

Jacek CZEKAŁA¹

TOTAL CHROMIUM AND NICKEL CONTENTS AND SOLUBLE FORMS OF THESE METALS IN COMPOSTS

OGÓLNA ZAWARTOŚĆ CHROMU I NIKLU ORAZ ROZPUSZCZALNYCH FORM TYCH METALI W KOMPOSTACH

Abstract: Composting is one of the methods of household sewage sludge management which ensures obtaining a product of high fertiliser quality, without the risk of soil contamination. Among preconditions is the appropriate chemical composition of the sewage sludge, especially with regard to the content of heavy metals, its stability as well as the proper choice of biodegradable wastes added to the sludge. The studies aimed at determining the impact of various organic substances added to sewage sludge on changes in the total content of chromium and nickel and water soluble forms of these metals in composts.

The experiment was carried out on the premises of an open compost plant using the method of compost piles which were made up of sewage sludge supplemented with industrial wastes from hemp or/and straw and wood chips, depending on the adopted experimental design. Composting until the end of the cooling phase lasted 93 days and the remaining 131 days were treated as the maturing phase. A tractor aerator was employed in the trial to spread, chop and aerate the composted material.

It was found that the strongest influence on the total content of chromium and nickel in composts was exerted only by the time of composting. In the case of soluble forms, time also exerted the strongest impact, although in the case of chromium compounds, additionally, the type of compost as well as the joint action of these two factors was also important.

Keywords: sewage sludge, organic wastes, composts, chromium, nickel

Introduction

Composting as a method for biological utilization of biodegradable wastes [1–3] has been known for ages and successfully used for utilizing the sewage sludge [4–8]. Data collected by Polish *Central Statistical Office* [9] revealed that 526.7 Mg of dry sludge was generated in Poland in 2010, including 20.7 % used in agriculture and 11.2 % stored in dumps. According to assumptions of National Plan for Wastes management [10], about 15 % of produced sludge are intended to be directed for composting in 2010 with perspectives of enhancing that proportion to 20 % in a future. Therefore, it is important to recognize in details all technological aspects as well as changes occurring

¹ Department of Soil Science and Land Protection, University of Life Sciences in Poznań, ul. Szydlowska 50, 60–656 Poznań, Poland, phone: +48 61 846 67 10, email: jczekala@up.poznan.pl

during composting process. It also refers to transformations of heavy metals that are integral part of sewage sludge [11, 12]. Heavy metals are present in sewage sludge at varied contents [13], which is reflected in composts produced using the sludge [14]. However, not only metals quantities, but also their chemical bindings have become the subject of studies for many years. It is associated, among others, with the risk estimation after sludge and other wastes introduced into the soil. Therefore, research upon the solubility of heavy metals forms contained in sewage sludge, thus their potential availability for plants, is an important element of composts assessment.

The study aimed at evaluating the influence of different bioorganic additives to municipal sewage sludge on changes in total contents of chromium and nickel and their water-soluble forms in composts.

Material and methods

The research was carried out in an open composting plant in 2007 applying mainly sewage sludge mixed – according to study scheme (Table 1) – waste hemp, wooden chips and/or straw. The percentage of individual components – recalculated onto dry matter – is presented in Table 1.

Table 1

Share in composts

Waste	Compost		
	1	2	3
	Share [%]		
Sewage sludge	30.6	32.8	37.6
Hemp waste	69.4	60.4	47.6
Straw	—	6.8	—
Wooden chips	—	—	14.8
Total	100	100	100

Sewage sludge, like other waste materials used, was characterized by various chemical composition, which is illustrated in Table 2.

Table 2

Selected properties of sewage sludge and organic wastes

Component	Dry matter	C _{org}	N _{tot}	C : N	C _{tot}	N _i _{tot}
	[g · kg ⁻¹ d.m.]				[mg · kg ⁻¹ d.m.]	
Sewage sludge	11.71 ± 0.39	481.3 ± 4.26	56.74 ± 0.69	8.48	158.80 ± 1.35	21.21 ± 0.54
Straw	90.44 ± 1.96	415.7 ± 1.11	46.39 ± 0.10	123.26	1.11 ± 0.06	0.93 ± 0.11
Hemp waste	77.62 ± 0.95	416.0 ± 2.14	10.05 ± 0.35	41.39	2.97 ± 0.24	2.74 ± 0.13
Wooden chips	45.58 ± 1.12	463.0 ± 1.07	3.36 ± 0.11	137.80	2.01 ± 0.04	2.05 ± 0.09

Organic materials were stacked up in layers in each prism with the straw as a bottom layer not taken into account in the qualitative balance. Prepared components were put in

a following sequence: straw – sludge – wastes, and then all these were shoveled using tractor aerator. The aerator shoveled, aerated, and crumbled material. The prism shoveling was made once a week during the first composting month, and then, depending on the temperature of composting matter. The process persisted 93 days, after which the prism was transferred onto its maturation place lasting another 131 days. In the course of the experiment, samples for analyses were collected but because of the quantities of data, the data presented in the paper include only information from the day of establishment of the trial (day 0), after 93 days (end of the cooling down period) and after the termination of maturing (131 days), *ie* the total of 224 days of the duration of the entire experiment.

The material for analyses in the amount of six samples was, every time, collected from the central area of the heap which, following their mixing and grinding, constituted a mean sample. All analyses were carried out in three replications.

Compost samples were subject to following determinations: dry matter – drier method at 105 °C, reaction – $\text{pH}_{(\text{H}_2\text{O})}$ – conductometry, organic matter – combusting at 550 °C, organic carbon – redox method with potassium dichromate in acidic medium, total nitrogen – Kjeldahl's method. Chromium and nickel were determined by means of *atomic absorption spectrophotometry* (AAS). Prior to analyses, total chromium and nickel were prepared by combusting samples (dry matter) at 550 °C and dissolving achieved ash in hot 3 mol · dm⁻³ HCl solution for 3 hours under cover. Soluble forms of both analyzed elements were obtained from the water extracts of composts (compost : water 1:10, w/v), part of which was evaporated till dryness, the remains were combusted at 550 °C (30 minutes), and the ash was dissolved in hot 3 mol · dm⁻³ HCl solution [15].

The statistical assessment of the obtained results was performed on the basis of the multifactorial analysis of variance and the significance of differences between means was determined using Duncan test at the level of significance of $\alpha = 0.05$. Calculations were carried out with the assistance of the STAT program.

Results and discussion

During the process of composting, organic matter undergoes decomposition the consequence of which is, among others, increase of ash quantities. This, in turn, causes observed increases of many elements in the composted material [16]. However, the rate of these transformations differs and, in general, varies between individual elements. For instance, Amir et al [17] determined a significant correlation between ash content in the composts from sewage sludge and Ni and Cu quantities soluble in water. On the other hand, no such correlation was found for Zn and Pb. Correlations between the above-mentioned parameters represent only a few of those that can be observed in composts. They appear to be the outcome of, among others, the initial content of chemical elements from individual constituents as well as the strength of their complexing with individual, primarily organic, constituents of wastes.

Transformations of compost constituents were strongly influenced by the time of composting as well as by the composition of the composting mass [2]. When

composting animal manure, above authors found the increase of majority of examined heavy metals contents, namely chromium and nickel. The demonstrated tendencies are, undoubtedly, associated with properties of the metal itself as well as with the bond stability with organic matter which, in turn, may exert impact on the dynamics of the release of individual metals during the composting process.

Taking into account data presented in the study, it is evident that the impact of experimental factors separately on the content of different forms of chromium and nickel varied.

The effect of the kind of compost, consequently, indirectly of their composition, on the total content of the two elements turned out to be non-significant ($p < 0.05$) (Table 3).

Table 3

Effect of the compost type, irrespective of the days of composting, on the content of chromium and nickel in composts [$\text{mg} \cdot \text{kg}^{-1} \text{ d.m.}$]

Compost	Chromium		Nickel	
	form			
	total	soluble forms	total	soluble forms
1	33.82	0.455 ^b	23.18	0.586
2	37.23	0.478 ^b	24.81	0.597
3	36.59	0.352 ^a	24.15	0.499

a, b – means marked with different letters in columns are significantly different at $p < 0.05$.

It was in contrast to results achieved by Yanez et al [18]. When composting the sewage sludge with various proportions of industrial waste of silver wattle, they found great initial differentiation of total chromium and nickel contents, the amounts of which increased along with the increase of the sludge share in the composting mixture. After composting complete (43 days), contents of both elements were lower in all composts than those determined at the experiment beginning day. In composts, this phenomenon is associated, most frequently, with the advancing degradation of organic matter in the process of mineralisation [19, 20]. This, in general, is accompanied by the increase in the ash content [21]. It is evident from the data [22] that, depending on the composition of composted mixtures, the increase in heavy metal concentrations in mature composts constituted from 14 % to 85 % in comparison with the initial content.

Changes in element contents in composts due to their initial composition also refer to macrocomponents, both in a view of compost type and the process duration, which was confirmed by Czekala [8]. On the other hand, data presented in Table 4 indicate a significant impact of time, as an experimental factor, on changes in total contents of chromium ($F = 144.30^{**}$) and nickel ($F = 146.91^{**}$). Attention should also be drawn to similar tendencies of changes for chromium and nickel contained in the same uniform groups in composts despite differences in the level of content of each element. In both cases, by the end of the cooling down phase (the 93rd day of composting), the content of Cr increased on average by 38.6 % and that of Ni – by 52.5 %. Compost maturation contributed to the reduction in the content of both elements but to a different degree.

The content of Cr amounted, on average, to $23.17 \text{ mg} \cdot \text{kg}^{-1}$ and that of Ni – to $18.23 \text{ mg} \cdot \text{kg}^{-1}$ (Table 4). This means that this decline amounted to about 44.1 % for total nickel and to about 52.8 % for total Cr in relation to the quantity from the cooling down phase.

Table 4

Effect of composting time, irrespective of the type of compost, on the content of chromium and nickel in composts [$\text{mg} \cdot \text{kg}^{-1} \text{ d.m.}$]

Days of composting	Chromium		Nickel	
	total	soluble forms	total	soluble forms
0	35.40 ^b	0.620 ^c	21.40 ^b	1.106 ^b
93	49.08 ^c	0.378 ^b	32.63 ^c	0.225 ^a
224	23.17 ^a	0.286 ^a	17.95 ^a	0.351 ^a

a, b... – means marked with different letters in columns are significantly different at $p < 0.05$.

No significant ($p < 0.05$) synergistic effect of the two experimental factors was observed on the level of total Cr and Ni content as well as of their unambiguous directions of their quantitative changes (Table 5).

Table 5

Impact of the cooperation of experimental factors on the total content of chromium and nickel and their soluble forms in composts

Element	Composts								
	1			2			3		
	Days of composting								
	0	93	224	0	93	224	0	93	224
Total content [$\text{mg} \cdot \text{kg}^{-1} \text{ d.m.}$]									
Cr	32.56	46.24	22.65	37.96	50.54	23.20	35.68	50.44	23.65
Ni	19.87	31.44	17.76	22.66	33.58	18.20	21.66	32.87	17.90
Content of soluble forms [$\text{mg} \cdot \text{kg}^{-1} \text{ d.m.}$]									
Cr	0.519 ^{de}	0.430 ^{cd}	0.418 ^{cd}	0.746 ^f	0.394 ^{bc}	0.294 ^b	0.596 ^c	0.312 ^{bc}	0.146 ^a
Ni	1.131 ^b	0.266 ^a	0.362 ^a	1.172 ^b	0.246 ^a	0.372 ^a	1.016 ^b	0.163 ^a	0.320 ^a

a, b... – means marked with different letters in rows are significantly different at $p < 0.05$.

This was probably caused by a strong influence of the time factor at the simultaneous negligible impact of compost composition. This possibility is indicated, among others, by investigations carried out by Jakubus [14] who demonstrated that chips and sawdust alone affected only slightly the total quantity of heavy metals in composts and significant differences in the content of heavy metals were only observed after the introduction into the compost mixtures of different quantities of sewage sludge. It seems that, when analyse the above problem, properties of the element itself should also be

taken into account as indirectly indicated by investigations carried out by Ko et al [23] who reported increased content of the examined metals in the course of the composting process but with the weakest dynamics in the case of chromium and nickel. However, it should be emphasised that such changes refer not only to micro- but also macroelements [8].

In the case of total contents of metals (Table 5), despite the above-mentioned lack of cooperation of the experimental factors, two phases of changes were observed. The first of them was connected with the increase in the Cr and Ni content during the first three months of the trial which, on average, constituted from 33.0 % to 42.0 % in relation to the initial content of chromium and from 48.2 % to 58.2 % in the case of nickel. The second phase was associated with quantitative losses of both elements both in relation to their content on the day of establishment of the compost heaps as well as during the phase of cooling down. The above changes could have been caused, primarily, by the high dynamics of organic matter degradation during the initial period of the composting process resulting in release of metals. On the other hand, their losses observed in mature composts were caused, to a considerable extent, by leaching during the autumn-winter period. Simultaneously, the observed greater dynamics in quantities of Ni could have resulted from easier release of the metal from organic bonds in relation to chromium, the element which forms relatively strong bonds with organic compounds [24].

Chromium and nickel are characterised by a relatively small albeit varying solubility. This is corroborated by data presented in Tables 3–5. It is evident from them that, out of the two metals, quantities of the easily available forms declined with the time of composting, but only with respect to chromium. The determined correlations resulted, to a certain degree, from the character of Cr and Ni bonds in sewage sludge. It was demonstrated [25] that, generally speaking, 80 albeit 90 % of chromium in sewage sludge occurred in poorly soluble or non-soluble bonds, whereas almost 20 % of Ni was found in bonds of residual fraction.

However, assessment of metal solubility in compost may differ depending on applied extracting agent. Krzywy et al [26], when used $0.5 \text{ mol} \cdot \text{dm}^{-3}$ HCl solution to evaluate some metals solubility properties, did not find any influence of the compost type and composting duration on qualitative changes of examined elements. However, large ionic strength of the extracting agent and its controversial usefulness for composts, should be also taken into account.

Regardless of these above remarks, own study revealed that chromium solubility decreased along with the composting duration on average from 1.75 % at the experiment beginning day to 0.80 % in matured compost. In the case of nickel, these changes were characterized by varied tendency in time from 5.17 % at the beginning to 1.92 % at the end of experiment.

Possibility to loose metals during composting process, namely under conditions of open composting plants, is another issue. During composting, when temperature in a prism arises, chemically bound water is released along with components of composted materials, which seems to be one of the most important sources of observed metal losses. The range of these losses depends on the chemical nature of individual elements bindings, namely on a solid fraction of composts.

Conclusions

1. Total contents of chromium and nickel in composts containing sewage sludge was significantly determined only by composting duration.
2. Along with time, total amounts of chromium and nickel in composts increased till the end of cooling phase with subsequent decrease at the final maturity stage.
3. No significant influence of the compost type and composting duration on total chromium and nickel content as well as water-soluble nickel forms in compost, was recorded.
4. The type of organic waste used for composting sewage sludge has differently influenced metals solubility, which was in turn substantially modified by the duration in composting.
5. Among all organic wastes, the addition of wood loggings decreased mostly the solubility, particularly of chromium.

References

- [1] Baran S, Drozd J. In: Komposty z odpadów komunalnych, produkcja, wykorzystanie i wpływ na środowisko. Drozd J, editor. Wrocław: PTSH; 2004: 7-27.
- [2] Kuo S, Ortiz-Escobar ME, Hue NV, Hummel RL. *Recent Res Devel Environ Biol.* 2004;1:451-513.
- [3] Amlinger F, Peyr S, Hildebrandt U, Müsken J, Cuhls C, Clemens J. Stand der Technik der Kompostierung. Richtlinie des Bundesministeriums für Land- und Forstwirtschaft, Umwelt und Wasserwirtschaft. 2005: 1-334.
- [4] Czyżyk F, Kozdraś M, Sieradzki T. *Zesz Probl Post Nauk Roln.* 2002;484:117-124.
- [5] Klärschlammkompost. Umweltinstitut des Landes Vorarlberg 2005:1-21.
- [6] Czeakała J, Sawicka A. *Woda – Środowisko – Obszary Wiejskie.* 2006;2(18):21-40.
- [7] Banegas V, Moreno JL, Moreno JL, Garcia C, León G, Hernández T. *Waste Manage.* 2007;27:1317-1327.
- [8] Czeakała J. *J Res Appl Agricult Eng.* 2009;54(3):43-48.
- [9] Ochrona Środowiska – Informacje i opracowania statystyczne. Główny Urząd Statystyczny, Warszawa 2010;193-196.
- [10] Uchwała Rady Ministrów Nr 233 z dnia 29 grudnia 2006 r. w sprawie “Krajowego planu gospodarki odpadami 2010”. Załącznik “Krajowy plan gospodarki odpadami 2010”. *Monitor Polski* 2006, Nr 90, poz. 946.
- [11] Czeakała J, Jakubus M. *Fol Univ Agric Stetin.* 200, *Agricultura.* 1999;77:39-44.
- [12] Bernacka J, Pawłowska L. Substancje potencjalnie toksyczne w osadach z komunalnych oczyszczalni ścieków. Warszawa: Monografie IOŚ; 2000.
- [13] Merrington G, Oliver I, Smernik RJ, McLaughlin MJ. *Adv Ecol Res.* 2003;8:21-36.
- [14] Jakubus M. Zmiany specjacji i bioprzyswajalności mikroelementów podczas kompostowania osadów ściekowych z różnymi bioodpadami. Poznań: Wyd. Uniwersytet Przyrodniczy w Poznaniu, *Rozprawy Naukowe;* 2010;405:1-156.
- [15] Wróblewska H, Czeakała J, Piotrowska M. *J Res Appl Agricult Eng.* 2009;54(4):185-189.
- [16] Czeakała J. In: *Mat I Ogólnopol Konf “Planowanie technologii kompostowania osadów ściekowych i innych bioodpadów”.* Kalifornia; 2003;28-34.
- [17] Amir S, Hafidi M, Merlina G, Revel JC. *Chemosphere.* 2005;59:801-810. DOI: 10.1016/j.chemosphere.2004.11.016.
- [18] Yañez R, Alonso JL, Diaz MJ. *Bioresour Technol.* 2009;100:5827-5833. DOI: 10.1016/j.biortech.2009.05.073.
- [19] Wagner DJ, Bacon GD, Knocke WR, Switzenbaum MS. *Environ Technol.* 1990;11:949-960.
- [20] Canarutto S, Petruzzelli G, Lubrano L, Guidi GV. *BioCycle.* 1991;32:48-50.
- [21] Czeakała J, Jakubus M, Mocek A, Owczarzak W. *Fol Univ Agric Stetin.* 200. *Agricultura.* 1999;77:45-50.

- [22] Czekala J. In: Mat. III Ogólnopol. Konf. "Planowanie technologii kompostowania osadów ściekowych i innych bioodpadów", Tarnowo Podgórne, 16-17 kwietnia 2008:75-82.
- [23] Ko HJ, Kim KY, Kim HT, Kim ChN, Umera M. Waste Manage. 2008;28:813-820.
DOI: 10.1016/j.wasman.2007.05.010.
- [24] Kyzioł J, Twardowska I, Schmitt-Kopplin Ph. Chemosphere. 2006;63:1974-1982.
DOI: 10.1016/j.chemosphere.2005.09.042.
- [25] Jakubus M, Czekala J. Polish J Environ Stud. 2001;10(4):245-250.
- [26] Krzywy E, Krzywy-Gawrońska E, Wołoszyk Cz, Iżewska A, Sałagan P. Zesz Probl Post Nauk Roln. 2009;537:199-205.

OGÓLNA ZAWARTOŚĆ CHROMU I NIKLU ORAZ ROZPUSZCZALNYCH FORM TYCH METALI W KOMPOSTACH

Katedra Gleboznawstwa i Ochrony Gruntów
Uniwersytet Przyrodniczy w Poznaniu

Abstrakt: Kompostowanie jest jedną z metod utylizacji komunalnych osadów ściekowych, zapewniającą otrzymanie produktu o wysokiej wartości nawozowej, bez ryzyka skażenia gleby. Jednym z warunków spełniającym takie wymogi jest prawidłowy skład chemiczny samych osadów, szczególnie pod kątem zawartości metali ciężkich, jego stabilizacja oraz właściwy dobór odpadów biodegradowalnych dodawanych do osadów. Przeprowadzone badania miały na celu określenie wpływu różnych dodatków organicznych do osadów na zmiany ogólnych zawartości chromu i niklu oraz ich wodnorozpuszczalnych form w kompostach.

Doświadczenie przeprowadzono na terenie kompostowania otwartej metodą przyz, które utworzono z komunalnych osadów ściekowych z dodatkiem przemysłowych odpadów z konopi lub/i słomy oraz zrębków drzewnych, w zależności od schematu badań. Kompostowanie do końca fazy schłodzenia trwało 93 dni i dalsze 131 dni w fazie dojrzewania. W pracy wykorzystano aerator ciągnikowy, który przerzucał, rozdrabniał i napowietrzywał kompostowany materiał.

Stwierdzono, że czynnikiem w największym stopniu wpływającym istotnie na ogólną zawartość chromu i niklu w kompostach był tylko czas kompostowania. W przypadku rozpuszczalnych form tych metali także czas działał najsilniej, a w odniesieniu do związków chromu dodatkowo rodzaj kompostu i współdziałanie obu czynników.

Słowa kluczowe: osady ściekowe, odpady organiczne, komposty, zawartość chromu, zawartość niklu