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ASSESSMENT OF PHYSICOCHEMICAL AND BIOCHEMICAL FACTORS OF URBAN STREET DUST

Studies concerned the composition of street cleansing residue (municipal waste with code 20 03 03) collected and accumulated on mound. The contents of macro- (C, P, S) and microelements (Zn, Cu, Pb, Ni, Cr, Mn, Fe) as well as enzymatic activity (dehydrogenase, catalase, alkaline and acid phosphatase, arylsulfatase) were determined in order to consider this material as a source of nutrients in agriculture. The study showed that the stored material consists mainly of mineral particles, poor in organic matter (mean content 2.905 g/kg) and fine fraction (particles of diameter less than 2 μm did not exceed 2 wt. %), with alkaline pH. Elevated levels of heavy metals (Cu, Pb, Ni, Cr, Mn and Fe) indicate that street cleaning residue is contaminated with these metals. In spite of relatively high content of phosphorus (mean 52.08 mg/kg) analyzed material should not be used for soil amendment as a source of P for plants, because of the accumulation of heavy metals, and also high contents of S-SO_4^{2-} (mean 56.38 mg/kg). Furthermore, low biological index fertility (*BIF*) calculated on the base of enzymatic activity of the collected waste, indicates that analyzed material has low ability to fulfil nourishing plant needs and might be a threat to the environment.

1. INTRODUCTION

Street dusts within urban areas represent a repository of multiple contributing sources of pollution including car vehicles emissions (wear of brake pads, tires, catalytic converters and fuel combustion process), chemical compounds used for deicing of streets, products of weathering of construction materials or concrete abrasion and others. Due to the origin of particles, street dusts contain heavy metals and other toxic components [1].

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The residue collected during cleaning of streets, called also road sediments, is qualified to municipal wastes, with a code No. 20 03 03. Street dusts consist of a mixture of mineral and organic materials – products of interaction of solid, liquid and gaseous contaminants emitted in the urban environment. Municipal solid waste usually contains high levels of phosphates, sulfates, chlorides, nitrogen compounds, calcium, magnesium, potassium, sodium and heavy metals which limit its management and utilization [2].

Studies on street dusts are limited to their chemical composition and the impact on human health [3–6]. A number of studies of street sediments have been directed at the degree to which they may contribute to the degradation of water resources [7]. There is no data available on the management of this waste collected in large quantities from roads, pavements and streets.

The accession of Poland to UE involved also European legislation on waste management, according to council Directive 75/442/UE [8] and a Directive 199/31/UE [9].

According to Regulatory of the Ministry of Economy and Labour of the year 2005, municipal waste storage with net caloric value larger than 6 MJ/kg is prohibited from 2013. Landfilling is the least preferable option for waste management and should be limited to the necessary minimum. Safe waste management and possible ways of its utilization should be predated by the identification of the chemical composition.

The aim of the present study was to assess physical, chemical and biological properties of municipal waste from dry cleaning of streets in order to establish its safe management instead of land filling.

2. EXPERIMENTAL

Study location. Material for the study is comprised of street cleansing residue (called also street dust, or road sediment) from dry cleaning of streets and public squares of Bydgoszcz community by the Municipal Services Company (53°12'N, 18°01'E; the Kujawy and Pomerania Province, central Poland). Bydgoszcz is located in temperate climate zone with the oceanic and continental influence. The area is characterized by annual precipitation typical of oceanic climate (533 mm) and thermal conditions common for the continental climatic zone. Mean annual temperature in the city is 7.8 °C; the coldest month is January (mean –2.3 °C) and the warmest is July with the monthly mean temperature 18.3 °C. Maximum precipitation is observed on July (72 mm) and minimum on February (20 mm). The waste with a code No. 20 03 03 was cumulated and stored on a large mound (103.0 m long and 5.0 m high) in the period of two years 2010–2012.

Laboratory analysis. From the mound of street dust 12 samples (depth of 40 cm) of the material were collected for the analysis. The samples were air dried and pass through the 2 mm sieve. Sampled material was treated like soil samples and analytical procedures used in the present study were similar as for the soil material [10].

The following analytical methods were used: total organic carbon (TOC) was determined with the TOC FORMACTS™ analyser Primacs provided by Skalar, pH in H₂O and pH in 1 M KCl measured potentiometrically (ISO 10390), the texture with the laser diffraction method applying the Masterssizer MS 2000 analyser. The content of available phosphorus (P_{E-R}) was determined with the Egner–Riehm method – DL, which involves the spectrophotometric measurement of the intensity of the colour of phosphorus-molybdenum blue formed by orthophosphoric ions with molybdenum ions in the presence of SnCl₂. The content of sulfate sulfur was determined by the Bardsley–Lancaster turbidimetric method [11] as modified by COMN-IUNG using an UV-visible spectrophotometer Evolution 201. The total concentrations of heavy metals (Zn, Cu, Pb, Ni, Cr, Mn, Fe) were assayed after mineralisation of the samples in the mixture of HF and HClO₄ as described by Crock and Severson [12]. The total contents of heavy metals were determined by the method of atomic absorption spectroscopy with the PU 9100X spectrometer (Philips).

Field-moist samples were sieved (2 mm mesh) and stored in a plastic box at 4 °C for not less than 2 days in order to stabilize the microbial activity and then were analyzed for selected redox enzymes: dehydrogenases [E.C. 1.1.1], catalase [E.C. 1.11.1.6] and enzymes of the class hydrolases: alkaline [E.C. 3.1.3.1] and acid [E.C. 3.1.3.2] phosphatase, and arylsulfatase [EC 3.1.6.1] activity within one week. Dehydrogenase activity (DEH) was determined according to Thalmann [13] with some minor modifications. Soil (1.0 g) was incubated for 24 h with 2,3,5-triphenyltetrazolium chloride (TTC, 3 mg/cm³ at 27 °C, pH 7.6. The produced triphenylformazan (TPP) was extracted with acetone and determined spectrophotometrically at the wavelength of 546 nm. The activity of catalase (CAT) in soil by the Johnson and Temple method [14] was measured by manganometric titration of the surplus of H₂O₂ under acidic conditions. The activity of alkaline (AIP) and acid (AcP) phosphatase was determined by the Tabatabai and Bremner method [15]. It is based on the colorimetric assaying of released substrate: *p*-nitrophenylphosphate (*p*NP) after incubation of soil with of MUB (modified universal buffer) at pH 6.5 for acid phosphatase and pH 11.0 for alkaline phosphatase samples for 1 h at 37 °C. The prepared soil samples (1.0 g) were incubated with an acetate buffer (pH 5.8), toluene and a potassium *p*-nitrophenyl sulfate solution at 37 °C for 1 h. Afterwards, 0.5 M CaCl₂ and 0.5 M NaOH were added and then the solution was filtered. The intensity of the color of *p*-nitrophenol that was formed was determined by reading the absorbance at the wavelength of 420 nm using a calibration absorbance curve versus the *p*-nitrophenol concentrations [16].

Based on enzymatic activities of the samples biological index fertility (*BIF*) was calculated according to Stefanic et al. [17]:

$$BIF = -\frac{1.5DEH + 100kCAT}{2}$$

where *k* is a proportionality factor equal to 0.01.

For the set of the data, arithmetic means (X) and median were calculated as well as a standard deviation (SD) and the coefficient of variation (CV) were estimated.

The coefficient of variation of analyzed parameters was calculated:

$$CV = \frac{SD}{X} \times 100\%$$

CV values of 0–15%, 16–35%, and >36% indicate low, moderate, or high variability, respectively.

All the assays were made in three replicates; the paper demonstrates the arithmetic means and ranges of the results. Besides, the results of the analyses of the features investigated were exposed to the analysis of simple correlation by Pearson's ($p < 0.05$), to define the level of dependence between the respective properties. The analysis of the correlation was performed in the STATISTICA 8.1 for WINDOWS software.

3. RESULTS AND DISCUSSION

Municipal wastes from the cleaning of streets and public squares varied in composition due to their source of origin [18]. Analysed material collected from Bydgoszcz community contained mainly mineral, coarse grains. The texture was classified according to Polish Society of Soil Science (PSSS) procedure [19] which showed the dominance of sand fraction (79.8–87.19 wt. %, Table 1).

Table 1

Texture and pH of studied street dusts

No. sample	Content of fraction wt. %			pH	
	Sand	Silt	Clay	H ₂ O	KCl
1	84.29	14.31	1.41	8.10	7.59
2	81.95	16.43	1.63	8.02	7.57
3	85.19	13.60	1.20	7.69	7.50
4	79.82	18.29	1.88	7.99	7.80
5	85.24	13.56	1.21	7.99	7.69
6	80.27	17.99	1.74	7.84	7.28
7	87.19	11.68	1.13	7.96	7.52
8	86.64	12.28	1.09	7.99	7.47
9	85.21	13.51	1.28	7.91	7.39
10	85.20	13.51	1.29	8.02	7.68
11	86.60	12.62	1.13	8.04	7.43
12	86.35	12.68	0.97	8.02	7.59

Such a high content of sand particles, characteristic of urbizems from Bydgoszcz agglomeration, indicates low sorption capacity of the material. Studied samples were neutral or alkaline ($\text{pH} > 7$). The alkalization of the material may be caused by carbonate particles, present in the waste due to weathering processes of building and concrete constructions. Other authors reported also the influence of alkaline dust from road aggregate limestone and deicing salts [3] used by municipal services.

Table 2

The content of some macro- and microelements in samples

Parameter	C_{org} [g/kg]	$P_{\text{E-R}}$	$S\text{-SO}_4^{2-}$	Zn	Cu	Pb	Ni	Cr	Mn	Fe [%]
	[mg/kg]									
Minimum	0.705	19.21	21.10	15.00	41.38	20.90	24.13	39.43	501	19.70
Maximum	9.600	95.47	101.18	28.23	90.45	94.25	37.93	52.08	641	33.37
Mean	2.905	52.08	56.38	23.71	69.85	56.84	30.64	44.05	582	26.82
Median	1.165	26.86	80.26	24.06	69.70	53.15	30.30	42.68	584	27.51
SD	3.34	22.63	26.34	3.49	16.21	23.59	3.95	3.77	36.18	3.79
CV, %	114.9	43.4	46.7	14.7	23.2	41.5	12.8	8.5	6.30	14.1

The content of mobile phosphorus ($P_{\text{E-R}}$), available to plants varied in a wide range: from 19.21 to 95.47 mg/kg, with the mean 52.08 mg/kg (Table 2). The results showed that the analyzed street sediment is relatively rich in phosphorus. Fertilizers industry seeks for the alternative sources of phosphorus, including wastes rich in this component. From the other hand, street dusts collected in a form of mound need to be reclaimed. However, the high variations of the mounded street dust (in respect to the phosphorus content variation coefficient $CV = 43.4\%$) suggests that the collected material varied due to the local point emissions, and also its composition has changed during storage mainly by leaching of soluble salts and mineralization of organic matter.

Fine particles in the atmosphere have both anthropogenic and natural origins. Natural sources include mainly windblown soils, whereas anthropogenic are largely due to combustion processes: fossil fuel burning and motor vehicle emissions [20].

The contents of $S\text{-SO}_4^{2-}$ varied from 21.10 to 101.18 mg/kg (mean 56.38 mg/kg), with the dominance of samples with high contents of sulfates (Table 2). According to soil standards analyzed, waste is contaminated with sulfates. Using that material as the soil amendment may acidify soil, accelerate the weathering processes of soil minerals and release of phytotoxic elements. Such an additive might also cause the increase of solubility and bioavailability of heavy metals in soil (Cd, Pb, Zn)

The results for heavy metals contents in the studied street dusts showed different level of contamination for each metal, except zinc. Total contents of zinc in analyzed material ranged from 15.00 to 28.23 mg/kg, with the mean value of 23.71 mg/kg. Ac-

ording to Kabata-Pendias and Pendias [21] mean concentration of Zn in surface horizons sandy soils is 24 mg/kg. Other metals in analyzed samples occurred in higher concentrations compared to the contents in the surface horizons of soil, with the mean value 69.85 mg/kg for Cu, 30.64 mg/kg for Ni and 582.0 mg/kg for Mn. High Cu concentration is connected with the fact that copper is linked with the wear-and-tear brake pads [20]. The content of lead within the range 20.90–94.25 mg/kg also indicated contamination with this element. The explanation for the elevated lead concentration in mounded street dusts is the leaded gasoline used in the past. It is also possible that at present time cars are still releasing lead via the wheel bearing. Other studies confirmed that urban dusts collected in streets are contaminated with trace metals. Wang et al. [4], Stone and Marsalek [5] observed accumulation of copper, zinc and lead in material from city roads. Irvine et al. [1] found Cu, Zn and Pb associated with urban and traffic areas.

Table 3

The activity of dehydrogenases (DEH), catalase (CAT), alkaline (AIP) and acid (AcP) phosphatase, arylsulfatase (ARS)

Parameter	DEH [$\mu\text{g TPF}/(\text{g}\cdot\text{day})$]	CAT [$\text{mg H}_2\text{O}_2/(\text{g}\cdot\text{h})$]	AIP	AcP	ARS	BIF
			[$\text{mmol pNP}/(\text{kg}\cdot\text{h})$]			
Minimum	0.071	0.030	0.443	0.421	0.053	0.084
Maximum	0.254	0.157	1.446	1.525	0.072	0.269
Mean	0.116	0.085	0.777	0.814	0.063	0.129
Median	0.101	0.087	0.672	0.725	0.065	0.111
SD	0.115	0.037	0.314	0.327	0.008	0.053
CV, %	99.13	43.53	40.40	40.17	12.69	41.09

Enzyme activities of soils are considered to be sensitive to pollution and have the further advantage of being easy to determine without expensive, sophisticated instruments [22]. Dehydrogenase activities in analyzed samples differentiated in a wide range: from 0.071 to 0.254 $\mu\text{g TPF}/(\text{g}\cdot\text{day})$, with the mean 0.116 $\mu\text{g TPF}/(\text{g}\cdot\text{day})$ (Table 3). The coefficient of variation calculated for this parameter was the highest, indicating the impact of different levels of heavy metals and sulfates on the activity of microorganisms responsible for this enzyme. In such a complex and contaminated environment, microorganisms access to the sources of carbon substrates is different. Dehydrogenase is an end cellular enzyme and occurs only inside intact, living cells. Dehydrogenases are particularly susceptible to heavy metals, and their activities are inhibited in the range of 10–90%, depending on the level of contamination. Hinojosa et al. [23] reported that enzyme activities decreased significantly with increasing degree of pollution (As, Bi, Cd, Cu, Pb, Zn): non-polluted soil showed the highest enzyme activity, polluted the lowest, and restored soil intermediate values. The greatest differences between the three levels of pollution were for urease, β -glucosidase and dehydrogenase activities. Shen et al. [22] studying the impact of a single metal contamination (Ag, Cu,

Hg, Zn) and their mixture on enzymatic activity of dehydrogenases and urease observed synergistic as well as antagonistic effects. The most inhibiting influence was reported in the case of silver and mercury. The dehydrogenase activity was not statistically related to contents of sulfur and other elements (Table 4). Levyk et al. [24], studying dehydrogenase activity in technogenic soils, observed that the activities of this enzyme are related to sulfate contents, however did not show statistical correlation between these parameters.

Table 4

Relationship between selected waste properties ($n = 12, p < 0.05$)

Variable		Equation	r	r^2
Dependent	Independent			
Mobile phosphorus	alkaline phosphatase	$y = 58.0488x + 6.9567$	0.807	0.651
	acid phosphatase	$y = 61.6098x + 1.9451$	0.891	0.794
	dehydrogenases	$y = 327.5034x + 14.2261$	0.744	0.554
	catalase	$y = 382.056x + 19.6052$	0.633	0.401
Sulfate	iron	$y = -5.1757x + 195.3653$	-0.745	0.557
	manganese	$y = -0.5659x + 386.0642$	-0.777	0.604
	chromium	$y = -5.4546x + 296.6447$	-0.780	0.608
	nickel	$y = -5.1243x + 213.3759$	-0.768	0.590
	lead	$y = -0.8874x + 106.8227$	-0.794	0.630
	copper	$y = -1.2178x + 141.4279$	-0.749	0.561

Catalase activity of studied deposited waste differed from 0.030 to 0.157 mg H₂O₂/(g·h), with the mean value 0.085 mg H₂O₂/(g·h), and a coefficient of variation 43.5%. Analyses of distribution indicated that the majority of the results for this parameter is higher than the mean value, which is confirmed by the higher median calculated for the catalase activity. Catalase can split hydrogen peroxide into molecular oxygen and water and thus prevent cells from damage by reactive oxygen species. Usually high concentrations of heavy metals lead to the increased formation of reactive oxygen species (ROS) responsible for the oxidative stress. Catalase is active over a wide pH range and its activity does not drop until the pH is below 3.5. However, in the studied samples pH was high and ranged from 7.69 to 8.10 in H₂O and from 7.3 to 7.80 in 1 M KCl.

Phosphatases are enzymes which catalyse the hydrolysis of organic phosphorus compounds to mineral forms. Their activities differentiated in the range 0.443–1.446 mmol pNP/(kg·h) (mean 0.777 mmol pNP/(kg·h) alkaline phosphatase) and 0.421–1.525 mmol pNP/(kg·h) (mean 0.814 mmol pNP/(kg·h) acid phosphatase) (Table 3). Similarly, the results for the phosphomonoesterases activities differentiated in a wide range, with the coefficients of variation $CV = 40.40\%$ and 40.17% for alkaline phosphatase and acid phosphatase, respectively. Lower median values than means indicated that majority of the results are smaller than mean values for these enzymes.

Arylsulfatases play a major role in the turnover and cycling of sulfur in soils by catalyzing the hydrolysis of ester sulfates, and thus releasing organically-bound sulfate into the soil solution [16]. The activity of this enzyme was fairly uniform ranging from 0.053 to 0.072 mmol *p*NP/(kg·h), with the low coefficient of variation – $CV = 12.69\%$ (Table 3). There was no statistical correlation between the content of sulfates and aryl-sulfatase activity, which may be caused by the inhibiting effect of heavy metals, particularly copper present in excess in analyzed material. Such an explanation is enhanced by the results of Wyzkowska et al. [25] who reported very strong negative impact of copper on arylsulfatase activity comparing to other enzymes.

For the estimation of the fertility value of the waste, the potential material for the soil amendment, multiparametric indicator of biochemical quality of the mounded street dusts was calculated. Dehydrogenases and catalase activities were the base for the calculation of the biological index fertility (*BIF*). The value of this index ranged from 0.084 to 0.269 (Table 3) and was lower than in the soil sampled from the dumping ground. Statistical analysis confirmed significant, positive correlation between alkaline and acid phosphates activities and the contents of mobile phosphorus in the analyzed waste ($r = 0.807$ and $r = 0.891$, $p < 0.05$) (Table 4).

There was also noted a positive significant correlation between the activity of dehydrogenases and the content of mobile phosphorus ($r = 0.744$, $p < 0.05$) (Table 4). Statistically positive correlation was also found between the catalase activity and the content of mobile phosphorus ($r = 0.633$, $p < 0.05$). Soil catalase activity is sensitive to soil biological factors and closely related with soil major nutrients. Soil catalase activity can be estimated through soil total P determination and can reflect soil salinity to a certain extent.

4. CONCLUSIONS

- The study showed that the analyzed mounded street dusts consist mainly of mineral particles, with the dominance of sand fraction.
- The contents of heavy metals were elevated, and the degree of contamination was different for each metal. The pollution degree were in the order of $Cu > Pb > Cr > Ni > Zn$.
- In spite of the high contents of phosphorus, analyzed material cannot be used as a soil amendment due to the contamination with metals, particularly copper, lead, nickel and chromium.
- High contents of sulfates in deposited material could be a threat for the soil environment thus limiting its utilization.
- Low value of the biological index of fertility (*BIF*) indicates that the analysed street dusts have low ability to fulfill nourishing plant needs.

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