Croatian
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International
Symposium on
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# PROCEEDINGS

1 - 6 June 2025
Hotel Bluesun Elaphusa 4*
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ORIGINAL SCIENTIFIC PAPER

# Effects of soil amendments on Cd availability in soil

Eva Smolnikar, Manja Potočnik, Kristina Ugrinović

*Agricultural Institute of Slovenia, Hacquetova ulica 17, Ljubljana, Slovenia (eva.smolnikar@kis.si)*

**Summary**
Agrotechnical measures may reduce bioavailability of cadmium (Cd) from soil. This research investigated the effect of repeated addition of different soil amendments (lime (L), lime + zeolite (LZ), lime + organic matter (LOM)) in uncontaminated field where excessive Cd in carrot was determined in previous years. Regular use of amendments affected soil chemical properties and bioavailability of Cd. The lowest pH, at all samplings, was determined in control, the organic matter (OM) increased above all in the upper level of LOM, cation exchangeable capacity at control was lower than at other treatments. Consequently, the highest bioavailable Cd was determined at control. In uncontaminated soil with elevated levels of plant available Cd, the level of available Cd may therefore be effectively lowered by manipulating soil pH and OM.

**Key words**: cadmium, lime, zeolite, organic matter, pH, cation exchangeable capacity

## Introduction

Cadmium (Cd) is one of the most ecotoxic metals, with harmful effects on humans, animals and plants. The presence of Cd in food is due to contamination of soil and water. Cd is transferred from soil and water to plants and aquatic organisms and accumulates in the food chain (NIJZ, 2023). European Commission Regulation 2023/915 of 25 April 2023 sets maximum levels for certain contaminants in food, including cadmium (EC, 2023). On average, Cd in soil is between 0.06 and 1.1 mg/kg and is an easily available element. Atmospheric deposition and the use of phosphate fertilisers are the main sources of cadmium inputs to agricultural soils, and can lead to elevated levels of cadmium in soils and crops, which can lead to increased dietary exposure to cadmium. Most of the cadmium contamination remains in the top 15 cm of the soil (Kabata-Pendias and Mukherjee, 2007).

In Slovenia the limit, alert and critical immission values for Cd in soil are written in the Regulation on limit, alert and critical immission values for dangerous substances in soil. The limit value (at which effects or impacts on human health or the environment are still acceptable) for Cd in soil is set at 1 mg/kg dry soil, the alert value (at which adverse effects or impacts on human health or the environment are likely to occur for certain types of land use) at 2 mg/kg dry soil and the critical value (at which contaminated soil is unsuitable for the production of plants for human or animal food and for water retention or filtration because of adverse effects or impacts on humans or the environment) at 12 mg/kg dry soil (UL RS, št. 68/96, 1996). In Slovenia soil Cd levels are higher than in other European countries due to the parent soil. According to the Geological Survey of Slovenia (n=817), the median Cd content of the surface layer (0-10 cm) is 0.47 mg/kg, so even a small increase in soil Cd (> 1 mg/kg) can pose a potential risk for Cd uptake into plants and further up the food chain (Gosar et al., 2019). Cd is most mobile in acidic soil, binding is weaker at pH higher than 5, and is relatively immobile in alkaline soil. Agronomic measures to reduce the Cd content in vegetable crops: higher pH, higher organic matter content, addition of Si- and clay mineral-rich materials contribute to a better cation exchange capacity (CEC) of the soil, soils with a higher CEC can bind more Cd, which reduces its availability (Lo et al. 1992; Kabata-Pendias and Mukherjee 2007). The effect of amendment on Cd concentrations in plants also depends on the soil and the amount of the amendment, so it is necessary to select the amendment according to the soil type (Keller et al., 2005). Analyses carried out within the framework of the Public Service in Horticulture for crops grown in soils with Cd concentrations below the immission limit confirm that the Cd content of garlic crops is mainly related to the amount of bioavailable Cd in the soil, rather than the amount of total Cd in the soil and that the amount of bioavailable Cd is influenced by both the soil pH and the soil organic matter content, with variations between varieties (Ugrinović et al. 2022, Smolnikar et al. 2024). Research on Cd uptake by plants, both in Slovenia and globally, has been mainly related to cultivation in soils with elevated Cd levels, often carried out in pot experiments. To investigate the effects of soil amendments on soil Cd availability, we designed a multi-year field experiment and present the results of the first three years in this paper.

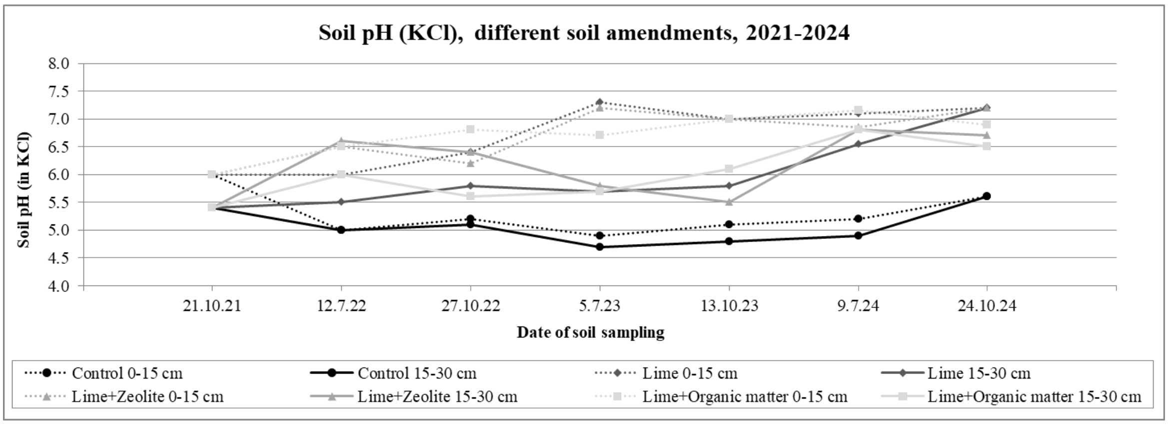
## Material and methods

A multi-year trial was designed in autumn 2021 on a plot in Gradišče near Murska Sobota, where Cd levels have been exceeded in the past in carrot crop. The soil properties (0 to 30 cm) of the experimental plot before the experiment are reported in Smolnikar et al. (2024). In brief, the soil is moderately acidic (pH 5.4), with low organic matter (1.6 %) and low cation exchange capacity (10.87 mmol 100 $g^{-1}$), low total but high available Cd (0.294 mg $kg^{-1}$and 0.013 mg $kg^{-1}$) The experiment is designed as a split-plot, where the main factor, in addition to the control (C), where only mineral fertilisers containing N, K and P are added, is the different soil amendments: lime (L) with Calcevita Agro (Intercal) 3 t $ha^{-1}$, lime with Calcevita Agro 3 t $ha^{-1}$ + zeolite flour (Montana) 1 t $ha^{-1}$ (LZ) and lime with Calcevita Agro (Intercal) 3 t $ha^{-1}$ + organic matter (LOM). The sub-factor in the trial is represented by 4 garlic varieties. The trial is conducted in a completely randomized design with 4 replications.

The previous crops and fertilisation in the growing seasons 2021/22 and 2022/23 are described in Smolnikar et al. (2024). In the growing season 2023/24 the previous crop was phacelia. In autumn 2023 the whole experimental plot was fertilised with 100 kg $K_2O$ $ha^{-1}$ (fertiliser with potassium chloride) and 24 kg N $ha^{-1}$, 48 kg $P_2O_5$ $ha^{-1}$, 96 kg $K_2O$ $ha^{-1}$. Each autumn the amendments were applied according to the experimental design and mechanically worked into the soil. To add organic matter to the main plot LO, green rye straw was incorporated in 2022, wheat straw was incorporated in 2023 and green mass of white mustard was incorporated in 2024. In March 2024, the trial was additionally fertilised with 54 kg N $ha^{-1}$,14 kg CaO $ha^{-1}$ and 10 kg MgO $ha^{-1}$. Before planting (autumn 2021, 2022 and 2023) and after harvesting (summer 2022, 2023 and 2024) of garlic, soil samples were taken with a probe from each of the main plots at depths of 0-15 cm and 15-30 cm. Due to budget limitations pH, CEC, organic matter, available and total Cd were determined in composite samples of all repetitions together, so only trends may be observed while the statistical differences between the treatments could not be tested. Soil pH was analyzed according to ISO 10390, CEC according to ISO 13536, soil organic matter according to ISO 10694, and Cd in soil according to ISO 16965.

## Results and discussion

Graph 1 shows soil pH fluctuations from October 2021 to October at different treatments. At all samplings, the lowest pH values at both depths were measured on the control plots, they ranged from 4.9 to 5.6 in the depth 0 to 15 cm and from 4.7 to 5.6 in the depth 15 to 30 cm, the maximum difference between the two layers was 0.3. For all treatments with soil amendments the pH values in the upper layer were higher (with the exception of LZ treatment in July 2022 where the values were almost equal), anyhow the differences between the two layers were much higher in the first two years (from 0.2 at LZ in October 2022 to 1.6 at L in July 2023 ) while in the 2024 they became much smaller or did not exist. The results show that the amendments increased the pH of the soil and that the effect in the first two years was more pronounced in the upper layer while with time also lower layer was affected. Ibrahim et al. (2023) also observed that zeolite application significantly increased soil pH and EC. Li et al. (2019) examend 175 studies on the effects of liming rate, lime application method, and liming material type on various soil chemical properties and crop yield, and concluded that most important variables that drive changes in soil pH and crop yield are liming rate and crop species. Soil conditions, such as soil organic matter and pH, are important for increasing pH in field-based experiments. Amendment of lime, biochar, by-products, manure, straw and combinations of them significantly increased soil pH and increased yield respectively, but it varied among crop types (Zhang et al., 2023).

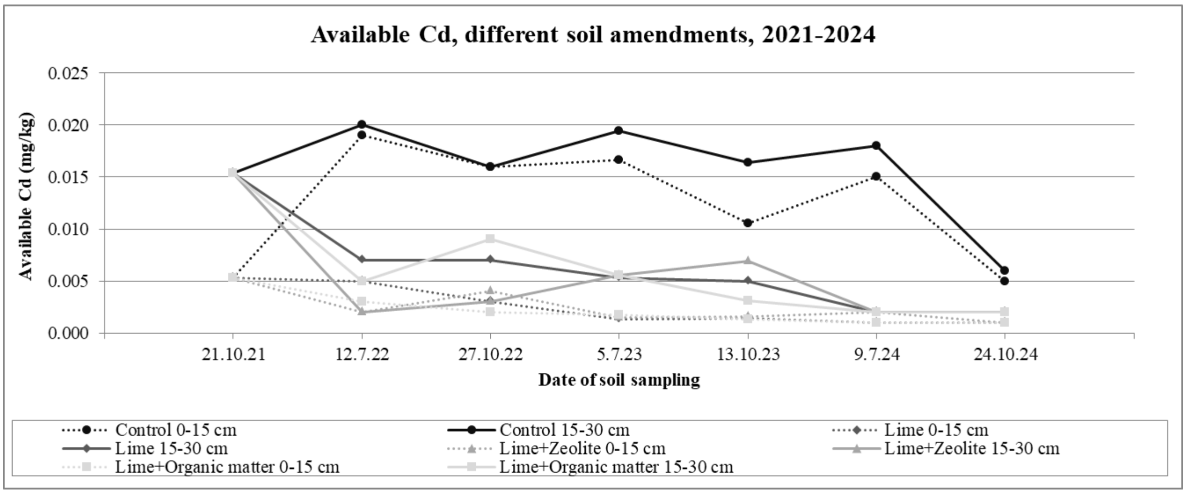



Graph 1. Soil pH (KCl), measured from October 2021 to October 2024

The highest soil OM (results are not shown) was, as expected, measured on LOM plots. Similarly, as pH, the OM first increased at the upper sampled layer and with time also at 15 to 30 cm.

CEC values (results are not shown) were the lowest at the control plots, with no difference between the layers and slight fluctuations over the time. The highest CEC values were determined at the upper layer of the plots with the amendments, and the increase of CEC is noticed over the time at both soil depths.

For total Cd (results are not shown), seasonal fluctuations may be observed, however on all plots, the measured content was 0.2 – 0.4 mg $kg^{-1}$.




Graph 2. Available Cd in soil, measured from October 2021 to October 2024

Graph 2 shows available Cd in soil, from October 2021 to October 2024. The highest concentrations of available Cd (0.02 mg $kg^{-1}$) were measured on the C plots. The lowest content (0.001 mg $kg^{-1}$) of available Cd was measured on 24.10.2024 at LZ and LOM plots. The results show that the amendments reduced available Cd in the soil and a trend of decreasing of available Cd over the time is noticeable at both depth of plots with amendments. It may be noticed (Graph 1 and 2) that with increasing pH and CEC bioavailable Cd content decreased. Li et al. (2024) reported that amendments increased soil pH and significantly decreased available Cd in the soil. Compared to the control, Cd bioavailability in soil was reduced by adding lime, lime+zeolite and lime+organic matter (Graph 1), what is in accordance with the expectations since lime and zeolite are known to elevate soil pH, and soil pH has significant role in Cd availability (Lu et al., 2017). Low pH leads to high solubility of Cd (Belimov et al., 2015). With increasing pH bioavailable Cd content linearly decreased (Shen et al., 2020).

## Conclusions

This research investigated the effect of repeated addition of different soil amendments (lime, lime + zeolite, lime + organic matter) on Cd bioavailability in uncontaminated soil with elevated level of plant available Cd. Research showed that Cd bioavailability was reduced after the application of the studied soil amendments, with increasing pH and CEC bioavailable Cd content decreased. The repeated application of amendments resulted in decreasing soil available Cd over the time at both soil depths, 0 to 15 and 15 to 30 cm, but the changes at upper level were quicker.

## Acknowledgement

The authors thank to the farmer who enabled the setup of the experiment on his field and helped with needed machinery operation and Breda Vičar form Agricultural Forestry Institute Murska Sobota at the Agricultural Forestry Chamber of Slovenia, Mojca Škof from the Agricultural Institute of Slovenia and Suzana Poplašen for their help with organisation and maintenance of the experiment. The authors acknowledge the financial support from the Slovenian Research Agency, the research core funding No. P4-0431 (Next Generation Agriculture) and the Slovenian Ministry for Agriculture, forestry and food, the founding of public service in vegetables and herbs (grant no. 2330-22-000006 and 2330-23-000079) and both for founding the project V4-2420.

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