.319	-0.29	-0.32	1.00	-0.31	0.137
Total susp.	**-0.64**	-	-0.10	0.05	-0.24	1.00	-0.23	-0.29	-0.09	-0.05

Bold means statistically significant value of correlation coefficient

small suspended particles from the bed and bottom sediments, resulting in an increased concentration of suspension in the runoff, significantly reducing the value of the reaction kinetics coefficient. The lack of significant correlation between the suspended solids and COD is the result of the fact that these indicator-forming substances occur mainly in dissolved form. On the other hand, the lack of correlation between the total suspended solids and BOD_5 is caused by the dominance of mineral form of suspension during filtration, which is why the share of volatile forms, representing organic pollutants is small.

The final equation describing the transformations of the analyzed pollution indicators during infiltration may be presented in the following forms:

$$C_{BOD5} = -0.527 \cdot t_{inf} + 2.121 \quad (2)$$

$$C_{COD} = 55.572 - 0.171 \cdot C_{Cl} + 0.657 \cdot \text{temp.} \quad (3)$$

$$C_{tot.susp.} = 251.795 - 0.600 \cdot k_0 - 0.423 \cdot C_{oxy} \quad (4)$$

The resulting multiple correlation coefficient in equation (3) amounted to R = 0.673 and is statistically significant at $\alpha = 0.05$ ($R_{calc} = 0.673 > R_{cr} = 0.444$) and 18 degrees of freedom. This provides a basis for evaluating the COD values in the filtrate with the 5% risk of error based on two features: chloride concentration and water temperature in the reservoir. However, it was found that only a partial regression coefficient describing the wastewater temperature is statistically significant at $\alpha = 0.05$ ($t_{calc} = 3.762 >$ ttabl $= 2.101$). The correctness of the selected model for the suspension transformations is evidenced by the high value of the multiple correlation coefficient R = 0.768. This coefficient is statistically significant at $\alpha = 0.05$ (critical value for 12 degrees of freedom is $R_{cr} = 0.532$). Partial regression coefficients also are statistically significant (at $\alpha = 0.05$) with zero-order kinetics and concentration of oxygen.

Conclusions

In the article the analysis of changes of contaminants contained in stormwater during the process of its treatment were made. Research was conducted on a real object located in Kraków. The basic element of the examineted stormwater treatment plant were reduction chambers, which act as an initial pretreatment of runoff and a retention and infiltration reservoir. The analysis included the most important indicators of pollution, which influenced quality of stormwater.

Based on the conducted analysis it may be concluded that COD, total suspended solids, and chlorides are the indicators which best determine stormwater quality. It was proved that only in the case of chlorides contained in wastewater samples collected from the reservoir was there a clear tendency for their higher concentrations in spring and summer in relation to the remaining months. The highest concentrations of heavy metals occur in the reduction chambers, but they are reduced in the reservoir and in groundwater. The reduction occurs as a result of sedimentation (hence the largest metal concentration in bottom sediments) and during sorption in soil during infiltration [5]. The existing risk of ground water contamination by pollutants present in sewage should be remembered. The risk of groundwater contamination is, however, not only related to the soluble pollutant fractions that potentially might be absorbed to the fixed soil particles, but can be due to adsorption on the mobile colloidal phase found in the pore water [28]. It was stated that the possibility of major pollutant removal from wastewater, such as: organic substances (BOD_5, COD), total suspended solids, chlorides, and heavy metals is determined by the sedimentation process that occurs in reduction chambers and in the retention-infiltration reservoir, as well as the process of infiltration through the soil bed. The best solution is to combine both processes, since then the best operation results of these devices are achieved. Transformations of organic pollutants and suspended solids may be described by simple stochastic models. The analysis showed that the transformations of these pollutants during infiltration depend on the reaction rate occurring in the bed and on the quality of water stored in the reservoir. The developed relationships can be used to predict the effect of retention-infiltration reservoirs on groundwater provided that there are similarities between soil and water conditions occurring in the vicinity of such facilities. In view of the fact that presented solutions for stormwater treatment use natural processes set in the ground and water, they should be commonly used. These solutions ensure the complexity of stormwater development, are characterized by higher reliability, and have great landscape value [29].

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