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Effect of silver nanoparticles supplied via sewage sludge on soil microbial communities

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Due to their biocide properties, silver nanoparticles (AgNP) are used in various manufactured products (textiles, medical products, home appliance…). Then, AgNPs enter sewage sludge treatments and reach agronomic soils via sludge application. Health and sustainability of agrosystems depend on diverse organisms, notably the microbial communities involved in biogeochemical cycles, which could be affected by these AgNPs.

Our aim in the ETNA² project was thus to assess the impact of AgNPs supplied via sewage sludge on soil microbial communities. The experimental design consisted in mesocosms of soils amended with sewage sludge submitted to anaerobic digestion in 4 different conditions: (i) supply of the commercial AgNP NM300K (including dispersant) (ii) supply of $AgNO_3$ (iii) supply of the dispersant only (iv) control without any amendment. In order to compare the impact of different routes of entry in the agrosystem, a 2nd set of microcosms were performed with direct exposure to silver (4 treatments: control soil and AgNP, $AgNO_3$, dispersant supplied directly on soil). After 35 days of incubation, we analyzed the diversity of the microbial community using Miseq sequencing of the 16S rDNA and the potential activities of respiration, denitrification and nitrification.

Microbial diversity was affected by silver supply but we cannot observe more intense effects of AgNP versus $AgNO_3$. Besides, sewage sludge application was the main driver with more effects on the microbial diversity than silver exposure.

If silver was supplied via sewage sludge, respiration and denitrification were not affected. However, in this case, a strong and significant decrease of nitrification was observed, whatever the silver form, AgNP or $AgNO_3$. On the contrary, when silver was applied directly in the soil microcosms a very different pattern was observed with a significant decrease in respiration and denitrification but no detectable effects on nitrification. Our results show that AgNPs did not exhibited more toxic effects than $AgNO_3$, probably due to aggregation and/or sulfidation of AgNPs. Besides, the opposite effects observed on nitrification and denitrification suggest a risk of imbalance of the N cycle and thus a possible decrease of the stability of the agrosystem.

Assisted phytoremediation of heavy metal contaminated soil

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Assisted phytoremediation process of Pb/Zn/Cd smelter-contaminated soil with stabilization amendments and specific plant species can be considered as a cost-effective option that reduces the mobility of heavy metals. Mainly two types of amendments are used for this purpose: organic and inorganic amendments as well as mixtures of them. Basically the applied amendments shall influence the stabilization of harmful compounds or/and delivery of beneficial for plants growth compounds. The first group includes mainly mechanisms based on chemical sorption processes or physical absorption processes. Numerous stabilization amendments for heavy metals in soils have been proposed, including alkaline materials (e.g., lime, calcium carbonate, lacustrine chalk, sulfurizing agents, magnesium oxide phosphate compounds (e.g., phosphate rocks, superphosphate, potassium phosphate, struvite), industrial residues (e.g., red mud, fuel ash, sewage sludge, compost), and biomass materials (e.g., shell powder, bone char, proceeded plants biomass, biochar), and these soil amendments have been shown to be effective at stabilizing heavy metals in assisted phytoremediation. The Pb/Zn/Cd smelter-contaminated soils are very difficult for remediation due to high toxicity and bioavailability of metals, the multi elemental contamination and thus undesirable effects of synergistic toxicity, as well as far-reaching physical changes in soils like low sorption capacity, intensive leaching and migration processes , low pH, low carbon and biogenic compounds. The results of amendments application provide the highly effective simultaneous stabilization of heavy metals. The second objective in the remediation process is obtaining the phyto-cover to realize the process of phytostabilization. The dense root system increases the degree of immobilization of metals, prevents secondary dusting and horizontal distribution of trace elements. Due to the large contaminated areas reaching hundreds of hectares surrounding smelters , the assisted phytoremediation seems to be the most reliable solution, even in comparison to natural monitored attenuation. The results proved the need to support the phytostabilization processes conducted on contaminated soils.

The research has been co-funded with the funds of NCN (National Science Centre Poland) and NCBR (National Centre of Research and Developement), under TechNabio project, acquired on the basis of the decision nr TANGO/266740/NCBR/2015.

A Novel *Pseudomonas fluorescens* Whole-Cell Biosensor for *in-situ* PAH Bioavailability Detection

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The burning of coal is the primary fuel source for the Polish nation [1], yet byproducts of this combustion are well-established toxins and carcinogens (cancer-causing agents) [2]. A notable class of these compounds are the polycyclic aromatic hydrocarbons (PAH's). While irrefragable connections have been established for PAH's toxicity, there remains a nescience of how mobile these compounds are in agricultural environments, and how this in turn affects public health. This is especially apposite in Poland, as both a significant sector of its workforce and cultural legacy lay in agriculture. Not all PAH's found within the soil are toxic to humans, as they must first pass through the skin and ultimately cell bilayers to be metabolized and intercolate with DNA [2]. This fraction is called the bioavailable fraction and can be measured using whole cell biosensors (WCB's) [3]. *Pseudomonas Fluorescens*, a soil bacterium with a known metabolism for soil PAH's [4]. Therefore, we have isolated genes involving this metabolism and seek to establish whether a there is a relationship between the concentration of in-situ PAH's from whence the bacteria are derived and their rate of expression of these genes to see if these genes are suitable as a bioreporter element in the WCB. Results will indicate whether these strains and genes can serve as the foundation for the WCB, in which rate of expression of the bioreporter element will directly correlate to artificially-induced fluorescence to be measured on site, such as with a mobile spectrometer [5]

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Eco-innovations in sewage sludge management

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The world “production” of sewage sludge is huge - if we calculate than 1 person could generate average 10-15 kg dry matter of sewage sludge, hence 7.6 billions people generate could achieve even 110 billions kg dry matter per year. Taking into consideration basic rule of circular economy (promoted by many developed countries) that scarce resources should be reused and not sent to landfills, sewage sludge ceases to be waste and becomes a valuable source [1]. It is mainly connected with its physical-chemical characters. Sewage sludge is composed mainly of organic matter–dehydrated (dry) sludge depending on applied stabilisation process contain on average 50–70% of organic matter and 30–50% mineral part (including 1–4% of inorganic carbon); 3.4–4.0% N; 0.5–2.5% P, as well as some other nutrients, including microelements [2]. It can be used as an energy resource for power and heat with conventional and emerging technologies, and can also be used in agriculture as a fertilizer or degraded soil remediation. The legislation of the European Union concerning the disposal of sewage waste is included in the Council Directive 86/278/EEC on environmental protection of 12 June 1986 (the so-called Sludge Directive). However sludge and sludge components may be recycled in a “productification” strategy, i.e. a strategy aimed at making products from sludge intended for sale in the market place [3]. It is several technologies to maximize energy recovery: co-treatment with grease-rich waste, improvement with enzymes or vitamins, disintegration by physical and chemical factors. In turn, the processing of sewage sludge into organic fertilizers (composts), organic-mineral fertilizers or substrates for plant cultivations are technological solutions proposed as an alternative for direct sewage sludge landscaping [4].

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Soil environmental genotoxicity: past and actual tools, future needs

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It is now clearly established that risk assessment and management strategies for chemicals, wastes, contaminated environments and materials should consider biological responses, including environmental genotoxicity. The characterization of terrestrial ecosystem contamination by genotoxicants requires the the assesment of their environmental and toxicological bioavailabilities and the identification of adverse effects at individual and population levels.

As in aquatic ecosystems (for review see [1]), environmental genotoxicity with field terrestrial species is assessed by means of markers focusing on genomic alterations and DNA damage, like DNA adducts (less used lately), nuclear abnormalities -as micronuclei- and DNA breaks. Epigenetic changes have not been investigated so far. The comet assay (with or without the use of endonucleases) has nowadays largely supplanted pre-existing techniques for DNA damage assessment. This technique of microelectrophoresis of isolated nuclei on microscope slides in agarose gels have been firstly described by Singh et al. (1988) [2] and is now applied in many fields of biology.
All these tools/techniques have firstly been used, optimized and validated with aquatic species. Their applications to soil species have secondary emerged and, for the comet assay for example, are now widespread with plants or vertebrate and invertebrate species. We will present briefly some results illustrating interests of the comet assay to approach the "genotoxic bioavailability" of terrestrial contaminants and as example their effects on earthworms.

In both aquatic and terrestrial environments, genotoxicity is generally measured in somatic cells, more scarcely at the level of germ cells. However, in some cases, it could be related to mutations, embryo mortality or reproduction impairment. Therefore, there is a need for works linking (1) genotoxicity in individuals and (2) population dynamics and genetics. Studies with gametes, early life stages and juveniles, in environmentally relevant conditions have to be conducted to reach such objectives.

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Importance of metal speciation for risk assessment of nanomaterials: the case of Ag in sewage sludge

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Ecotoxicity of Ag nanoparticles has been widely reported in the literature. However, most of the toxicity studies do not take into account the environmental transformation that the particles may undergo once released from their initial product. To more accurately assess the environmental risks of Ag NPs, it is necessary to investigate the environmental transformations of Ag NPs in environments that are consistent with their anticipated release pathways and exposure routes. One of the major release pathway for silver NPs in consumer products is through discharge to the sewer system. These materials are released to a wastewater treatment plant (WWTP) and accumulate in sludge produced during the wastewater treatment process. Part of these sludges are finally used as a fertilizer on crops.

Here, we will show the importance of studying the speciation of Ag during the lifecycle of the product in order to better predict the risk associated with nanoparticle release for the environment and in particular for terrestrial compartments in the context of the use of sewage sludge as fertilizer. In particular, we will see how transformation to silver sulfide strongly affect nanoparticles properties and toxicity.

ETNA2 project: Silver ecotoxicology in terrestrial environments

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Due to the increasing incorporation of silver nanoparticles (AgNP) in consumer products, silver contamination of sewage sludge may increase and have environmental impacts. Indeed sewage sludge are sometimes used in agriculture as fertilizers. In such a context, our project ETNA2 propose to monitor the silver concentrations in selected sewage sludge coming from southern Poland during 2 years and examine their evolution in term of concentrations. In parallel, the assessment of the terrestrial ecotoxicity of silver ions, silver nanoparticles (AgNP) and their transformation products (sulphides of silver) will be conducted. Therefore, such ecotoxicological assessment will be done using key organisms of soil functioning which are affected by chemical contamination: microorganisms and earthworms. Exposures of the ecotoxicologically important test species *Eisenia fetida* were conducted in mesocosms containing agricultural reference soil contaminated by sewage sludge, Ag ions, AgNP or silver transformation products. These compounds were added to the soil or through the sludge after fermentation. Our aim is to address the lack of informations concerning the question of silver in soil ecotoxicology. The impact of Ag on soil microflora communities was explored as preliminary experiments evidenced the bactericidal properties of Ag in this environmental context. A better understanding of the effects of Ag, depending on its form (sulphides from WWTP sludge, Ag ions and AgNPs) will be achieved mainly through genomic and trancriptomic approaches combined with full physico-chemical characterization. Analysis will be conducted to make a link between silver evolution/ behavior in sludge and soils and their terrestrial ecotoxicity.

The sustainable technologies in agriculture and soil remediation – TechNabio powered by GreenBack Ltd

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The concept of sustainable development has recently found a wide range of applications. The principles of this agenda comes from forestry. In the beginning they were related to the management of wood production, in way that ensures the highest possible income with the regard of multi-generational production contexts. The literature and legal acts, provide also a another definition of this principles. According to those documents the sustainable development is the way of production management, that takes into account the combined economic, social and environmental aspects.

With regard to agriculture, the principles of sustainable development are almost unchanged. In practice, they are concerned on the natural resources management, in way, that allow to maintain a high soil productivity, not only for a short period but also for many years. At the same time, all activities within the indicated scope, should not have a negative impact on the both human health and environment. It is also important that conducted works generates income, that allow to provide a constant development of production unit.

In recent years, many new technologies and methods, aimed to solve issue with the unsustainable agriculture were been developed. Some of them includes a immobilization process. Those methods are based on the natural modification of the soil environment in way, that allow to provide a more effective nutrients management.

The simplest technique, that can improve the soil sorption capacity, is the direct application of fertilizers that are rich in organic matter, mineral compounds with a large active surface or humic acids in solid or liquid form. One of the most interesting solutions within this sector is a product developed as a result of the TechNabio project. The prepared solution is consisted of humic substances encapsulated inside a biodegradable polymeric capsule. The advantage of this solution is the ability to precise delivery of active substance, to place where it can effectively work.

More information on these preparations can be found on the project website:
www.technabio.com

All business contacts and distribution options can be also found at:
www.greenback.net.pl.

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WATER TREATMENT SEDIMENTARY BY BIOLOGICAL METHODS

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Abstract

In the wastewater treatment process, significant amounts of sludge are generated, which due to the high content of organic substances, minerals, toxic compounds as well as sanitary condition are neutralized during the classic processes where a certain amount of sediment liquid separates from sediments. These processes include, among others: gravity, flotation or mechanical concentration of crude sludge, mechanical dehydration of digested sludge, stabilized sludge concentration, aerobic or anaerobic stabilization.

On this paper discusses the management of sedimentary water in municipal wastewater treatment plants, which is inherently related to the treatment as well as the disposal of sediments by reducing the volume and exclusion of their harmful impact on the environment. The classification of sedimentary waters, characteristics of the physical and chemical composition was described and methods for their purification were described.

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Sewage sludge, silver nanoparticles and terrestrial environments: state of the art and involved work

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The fast increase of the global population, urbanization, industrialization and the improvement of technologies used in wastewater treatment plant have led to a strong increase of the production of sewage sludge. Because of the high organic matter and nutrients content, sewage sludge can be applied as a fertilizer, but some contaminants shall be strictly monitored. In Europe, legislation focused on: seven metal trace elements (cadmium, chromium, copper, mercury, nickel, lead and zinc) and organic traces compounds (7 polychlobiphenyls and 3 polycyclic aromatic hydrocarbons (fluoranthene, benzo(b)fluoranthene and benzo(a)pyrene)). Still, some potentially dangerous contaminants, e.g. silver nanoparticles are not regulated at present.

Due to their biocidal properties, silver nanoparticles are among the most frequently used nanomaterials (in more of 300 products and production estimated around 500 tons per year). Releases in the environment through wastewater treatment plants, linked to the life cycle of products containing nano-silver, can cause a contamination of ecosystem and ecotoxicological and/or health effects [1].

Many research aimed on the assessment of the risks and dangers associated with the use of silver, nano-silver and their derivatives on organisms and ecosystems. Recent works have shown that the nano-silver 1) decrease the diversity and the quantity of soil microorganisms [2], 2) are accumulated in plant and animal tissues [3,4] and 3) cause biological effects on studied organisms. Nevertheless, the understanding of their effects on the terrestrial ecosystem is still incomplete and many questions subsist.

This work aims on the effects of the nano-silver toxicity in terrestrial environment, mainly throught its effects on organisms living in close contact with soil, to characterize it and to understand its mechanisms of action on organisms.

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Plant-based composts for veganic agriculture

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In recent years we are observing a gradual shift from conventional agriculture to organic agriculture (this also includes veganic farming). Organic food is considered to be healthier and safer for people. Organic farming has also less environmental impact in comparison to conventional farming. Conventional agriculture uses chemical and mineral fertilizers, pesticides, animal based fertilizers (such as manure, composts from animal parts, feather meal, bone meal, etc.), and thus can result in greenhouse gas emissions and run-off of the excess nitrogen from fertilizers. Also, organic agriculture uses organic fertilizers and composts that are produced from animal derived materials. The application of animal derived organic fertilizers such as manure – the most commonly used in agriculture – may pose health threats as e.g. manure may contain intestinal and parasitic diseases, antibiotic and growth hormones residues. With the growing interest in vegan diet and veganic farming (veganic farming rejects fertilizers made from animal sources), there is a need for plant-based composts that can be used for growing plants for vegan consumers.

There is a potentially vast group of waste materials that can be used in composting in order to produce high quality plant-based composts for veganic agriculture. This includes green waste, hays, straws, seaweed, plant waste and by-products from food processing industries. However, the challenge lies in achieving the proper balance of nutrients in composting mixtures, especially nitrogen, carbon and phosphorous.

There is little known about the potential of various waste materials of plant origin for producing composts that can be used for veganic agriculture. Therefore, the overall goal of this contribution is to review the current state of the art and to analyze the potentials of producing plant-based composts that can be used in vegan agriculture.

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Characteristics of biochar-added vermicomposts from sewage sludge

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Biochar is an effective amendment in composting of various organic waste and the obtained composts. Some studies also demonstrate that biochar can have a positive effect on vermicomposting by facilitating the growth and reproduction of earthworms. This is mostly due to the fact that biochar added to the mixtures of organic waste improves total porosity and water holding capacity, provides macro and microelements and reduces the bioavailability of heavy metals to earthworms. However, little is known about the properties of biochar-added vermicomposts and their potential applications.

The overall goal of this study was to characterize the vermicomposts obtained from two types of mixtures: (1) sewage sludge and wheat straw and (2) sewage sludge and woodchips. The treatments included addition of biochar (0%B, 4%B, 8%B on wet basis): (1) prior to composting and vermicomposting and (2) after composting but prior to vermicomposting. The properties of biochar-added vermicomposts differed depending on the type of bulking agent and the origin of biochar.

All vermicomposts demonstrated low pH (5.25-5.61) which makes them suitable for the use as a horticulture substrate or an organic amendment for calcareous soils. In addition, depending on the initial properties of the composting mixtures the biochar-added vermicomposts demonstrated higher phosphorous and potassium concentrations. However, concentrations of some heavy metals, e.g. chromium were elevated and exceeded the permissible values.

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FLUIDIZED-BED CHEMICAL-LOOPING-COMBUSTION OF SOLID-FUEL

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ABSTRACT

Chemical looping combustion (CLC) is one of the most promising CO_2 capture technologies, with the potential of reducing the costs and energy penalty in comparison to other pro-CCS technologies. In CLC process oxygen necessary for fuel combustion is supplied by metal oxides called as oxygen carriers, which circulate between two interconnected fluidized-bed reactors. The first is a fuel reactor (FR) and the second is an air reactor (AR). In fuel reactor the oxygen carrier is reduced and fuel is burned. The reduced oxygen carrier is re-oxidized by air in air reactor and returns to the fuel reactor to start a new redox cycle.

This work presents the results from experiments on the 5 kW FB-CLC-SF test rig. The unit was operated with polish bituminous coal and biomass using different types of oxygen carriers. The main flue gas components were measured by using FTIR analyser whereas the oxygen levels at the outlets of AR and FR were controlled by paramagnetic analyser and zirconium sensor, respectively. The pressure was controlled by pressure sensors, while the temperature was measure by thermocouples. The capacity and reactivity of OCs seem to remain unchanged (or only slightly decrease) after few-hour operation under fluidized bed-CLC conditions. FB-CLC-SF test rig operates smoothly when natural OC is used, whereas other OCs cause the some problems with solids agglomeration and sintering. The experimental results of pollutant emissions (Idziak, 2017) and fluidized-bed kinetics were compared with the numerical results obtained from CeSFaMB simulator (Krzywanski, 2016; Zylka, 2017).

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PRECIPITATION OF STRUVITE FROM SEWAGE SLUDGE

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Nowadays, the rapid development of new technologies also applies to sewage treatment plants. Despite the various possibilities of sewage sludge management, a significant part of them is still stored in sewage treatment plants. One of the possibilities their management is the recovery of phosphorus and nitrogen, which are components of fertilizers. About 90% of phosphorus compounds are accumulated in sewage sludge. [1] The most beneficial forms in which we can recover phosphorus are calcium phosphates, as well as struvite - (NH_4) Mg $[PO_4]$ • $6H_2O$. Phosphorus and nitrogen contained in the struvite are released into the soil slowly, which is why it is a highly valued product. Struvite recovery technologies from sewage sludge are not yet widely used due to their low economic aspect. Research is being carried out to optimize the precipitation process. [2]

The aim of the research was to determine the most favorable concentration of Mg^{2+}, NH_4^+ ions necessary to precipitate struvite, at which its greatest mass was obtained. The tests carried out consisted of two stages, the first consisting in the precipitation of struvite deposits in the aqueous solution; second struvite recovery from fermented sewage sludge.

The following different concentrations were used in the tests: Mg^{2+} in the form of a solution of $MgSO_4$ • $6H_2O$, NH_4^+ in the form of NH4Cl and PO_4^{3-} in the form of KH_2PO_4; solutions were prepared on the basis of distilled water. A constant pH of 9 was used, and a reaction temperature of 20-22 ° C. In the first stage the largest mass (3.14g) was obtained in concentrations of: 300mgNH_4^+ / dm^3 and 100mgPO_4^{3-} / dm^3 i 10mgMg^{2+} / dm^3, while in the second stage the maximum mass (6.43g) was obtained for concentrations 150mgNH_4^+ / dm^3 and 60mgMg^{2+} / dm^3. [3]

Key words: phosphorus, struvite, sewage sludge, management of sewage sludge

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Application of assisted bioremediation in the removal of petroleum contaminants

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The contamination of the environment caused by petroleum compounds entail the necessity of taking some operations which lead to its remediation. Technology used to eliminate this type of contamination from the natural environment is bioremediation techniques. A process of bioremediation is precisely related with the activity of microorganism (bacteria, fungi) and causes degradation or transformation contaminants into less toxic compounds. Bioremediation is environmentally friendly methods without any harmful effect. The activity of microorganisms on the degradation of contaminants depends on some physico-chemical factors such as: oxygen concentration, pH, temperaturę and prevalent amount of nutrients (carbon, nitrogen, phosphorus). In the thesis, the ability of decomposition of petroleum compounds via bacteria as well as fungi were analyzed. Biopreparations were added two ways: in a free living form and moreover as an immobilized ones.

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Analysis of the influence of the compost mix composition on the thermophilic phase

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The paper presents the influence of selected substrates (grass, an organic fraction of municipal solid waste, barley straw, energy willow, coal mud, sewage sludge from sewage-treatment plant "Warta" and a biopreparation) used to create compost mixes on the course of thermophilic phase. It was verified that the combinations would allow for temperatures sufficient for the hygienisation of the compost and increase the duration of the high temperature phase. The experiment was conducted for 8 weeks (4 weeks of composting in bioreactors + 4 weeks of compost maturation in natural conditions) for various combinations of substrates and their shares. The influence that additional external warming had on the course of the thermophilic phase was also analyzed. During the experiment, the following parameters of the compost masses were analyzed: temperature, humidity, Kjeldahl nitrogen, total carbon, organic matter content, presence of bacteria such as *Escherichia coli* and *Salmonella* sp. and *Ascaris lumbricoides* eggs. The mix that generated the most heat in the thermophilic phase (56,3°C) consisted of 60% grass, 20% organic fraction of municipal solid waste and 10% mud. In addition, it reached one of the longest thermophilic phases and was the only one to reach full hygienisation as determined by the absence of *Salmonella* sp., *Escherichia coli* and *Ascaris lumbricoides* eggs after four weeks of the composting process. The use of thermal insulation influenced the increase of temperature in the thermophilic phase and extended its duration [1].

Key words: thermophilic phase, compost, composting, organic fertilizer, compost mix composition

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Acidity of vapor plume from cooling tower mixed with flue gases emitted from coal-fired power plant

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Acidity of products resulting from the reaction of flue gas components emitted from a coal-fired power plant with water contained in a vapor plume from a wet cooling tower was analyzed in a close vicinity of a power plant (710 m from the stack and 315 m from the cooling tower). Samples of this mixture were collected using a precipitation funnel where components of the mixed plumes were discharged from the atmosphere with the rainfall. To identify situations when the precipitation occurred at the same time as the wind directed the mixed vapor and flue gas plumes above the precipitation funnel, an ultrasound anemometer designed for 3D measurements of the wind field located near the funnel was used. Precipitation samples of extremely high acidity were identified - about 5% of samples collected during 12 months showed the acidity below pH = 3 and the lowest recorded pH was 1.4. During the measurement period the value of pH characterizing the background acidity of the precipitation was about 6. The main outcome of this study was to demonstrate a very high, and so far completely underestimated, potential of occurrence of episodes of extremely acid depositions in the immediate vicinity of a coal-fired power plant.

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The directions of the research on earthworms in the Faculty of Biology and Agriculture at the University of Rzeszów (1984-2017)

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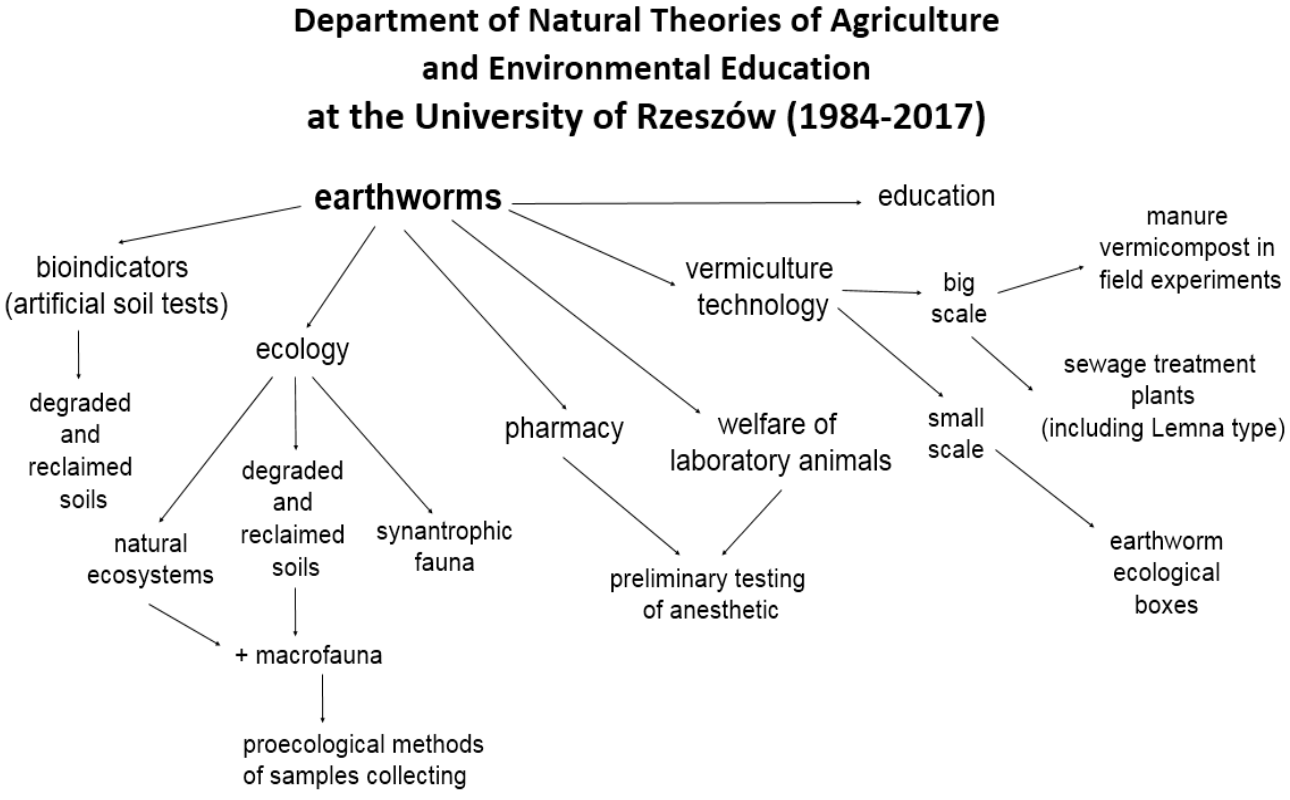
Research on earthworms has been conducted in the Department of Natural Theories of Agriculture and Environmental Education since the year of 1984. They began by recognizing the qualitative and quantitative structure of the Lumbricidae populations in Carpathian beech forest. To date, such studies have been conducted to evaluate the populations of these invertebrates in different ecosystems and ecosystems altered anthropogenically. In the 1990s, research into the possibilities of using vermiculture for the utilization of various organic wastes was started, which continues today also in connection with educational activities.

Between 1994 and 2005, five national scientific conferences "Ecological and economic importance of earthworms" were organized in Rzeszów.

These and some other directions of the new research conducted on earthworms are presented in the diagram below.



Analysis of the potential use of struvite

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Progressive degradation and devastation of soils is one of the main problems occurring in Poland, the important aspect of which is the introduction of a significant amount of pollutants, a reduction in the content of nutrients and humic substances in the soil. Disruption of any of its functions can contribute to its rapid degradation and difficulty in restoring its resources. The use of fertilizers has thus become an inseparable element of plant breeding, which allows to increase the content of nutrients mainly nitrogen, phosphorus or potassium needed for the proper growth and development of plants. This work focuses on the analysis of the applicability of struvite as a fertilizer. Struvite is a hydrated ammonium magnesium phosphate of chemical formula: $MgNH_4PO_4.6H_2O$. Struvite is a mineral, inorganic chemical compound, crystalline, rapidly bubbling in the form of white powder. Struvite crystals contain two important macroelements necessary for the growth and development of plants - phosphorus and nitrogen. Another important fact is that it exhibits a relatively low solubility, this means that it is a slow-release fertilizer, slowly dissolving in the soil and the plant itself stimulates the intensity of the collection. At present, acquiring struvite for economic purposes is unprofitable, however, the natural phosphorus deposits are constantly narrowing, which in the future is forecasting the search for alternative sources of phosphorus and the possibility of using struvite in agriculture. Some European countries, such as Sweden, Switzerland, the Netherlands and Denmark, due to the exhausting sources of apatites and phosphates from which phosphate fertilizers are produced, are moving towards introducing new regulations on the recycling of phosphorus from various sources, especially secondary ones. The natural source of struvite is decomposing organic material. Struvite may precipitate in sewage sludge after anaerobic fermentation processes in liquid sediments after animal cultures as well as in sediments after biological wastewater treatment.

Key words: Struvite, fertilization, phosphorus recovery

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Influence of Dimilin 25WP on the earthworms Allolobophora chlorotica

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Keywords: *Allolobophora chlorotica,* Dimilin 25WP, ecotoxicology, population characteristics, coelomocytes

Earthworms are an important and representative group of inhabitants of the soil environment. They can contain up to 70% of biomass, which is why they are commonly used in ecotoxicological tests to assess the impact of chemical substances on the environment. Chemical stress affects the zooedophon representatives differently, even in the so-called environmentally safe doses recommended by the manufacturers.

The aim of the present studies was to check the impact of Dimilin 25 WP on the earthworms *Allolobophora chlorotica.*

Mature (*clitellum*) earthworms *Allolobophora chlorotica* were collected by hand-sorting method from the experimental garden of the Institute of Zoology of the Jagiellonian University (Kraków). To the containers filled with 300 ml soil (Kronen Universalerde – garden soil; pH ($CaCl_2$) 5,5-6,5; N – 200-450 mg/l; P_2O_5 – 200-400 mg/l; K_2O – 300-500 mg/l; ISO 9001 2000) contaminated before respectively 0.078 g and 0.0078 g Dimilin 25 WP introduced 5 adult (*clitellate*) earthworms *A. chlorotica* (BW: 0.379 ± 0.091 g)**.** Dimilin 25WP belongs to the inhibitors of chitin biosynthesis from the group of acylurea (benzylurea) preparations (active substance – diflubenzuron). Soil samples were allowed it equilibrate for 24 h before. The experiment was performed in four replication in comparison with the control group. Soil in the containers checked by hand-sorting method after 3, 6, 9 and 12 weeks. At this time survival, body weight and reproduction were checked. At the end of the experiment, the surviving earthworms were stimulated for 1 minute with 4,5V electric current to expel coelomic fluid with coelomocytes (3 ml PBS with 2g/l EDTA 1 min; 2% formalin 24h) and counted in a Burker haemocytometer. Experiment carried out for 12 weeks in 2015 in laboratory conditions (18 ± 2 ^oC; 24 light), fed on horse manure.

Application of Dimilin 25 WP in both studied concentrations significantly decreased the biomass of the population and the individual body mass. Insecticide reduced the total number of coelomocytes *A. chlorotica* and reduced the probability of survival of the earthworm population compared to the control group.

IMPACT OF ADDITION OF PHOSPHORUS COMPOUNDS CONTAINED IN SEWAGE SLUDGE ON PLANT GROWTH

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Phosphorus is a biogenic element necessary for the proper functioning of all living organisms. In nature it is widespread in the various various compounds [1]. For plants, the only available form is the form of phosphates contained in the soil solution. Phosphate fertilizers are used throughout the world to improve soil quality in crop fields to create the best conditions for plant breeding. If the rate of phosphorus exploitation will be as high as before, natural sources of phosphorus will run out over the next several decades [2,3]. Therefore, there is an increasing interest in the effective use of waste containing large amounts of phosphorus compounds, which include sewage sludge. The phosphorus content in the dry mass of sewage sludge or sewage sludge ashes ranges from several (2.62% - for sewage sludge) to a dozen or so percent (13.4% - for ashes) [4].

The main goal of research was to compare the effect of the addition of phosphorus compounds from various sources (sewage sludge, synthetic struvite and fertilizer) for growth and biomass of plants (mustard and rape). The plant biomass was grown in vitro on soil extracts with appropriate additives in a phytotron chamber for 4 weeks. Based on the obtained results, stated that sewage sludge has a positive effect on general plant growth. Plants grown on a medium with the addition of sewage sludge were characterized by a higher mass and length of stalks and roots, both in the case of rape and mustard. Farther for rapeseeds this parameters reached the highest values and was better than using a phosphate mineral fertilizer. In addition, the plants were better hydrated. In the conducted experiment, struvite showed no particular effect on plant growth. Struvite has an impact of increase length and water content in stalks and roots [5].

Key words: phosphorus, phosphorites, natural phosphorus raw materials, sewage sludge, natural fertilizers, waste management, sewage sludge management

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Toxicity tests of ketoprofen and diclofenac on *Daphnia magna*

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The acute toxicity of selected pharmaceuticals from group of nonsteroidal and anti-inflammatory drugs (NSAIDs) – ketoprofen, diclofenac has been evaluated within this study using DAPHTOXKIT F^{TM}. The main goal of studies was toxicity analysis of individual pharmaceuticals and the mixture of them, performed on aquatic organisms – *Daphnia magna.* Toxicity effects were tested by means of half-maximal effective concentration (EC_{50}) and lethal concentration (LC_{50}) on 3 populations of *Daphnia magna*. The EC_{50} values ranged from 47 to 71 mg L^{-1} for diclofenac and from 33 to 52 mg L^{-1} for ketoprofen. The average LC_{50} values for ketoprofen, diclofenac and their mixture are: 76 mg L^{-1}, 103 mg L^{-1} and 58 mg L^{-1}, respectively. According to EU Directive both pharmaceuticals can be classified as harmful. Toxicity tests showed that ketoprofen is more toxic than diclofenac. The study exhibited synergistic interaction because toxicity effects of the mixture was 10 - 15% greater compared to single pharmaceuticals. The toxicity data obtained within this study revealed that occurrence of ketoprofen and diclofenac in the water pose side-effects and direct threat to aquatic organisms. The future studies should be extended to examine the chronic toxicity of pharmaceuticals.

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Biochar as an alternative filler for biodegradable composites

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Biochar is a carbonaceous material obtained from pyrolysis of various organic materials. Till now, there is a number of potential applications of biochar that include using biochar as an innovative fertilizer or soil improver for agriculture, a sorbent for wastewater treatment, an amendment for composting and vermicomposting. Recent studies demonstrate that biochar has a potential as an additive or filler in production of composites from biodegradable polymers. Biodegradable polymers, e.g. poly lactic acid (PLA), used for production of various biodegradable materials (e.g. accessories for agricultural use), are expensive, and thus the use of them can be limited. Therefore, one of the challenges is to reduce cost of these materials by substituting portions of biodegradable polymers with cheaper fillers such as biochar. Biochar can be obtained from organic waste and residues through pyrolysis and used as a filler in production of biodegradable composites. Some recent studies demonstrate that biochar added to biodegradable polymers can improve mechanical, thermal and physico-chemical properties of biocomposites. Also, converting organic waste into a solid carbonaceous material – biochar can be consider one of the waste management strategies. Such approach follows the principles of circular economy and sustainable agriculture.

The overall goal of this contribution is to: demonstrate the potentials of different biochars as alternative fillers in manufacturing biodegradable composites, analyze benefits and limitations of biochar used as a filler in biodegradable composites, and to discuss challenges and future research in this area.

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Adsorption diclofenac sodium on activated carbons. Influence of pH and temperature

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1. Introduction

Sources of pharmaceuticals in surface waters:

The presence of pharmaceuticals in water is attributable to : hospital waste, pharmaceutical industry, veterinary, household waste, farms.

The most common pharmaceutical compounds in the environment, belong to the groups of: antiinflamatory and analgestic drugs, beta-blockers, abtibiotics, lipid regulators, steroids and hormones (Nicolau, Ultra-Riverra).

2. Materials and methods

Materials

The starting solid materials used in this work were: two granular activated carbons: ROW 08 Supra, F-300. ROW 08 Supra manufactured in the Netherlands, by NORIT, F-300 manufactured in Belgium, by Chemviron. Diclofenac-Na were supplied from Sigma-Aldrich.

Method

The measurements were carried out on monocomponent model solutions containing 125 ml of diclofenac sodium, to which 0.5 g of activated carbons were added. Initial concentrations of the tested compounds ranged from 0.5 to 4 mmol / dm3. The test solutions were placed on a shaker, the mixing time was 10 h, the static contact time was 14h. The pH range in which the tests were carried out ranged from 6-10 and the temperature range from 20-40^{o}C

3. Results and discussions

Effect of pH

Adsorption of diclofenac sodium on ROW-08 and FG-300 activated carbons decreased with increasing pH. Adsorption was most effective at the solution pH of 6 and the lowest at a pH of 10.

Effect of temperature:

Adsorption of sodium diclofenac on active carbons ROW-08 and FG-300 increased with increasing temperature. The most effective was at 40^{o}C, less at 30^{o}C and 20^{o}C.

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Positive effects of vermicompost on soil water retention

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Degradation of soil often leads to lowering its ability to hold water, which not only lowers potential to utilize the land to produce crop but may also lead to lack of natural buffer to contain rainfall and in consequence to local flooding. As amount of organic matter in soil decreases, it gets more and more permeable for water. In case of climates where the water is scarce and the rainfall is rare this leads to irreversible damage to terrain as the arid areas are growing because plants are not able to develop in such dry conditions. Such barren areas can form due to natural wind erosion but also due to anthropogenic activity such as deforestation and heavy metal pollution – in case of the former it may cause faster permeation of toxic compounds to groundwaters. A number of papers involving use of vermicompost in soil mixes were reviewed to check for results on water retention among overall improvement of the state of the soil. In all analysed papers this organic fertilizer had positive effect on increasing the organic matter content. Amount of total nitrogen and phosphorus was also higher than in control groups, however it was noted that the available nutrients were usually released gradually. In case of microbial activity the addition of easily degradable substances supported growth in temporal bacterial activity, that lowered after those readily available nutrients depleted. Furthermore researchers observed beneficial influence on plants in scenarios involving potential water stress. Vermicompost is reported to playing a significant role in case of long term field tests with limited water availability. While this results were observed in case of other organic fertilizers (such as manure and compost) the vermicompost is reported to have the most notable effect of them all.

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ANALYSIS OF THE EFFICIENCY OF OBTAINING PHOSPHORUS FROM SEWAGE SLUDGE

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Phosphorus as a biogenic element is essential for growing plants. The fertilizers used most often in the form of P_2O5, the source of which are natural deposits of phosphorites and apatites. It is estimated that more than half of the natural source of phosphates for the production of fertilizers will be exhausted over the next 90 years.Therefore, methods of effective recovery of phosphorus from waste can be identified: urban waste water, sewage sludge, waste from the meat industry. In sewage treatment plants there are large reserves of unused phosphorus. About 90% of the phosphorus compounds reaching the sewage treatment plant is stored in the sludge. Phosphorus compounds can be recovered directly from sewage sludge or after thermal treatment from ash or slag. The phosphorus content in the dry mass of sewage sludge or ash from sewage sludge ranges from a few (2.62%) to a dozen or so percent (13.4%). Higher phosphorus content can be observed for more concentrated ashes. The content of% phosphate ions increases significantly with increasing temperature (21.4% at 600 ºC-23.9% - at 950 ºC). The ash from sewage sludge is an interesting and at the same time rich source of phosphorus, and there are several possible and economically justified methods of extracting phosphorus [1, 2] One of the simpler and cheaper methods seems to be reaction with phosphoric acid, which gives the effect of fertilizer, which is, however, still burdened with excessive amounts of heavy metals. It is estimated that the recovery of phosphorus, according to different methods, is at 80-90% The most beneficial forms in which we can recover phosphorus due to bioavailability are calcium phosphates, as well as struvite - (NH_4) $Mg[PO_4] \cdot 6H_2O$ - containing 58% P_2O_5, which does not damage the roots plants.

Key words: phosphorus, sewage sludge, sludge management, methods of phosphorus recovery

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THE USE OF BIOCHAR IN COMPOSTING

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Composting is the biological decomposition and stabilisation of organic matter derived from plants, animals or humans through the activity of diverse microorganisms under aerobic conditions. During that process, part of the organic matters is mineralized to CO_2, whereas the rest is transformed to humic substances, which represent a valuable mechanism of organic matter stabilization. However, the emission of greenhouse gases from composting of organic wastes is a serious problem [1,2]. Recent research shows that the addition of biochar during composting significantly increases the efficiency of this process [3,4]. Biochar is produced by organic matter thermal treatment at oxygen deficiency e. g. by pyrolysis or gasification, resulting in three products: char, gas and tarry oils. The addition of biochar during composting results, among others, in :

- increase in temperature (on average by 10 ° C),
- extension of the thermophilic phase,
- reduction of nitrogen losses during composting by sorption of NH_3 gas and water-soluble NH_4 ions,
- reduction of gas emissions, e.g. CH_4, N_2O, H_2S or CO_2,
- increase of air porosity in the heap and thus enable proper oxygen transport,
- drainage of water and heat from the heap during composting,
- increase in the activity of microorganisms,
- limiting the bioavailability of organic pollutants and heavy metals for living organisms,
- increase in water retention,
- giving the new properties to composts.

Depending on the properties, biochar in composting can function as:

- structure-generating material,
- functional additive, eg limiting greenhouse gas emissions, as well as nitrogen losses in the final product
- a carrier for microorganisms,
- filler for biofilters [1-4].

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The CeSFaMB simulator in modeling of CLC process

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Chemical Looping Combustion (CLC) is an important technology from the environmental protection point of view. The CLC process uses solid oxygen carriers for the fuel combustion. The metal oxides circulate between the air reactor and the fuel reactor. Absolute absence of air in the combustion chamber allows to obtain the exhaust gas containing mostly CO_2 and H_2O. The condensation of the steam allows to obtain almost pure CO_2, which is ready for storage [1].

The software "*Comprehensive Simulator of Fluidized and Moving Bed equipment*" (CeSFaMB) constitutes a comprehensive environment to simulate bubbling and circulating fluidized-beds as well as downdraft and updraft moving-beds [2,3].

The CeSFaMB simulator has been improved and successfully validated and applied since 1987. The program is prepared to deal with a wide range of possibilities, processes, and equipment designs. The simulator results have been compared against operations data from several real operations at various scales, always achieving low deviations between simulation results and real operational conditions.

The new fourth generation of CeSFaMB software greatly expands the range of cases able to be simulated in processes occurring in fluidized bed. The 4-th generation includes the Chemical Looping Combustion, allows much more flexibility on setting parameters related to fluidization dynamics, provides more methods to control and influence reaction rates, additional methods to facilitate convergences, as well many other features.

The CeSFaMB was successfully used in the works [1-9], dealing with CLC technology. These scientific works confirm that CeSFaMB simulator is a useful tool for the analysis of Chemical Looping Combustion process.

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