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# The effect of Spent Mushroom Substrate field storage conditions on its leachate composition

Passive weathering in a field is a popular method of Spent Mushroom Substrate disposal. During this process rain and snowmelt water percolates through SMS piles and a large amount of solutes is leached out. Leachate contains substantially high concentrations of inorganic salts, that contribute to soil and groundwater salinity. In order to examine to what extent salts are leached from SMS piles, laboratory-scale lysimeter study was carried out. It was performed on two SMS substrates stored in the field for 3 years (substrate "A") and 1 year (substrate "B") respectively. Leaching experiment was conducted for 21 days, simulating annual rainfall cycles in Poland. Effluents were controlled for changes in chemical composition. Analysis included: moisture, pH, conductivity (EC), ions concentrations: $Cl^-$, $NO_3^-$, $SO_4^{2-}$, $K^+$, $Na^+$, $Ca^{2+}$, $Mg^{2+}$, $Fe^{3+}$, $Mn^{2+}$, $Zn^{2+}$, total carbon (TC) and total nitrogen (TN) measurements. Leachate composition was dominated by $Na^+$, $K^+$, $Ca^{2+}$, $Mg^{2+}$, $Cl^-$ and $SO_4^{2-}$ concentrations. To describe the leaching dynamics seven mathematical models were fitted to the data. For the majority of components the function that best illustrated weathering process was a quadratic function, although $Ca^{2+}$ leaching was best illustrated by a power function and $Cl^-$ release by a logarithmic one. After three weeks the quantity of inorganic salts eluted from 1 $kg_{dw}$ of SMS reached 16.8 g for substrate "A" and 43.9 g for substrate "B". Obtained results indicate that improper management of SMS may result in excessive soil salinity.

Keywords: mushroom production, spent mushroom substrate, weathering, leachate, soil salinity

## Introduction

*Agaricus bisporus* cultivation is an important and ever-growing sector of agriculture. It represents approximately 90% of the total fungi production in Poland, estimated at 200 000 tons per year [1, 2]. Such high production rate consumes annually 1.3 million tons of cultivation material [3]. After harvesting, significant amount of residual material is no longer suitable for reuse and becomes a by-product of cultivation process called Spent Mushroom Substrate (SMS). After composting this substrate becomes a Spent Mushroom Compost (SMC), which contains large quantities of organic and inorganic compounds easily accumulated by plants [4-7]. Fresh SMS typically contains approximately: 0.5% nitrogen, 0.5% phosphorus, 0.5% potassium, 4÷6% calcium and 18% of organic matter and therefore is frequently used as a fertilizer [2, 8]. Before application into soil, SMS is placed in piles and subjected to aging process (so-called passive weathering), usually lasting two years. Rain and melted snow enter the piles and large quantities of

organic matter [9] and mineral compounds [10-12] are leached into soil. Excessive amounts of $Na^+$, $K^+$, $Ca^{2+}$, $Mg^{2+}$, $SO_4^{2-}$ and $Cl^-$ ions are responsible for soil salinity and constitute major limiting factor for agriculture. Leaching intensity depends largely on SMS and SMC composition, humidity and storage conditions. Results obtained by Guo et al. [13] showed that SMS can release significant amounts of salts under conditions favoring leaching. They reported that concentration of water - soluble $Cl^-$, $NO_3^-$, $Ca^{2+}$, $Mg^{2+}$, $Na^+$ and $K^+$ ions in soils underneath SMS piles after 2 years weathering time, were 4 to 20 times higher compared to unaffected soil. In addition, they demonstrated that piles height strongly affects leaching rate. The concentrations of salts and soluble organic matter in leachate resulting from SMS piles stacked at 90 and 150 cm height were several times higher compared to 50 cm piles and significantly exceeded the permissible level [14]. There are few scientific reports covering solute release kinetics from SMS and SMC [18-21]. Most of the available kinetic models concern elution from soil [14-17]. Leaching simulations conducted by Stewart et al. [17] indicate that nitrogen release from SMS amended soil followed zero order model: $N_t = k \cdot t + c$, where $N_t$ is nitrogen net release, t is time from the beginning of the incubation period and c is a constant value. To date, there is no explicit mathematical description illustrating salts release from SMS, which is of special importance concerning SMS-pretreatments before fertilization. In order to prevent the negative effects of improper SMS management, knowledge about solute release kinetics is essential.

The purpose of this study was to:
- examine the concentrations of selected compounds released from SMS in laboratory conditions,
- determine the influence of SMS storage time on organic and inorganic compounds release degree.


## 1. Materials and methods

Two Spent Mushroom Substrates "A" and "B" stored in field for three years and one year respectively, were used in this study. The SMS were collected from mushroom producer, "Polok" company in Kryry (Poland). During sampling the SMS substrates weren't mixed with a soil layer. Lysimeter experiments were performed at room temperature (21°C) in PVC pipes (102 mm in diameter), for 21 days. Portable lysimeters were equipped with containers for effluents. The water-loading rates were equal to a moderate rainfall intensity in Upper Silesia region [22]. Piles height was 70 cm. SMS oven dry mass in columns A and B was: 2.41 kg and 1.87 kg respectively. Deionized water was loaded to the columns through the whole cross-section. Leachate samples were collected daily and stored at 4°C until analysis. For pH and conductivity measurements inoLab multilevel 3 apparatus (WTW) was used. Alkalinity/acidity measurements included using SenTix 81 electrodes (WTW) and conductivity was determined using 325 TetraCon sensor (WTW). For quantitative and qualitative analysis of carbon and nitrogen contents TOC Multi N/C analyzer (Analytik Jena) was used. Chlorides, nitrates and sulfates

concentrations were measured by ion DX-120 chromatograph (Dionex) equipped with a conductivity detector CDM-3 and ASRS-Ultra (4 mm) suppressor, IonPac AS-14A + AG-14A column was used. The analysis was performed at 20°C, using 8 mM $Na_2CO_3$ + 1 mM $NaHCO_3$ as eluent with a flow rate 1 $cm^3$/min. The concentration of ions $Ca^{2+}$, $Mg^{2+}$, $Na^+$, $K^+$, $Fe^{3+}$, $Zn^{2+}$ and $Mn^{2+}$ was determined by means of the AAS method using flame atomic absorption spectrometer SpectraAA Varian-880. Results analysis was performed using Statistica 9.1 (StatSoft).

## 2. Results and discussion

Lysimeter study allowed to track changes in chemical composition of SMS filtrate. Leaching behavior of individual SMS compounds is presented in the form of elution curves (Figs. 1 and 2). According to [14] total mass of weathered components was calculated as follows:

$$M_a = C_{ai} \cdot V_i$$

where: $M_a$ is maximum amount of releasable component during single loading, mg, $C_{ai}$ is component concentration in the sample, mg/L, and $V_i$ is the volume of the sample eluted from a single load, L. Results are presented as the cumulative mass of the substance eluted from 1 $kg_{dw}$ (dry weight) of SMS, calculated by summing the masses of the substance released at each loading from the start of the experiment:

$$I_t = \left( \sum_{j=1}^{j} M_j \right)$$

where: $I_t$ - the cumulative mass of eluted substance, mg/$kg_{dw}$, $M_j$ - amount of substance released from a single loading j (j = 1...21), mg/$kg_{dw}$.

Due to the high moisture, SMS substrate did not require pre-saturation to a state of maximum water capacity and the effluent volume from the first day of loading was over 90%. Water content for substrate "A" and "B" was 48.7% and 56.3% respectively. The younger substrate was characterized by greater hydration degree compared to substrate "A", which significantly accelerated elimination of organic and inorganic compounds from SMS, especially in the first days of weathering.

Leachate pH was changing during experiment and for substrate "B" it fluctuated in the range 6.56÷7.06, while for the substrate "A" it was 7.03÷7.43. These values indirectly reflect SMS mineralization degree, since neutral pH is typical for stabilized compost. It is estimated that the optimum pH for mature compost should be in the range 6.5 and 8 [23, 24]. A slight increase in pH toward alkalinity for substrate "A", stored for longer period, was probably due to the presence of carbonate and bicarbonate ions in leachate, as a result of TOC decomposition. The organic carbon release from SMS was correlated with nitrogen loss. The C:N ratio in the effluent ranged from 1.3 to 1.87 for substrate stored for 3 years and 0.79 to 0.82 for the younger one, and was altered by substrate age, while the optimum C:N ratio should

be approximately 13:1 [3]. Lower than recommended C:N ratio indicates SMS incomplete stabilization and excessive release of ammonium nitrogen.
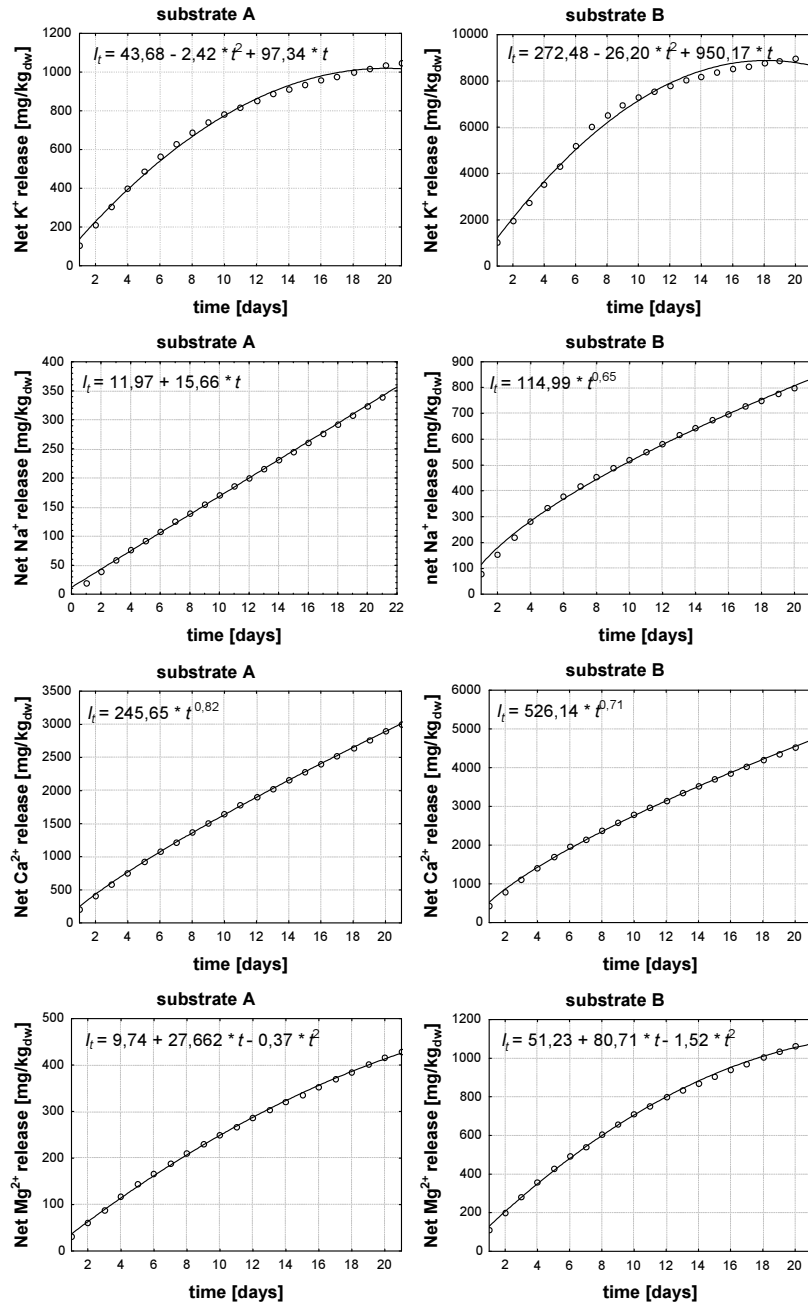
**substrate A**

$I_t = 43,68 - 2,42 * t^2 + 97,34 * t$

Net K⁺ release [mg/kg_dw]

**substrate B**

$I_t = 272,48 - 26,20 * t^2 + 950,17 * t$

Net K⁺ release [mg/kg_dw]

time [days]

**substrate A**

$I_t = 11,97 + 15,66 * t$

Net Na⁺ release [mg/kg_dw]

**substrate B**

$I_t = 114,99 * t^{0,65}$

net Na⁺ release [mg/kg_dw]

time [days]

**substrate A**

$I_t = 245,65 * t^{0,82}$

Net Ca²⁺ release [mg/kg_dw]

**substrate B**

$I_t = 526,14 * t^{0,71}$

Net Ca²⁺ release [mg/kg_dw]

time [days]

**substrate A**

$I_t = 9,74 + 27,662 * t - 0,37 * t^2$

Net Mg²⁺ release [mg/kg_dw]

**substrate B**

$I_t = 51,23 + 80,71 * t - 1,52 * t^2$

Net Mg²⁺ release [mg/kg_dw]

time [days]

Fig. 1. The cumulative release of potassium, sodium, calcium and magnesium washed from 1 kg_dw of substrate "A"- stored for 3 years (since 2008) and substrate "B"- stored for 1 year (since 2010)

Figure 1 presents the cumulative amounts of potassium, sodium, calcium and magnesium released from SMS. The total amount of cations washed from substrate "B" weathered for a shorter time period, was significantly higher compared to substrate "A". During 21 days of weathering the 70 cm SMS pile released (per 1 kg of SMS) 43.9 g of inorganic salts from substrate "B" and three times less - 16.8 g from substrate "A". Similar results were previously described by Guo at al. [25]. They calculated that the amount of inorganic salts released from 90 cm pile during 2 years of weathering was 26.6 g from 1 kg of SMS. From substrate "B" in largest amounts were eluted (in ascending order): $Fe < Zn < Mn < Na < Mg < Ca < K$, and from substrate "A": $Mn < Fe < Zn < Na < Mg < K < Ca$. Chemistry of leachate was therefore dominated by $Na^+$, $K^+$, $Ca^{2+}$, $Mg^{2+}$ cations. The total amount of potassium and calcium released from substrate "B" was 9033 $mg/kg_{dw}$ and 4708 $mg/kg_{dw}$ respectively. Sodium and magnesium release degree was lower and amounted to 820 mg $Na/kg_{dw}$ and 1090 mg $Mg/kg_{dw}$. Following three weeks the amount of base elements leached from substrate "A" was 1048 mg $K/kg_{dw}$, 3003 mg $Ca/kg_{dw}$, and 429 mg $Mg/kg_{dw}$ respectively. The excess release of sodium, calcium or potassium into soil causes decrease in its bioavaliability, since these elements compete for binding sites in the roots [26]. Ions elution from SMS was accompanied by electrolytic conductivity (EC) decrease. For younger substrate "B" EC was 17 490 µS/cm, and after 21 days reduced to 3570 µS/cm, while for substrate "A" the initially 5830 µS/cm EC value was depleted to 2950 µS/cm. Guo and Chorover [14] also observed significant conductivity decrease from 50 000 µS/cm to 3000 µS/cm during SMS weathering for 180 days.
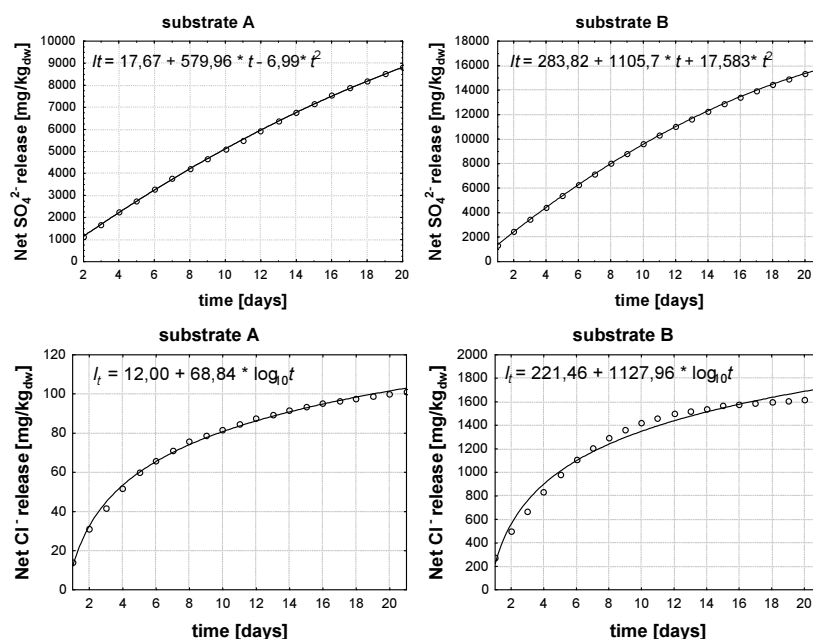


**Fig. 2. The cumulative release of $SO_4^{2-}$ and $Cl^-$ from substrate substrate "A"- stored for 3 years (since 2008) and for substrate "B"- stored for 1 year (since 2010)**

Figure 2 shows the cumulative amounts of chlorides and sulfates released during the leaching experiment. The total amount of sulfates released from SMS after 21 days for substrate "B" was 15 830 mg/kg$_{dw}$ and for substrate "A" - 9082 mg/kg$_{dw}$. The total amount of chlorides was lower and amounted to 1626 mg/kg$_{dw}$, for substrate "B" and only 101 mg/kg$_{dw}$ for substrate "A". Chlorides and sulfates leaching during first 15 days of the experiment proceeded more intensively for substrate "B", as evidenced by higher slope values on graphs presenting $I_t = f(t)$ relationship, compared to substrate "A" graphs. According to the scale of toxicity [2], the sum of chlorides and sulfates washed from substrate A and B was highly toxic to plants. The mean concentrations of sulfates, 2576 mg/L for substrate "B" and 2017 mg/L for substrate "A" do exceed the limit values defined by the Regulation of Minister of Environment of 28 October 2009 on conditions that have to be met, when discharging sewage to water or to soil and on substances particularly hazardous to aquatic environment which therefore contribute to soil salinization [28]. Exceeded salts concentration in SMS leachate might also affect soil filtration ability by promoting its transformation into liquid state, even despite low water contents.

To describe leaching dynamics of organic and inorganic compounds from SMS the corresponding known-functions were selected:

| | | |
|---|---|---|
| Linear function: | $I_t = a \cdot t + b$ | (1) |
| Hyperbolic function: | $I_t = a \cdot 1/t + b$ | (2) |
| Logarithmic function: | $I_t = a \cdot \log_{10}(t) + b$ | (3) |
| Quadratic function: | $I_t = a \cdot t^2 + b \cdot t + c$ | (4) |
| Power function: | $I_t = a \cdot t^b$ | (5) |
| Exponential function: | $I_t = a \cdot b^t$ | (6) |

and one literature-source model [7, 29] which describes leaching/mineralization of carbon, nitrogen and sulfur from the soil, when substrate is unlimited:

$$I_t = M_{max}\left(1 - e^{-k_1 t}\right) \qquad (7)$$

where: $I_t$ - is the amount of cumulative net mineralization/release (mg/kg) over the time period t, days, t - time, days, $k_1$ - first-order exponential rate parameter, a, b - regression parameters.

The best-fitting model was selected basing on two parameters: maximum determination level (maximum correlation between predicted and empirical data) and minimum loss function (sum of squared errors). Obtained results are summarized in Table 1. Trend function was estimated by least squares method.

The break-through curves for $Na^+$ (substrate A) and $Ca^{2+}$ were best fitted by power function and for $K^+$ by quadratic model. Time-dependent elution profiles reflects ions mobility in soil solution. Sulfates release was best described by quadratic function - the correlation coefficient R = 0.999, while chloride leaching process was best described by logarithmic function - the correlation coefficient

R > 0.99. Leaching inorganic salts from SMS proceeded more intensively in early stages of the experiment (elution slope values presented in Figures 1 and 2. For example, potassium leaching occurred more rapidly until the 18-th day of the experiment (similar to the course of the exponential function), while for chlorides till the 10-th day. In leaching study Lohr et al. [30] indicate that potassium release from SMS was exponential, while Ca initially fast release after a few weeks was slower and more gradational in nature.

Table 1. **Evaluation of model parameters**

| Parameter | Substrate | Storage time years | Model | Adj. $S_{sgr.}$, % | $SS_{res.}$ | $R^2$ |
|---|---|---|---|---|---|---|
| Fe | A | 3 | 4 | 98.27 | 0.021 | 0.991 |
| | B | 1 | 4 | 98.98 | 0.023 | 0.994 |
| Mn | A | 3 | 4 | 98.65 | 0.005 | 0.997 |
| | B | 1 | 4 | 98.88 | 0.07 | 0.998 |
| Zn | A | 3 | 4 | 97.98 | 0.08 | 0.988 |
| | B | 1 | 4 | 99.85 | 0.006 | 0.999 |
| K | A | 3 | 4 | 99.56 | 6736.85 | 0.997 |
| | B | 1 | 4 | 99.24 | 873 880.85 | 0.996 |
| Na | A | 3 | 1 | 99.95 | 39.00 | 0.999 |
| | B | 1 | 5 | 99.34 | 4768.00 | 0.996 |
| Ca | A | 3 | 5 | 99.97 | 3410.30 | 0.999 |
| | B | 1 | 5 | 99.91 | 27 527.77 | 0.999 |
| Mg | A | 3 | 4 | 99.92 | 206.05 | 0.999 |
| | B | 1 | 4 | 99.88 | 1961.04 | 0.999 |
| Cl | A | 3 | 3 | 99.63 | 43.52 | 0.998 |
| | B | 1 | 3 | 98.56 | 46784.52 | 0.992 |
| $NO_3^-$ | A | 3 | 4 | 99.05 | 98709.75 | 0.995 |
| | B | 1 | 4 | 99.12 | 1 358 712.83 | 0.995 |
| $SO_4^{2-}$ | A | 3 | 4 | 99.99 | 13790.98 | 0.999 |
| | B | 1 | 4 | 99.99 | 24 189.57 | 0.999 |
| IC | A | 3 | 4 | 99.96 | 51.66 | 0.999 |
| | B | 1 | 4 | 99.95 | 200.15 | 0.999 |
| TC | A | 3 | 4 | 99.80 | 6661.19 | 0.999 |
| | B | 1 | 4 | 99.62 | 65 099.19 | 0.998 |
| TN | A | 3 | 4 | 99.22 | 7737.23 | 0.996 |
| | B | 1 | 4 | 99.01 | 247 535.58 | 0.990 |
| TOC | A | 3 | 4 | 99.69 | 6381.96 | 0.998 |
| | B | 1 | 4 | 99.56 | 66 568.73 | 0.997 |

Conducted studies have shown that during SMS weathering substantial amount of solutes is released into soil environment. Excessive soil salinization contributes to its physical deterioration and leads to irreversible chemical changes in sorption

complex within a soil, adversely affecting crops quality. To avoid soil salinity the proper management of SMS should therefore cover: more than the commonly used 2-year weathering period, less than 70 cm piles height, as well as appropriate time intervals between successive storage and irrigation of saline soil. Artificial irrigation as well as aeration during weathering fastens the process of SMS stabilization by reducing the time for biological activity within the SMS.

## Conclusions

According to the Regulation of the Minister of Environment from 27 September 2001, mushroom spent is classified in the group of wastes from agriculture, horticulture, aquaculture, fisheries, forestry and food processing, under catalogue number 02 01 99 specified as "other wastes" [31]. However, Polish legislation inadequately addresses the issues of its management and do not properly specify SMS storage conditions in the field. Laboratory-scale experiment confirmed that even mature SMS weathered for 3 years can still release significant amounts of dissolved solids. Therefore longer than regulated 2 years aging period is necessary to protect the soil from excessive salinity. Legitimate approach in controlling SMS passive weathering should be also to determine the kinetics of this process. Conducted experiments also revealed that storing SMS in 70 cm piles can result in excessive soil salinity, which is contrary to standards established by the Department of Environmental Protection in Pennsylvania (PADEP) [32] regulating piles height at 50 cm from the ground surface. After solving this agriculture related problems SMS can be successfully stored in the field. However, it requires some early treatments like desalination, prolonged leaching and recomposting for given advantages. Obtained results can be of significance in the light of SMS management regulations and practices used by farmers.

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## Wpływ warunków leżakowania odpadu popieczarkowego na polu na skład jego odcieku

Leżakowanie na polu jest popularną metodą zagospodarowania zużytego odpadu popieczarkowego (Spent Mushroom Substrate). W trakcie tego procesu wody opadowe oraz roztopowe przenikają przez pryzmy SMS i przyczyniają się do powstawania odcieków zawierających wysokie stężenia soli nieorganicznych, powodujących zasolenie środowiska wodno-gruntowego. W celu zbadania, w jakim stopniu składniki mineralne są wymywane ze zużytego odpadu popieczarkowego, przeprowadzono lizymetryczne badania laboratoryjne. Do badań użyto dwóch odpadów SMS, substratu „A" leżakującego przez 3 lata oraz substratu „B" składowanego w warunkach polowych przez rok. Eksperyment prowadzono przez 21 dni, symulując warunki wymywania, typowe dla opadów na terenie Polski. Zakres analiz obejmował następujące oznaczenia: wilgotność, pH, przewodnictwo właściwe (EC) oraz stężenia: $Cl^-$, $NO_3^-$, $SO_4^{2-}$, $K^+$, $Na^+$, $Ca^{2+}$, $Mg^{2+}$, $Fe^{3+}$, $Mn^{2+}$, $Zn^{2+}$, węgla całkowitego (TC) i azotu całkowitego (TN). Skład odcieku był zdominowany przez jony: $Na^+$, $K^+$, $Ca^{2+}$, $Mg^{2+}$, $Cl^-$ i $SO_4^{2-}$. Do opisu dynamiki wymywania tych składników użyto siedmiu modeli matematycznych. Dla większości składników przebieg wymywania najlepiej ilustrował model funkcji kwadratowej, w przypadku potasu funkcja potęgowa, a w przypadku chlorków funkcja logarytmiczna. Na podstawie krzywych wymywania stwierdzono, że po trzech tygodniach prowadzenia procesu ilość soli nieorganicznych wypłukana z 1 kg zużytego podłoża wynosiła w przypadku substratu „A" 16,8 g, a w przypadku substratu „B" 43,9 g. Uzyskane wyniki wskazują, że niewłaściwy sposób zagospodarowania zużytego podłoża z produkcji pieczarek może być przyczyną nadmiernego zasolenia gleby.

**Słowa kluczowe:** produkcja grzybów, odpad popieczarkowy, leżakowanie, odciek, zasolenie gleby