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Phytoremediation of sediment polluted with organic pollutants

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Introduction

Environmental pollution has been emphasized in recent decades as one of the main consequences of rapid development, the generation of large amounts of waste containing high levels of contaminants (Zhang et al., 2020). The use of plants in reducing pollution, i.e., phytoremediation, is the most acceptable method of decontamination from an environmental point of view. In this process, plant species are used to remove pollutants or render them harmless by extraction, sequestration, degradation, or detoxication (Rascio et al., 2011; Pandey et al., 2019; Zhang et al., 2020). It is well known that non-hyperaccumulating *Brassica* species have potential for heavy metal accumulation and can tolerate high concentrations of heavy metals in their shoots. However, there is a little data on phytoremediation of organic pollutants. Thus, the objective of this study was to assess if the energy crops, has potential to be used for phytoextraction of organic pollutants such as PAHs, PCBs and mineral oil from soil from POT trials. The effect of different type of rapeseed potential to uptake organic pollutants was compared to other energy crops such as sunflower, hemp, white mustard.

Materials and methods

Soil/sediment used in POT tests was collected at the Serbian pilot site (45°34'49.83"N; 20°45'41.49"E). Unpolluted sediment used as control was collected at Special Nature Reserve “Zasavica” which has chemical properties similar to sediment at the pilot site. POT experiments were performed on open air A pot experiment with polluted sediment started on May 17th and lasted to July 28th 2021. Pots were filled with 20 kg of polluted sediment each. On May 18th sowing was performed. Following energy crops were selected for pot trials: rapeseed (Brassica napus), white mustard, WM (Brassica alba), sunflower, SF (Helianthus annuus) and hemp, HE (Cannabis sativa) and sorghum (Sorghum bicolor). All energy crops were sown in 3 replicates. Plants sown in unpolluted sediment showed also low germination and slow development and it was discarded. Three days after sowing, pots with only rapeseed were treated with commercial PGPR products (without treatment labelled as OR_0; Trifender Pro labelled as OR_T; Panorama Bio Plus labelled as OR_P and Bio Eho labelled as OR_B) and after six weeks ammonium nitrate fertilizer was applied. Pots were irrigated manually by adding 2.5 L of water. Soil samples were collected from each pot at the beginning of pot experiment and after the harvest. The OC content was determined by TOC analyzer (LiquiTOCII, Elementar, Germany) after acid pre-treatment of the sediment to remove inorganic carbon. Cation exchange capacity (CEC) was determined according to EPA method 9080 (USEPA, 1986a). Analytical methods used for soil characterization are given in the Table 1.

Table 1. Analytical methods for soil/sediment characterization

Parameters	**Method**	**Method detection limit**
Texture - granulometric composition	ISO 11277:2009	0.1%
pH	ISO 10390:2005	0.02
Hydrocarbons (TPH)	ISO 9377-2:2000(E) and EPA8000B)	25 mg/kg
Polyaromatic Hydrocarbons (PAHs)	GC-MS (series of EPA method)	0.003 mg/kg
Polychlorinated biphenyl’s (PCBs)	GC-ECD (series of EPA method)	
Bioavailable fraction of organic pollutants	Spasojevic et al., 2015	

Results and discussion

Soil characterization

Based on the TOC content contaminated sediment can be considered as rich in organic carbon (2.87±0.7). TOC in agricultural soil used as control was about 1.23%. According to the CEC value contaminated sediment can be classified as light-colored loams and silt loams. The control soil and contaminated sediment have similar texture.

There is slightly higher clay content (up to 30%), and lower send content in the contaminated sediment compared to the control soil samples. pH for both was in range 7.76-8.07.

Results of phytoremediation

Of the PCB congeners measured, the higher molecular weight (HMW) congeners were abundant and mostly dominated by hexa-, penta-PCB and in the range 38-70 µg/kg for both sampling seasons. This could be a consequence of the historical use of common technical PCB mixtures, such as Clophen A60 and Aroclors 1254 and 1268 since these commercial products mainly contain hexa-, hepta-PCB (PCB138, PCB153, and PCB180 as most abundant constituents). The highest concentration of PCBs was detected at the beginning of the experiments (37-70 µg/kg), while its concentration decreased by a factor of around two over the course of the experiment (ranged from 15 to 33 µg/kg). In both cases, the bioavailable fraction was in the range from 7 to 34 µg/kg and was higher in May at the beginning of the experiment. At the end of the experiment, the bioavailable fraction for ∑PCBs increased in the following order: OR_P < OR_T < OR_0 < SF < HE < OR_B < WM, indicating that the increase in the bioavailable fraction was not consistent with the ∑PCBs for the same period.
The Σ16 PAHs varied and ranged between 341 and 1395 µg/kg (mean: 633 µg/kg; median: 422 µg/kg) at the start and decreased, ranging from 270 to 924 µg/kg (mean: 407 µg/kg; median 309 µg/kg) at the end of the experiment. Similarly, to the PCBs, for all analyzed samples during both sampling seasons, ∑16PAHs in soils was dominated by HMW PAHs (4, 5 and 6 rings) which were abundant and contributed on average from 74-95% of the ∑16PAHs. At the end of the experiment, ∑16PAHs decreased compared to those samples taken at the start. However, ∑16PAHs of the bioavailable fraction was in the range 44 to 89 µg/kg at the beginning of the experiment and slightly higher at the end of experiment 49-124 µg/kg, indicating that during the 120-day treatment and cultivation of the soil the bioavailable fraction of PAHs increased. The obtained values ∑16PAHs for the POT experiment at the end indicate that the bioavailable fractions increased in the following order OR_0 < OR_P < OR_T < HE < SF < OR_B < WM, whereby the greatest bioavailable fraction was obtained for WM and was about 124 µg/kg. It is assumed that the main mechanism accounting for these results is the sorption mechanisms of PAHs on the soil organic carbon and root systems of the cultivated plants, which are responsible for a decrease in PAHs concentrations in the soil at the beginning.
For all analyzed samples, TPHs were between 557 and 1273 mg/kg in May and decreased to 128 to 755 mg/kg in August. The median value of 337 mg/kg obtained at the end of the experiment was lower than the median value of 667 mg/kg obtained at the start, indicating a decrease of detected concentration over the 120 days. At the end of the pot experiment, the content of TPHs in the bioavailable fraction was investigated and generally increased in the following order OR_P < OR_0 < OR_T < OR_B < WM < SF < HE. The bioavailable fraction decreased during the experiment by a factor of two in comparison to the values obtained at the beginning.

Conclusion

The mechanisms of organic pollutants uptake by plants are numerous and complex. Based on the obtained it can be concluded that the content of organic pollutants (PAHs, PCBs, TPH) decreased during the course of the experiments. Bioavailable fraction of the investigated organic pollutants is lower compared to started concentration. Further research should be focused on testing different plants (ie Ricinus) which could potentially have higher accumulation potential, but could be same or higher biomass producer as rapeseed.

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