PoLaRecCE

fertilization needs with respect to local/environmental conditions

SUBJECT * MERGEFORMAT Best available practices and on-site techniques for environmental site assessment

Authors

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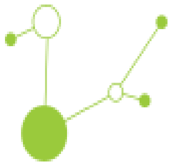

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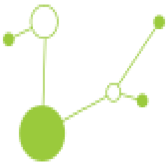

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Executive summary

The deliverable 2.1.3 provides a protocol with guidelines explaining how to estimate the fertilization needs on the investigated pilot sites. It refers to national guidelines of fertilization management. Further, an overview is made about the state-of-the-art methods used to determine the most plant growth promoting nutrients nitrogen (N), phosphorous (P) and potassium (K). A short literature review is made about remediation techniques of contaminated soils and provides recommendations about suitable methods which should be used to support the immobilization of the potentially toxic elements. We identified three promising soil amendments (biochar, zeolite and chitosan) which are able to immobilize heavy metals and therefore support the preservation or restauration of the biological and agricultural function of contaminated soils for a non-food agricultural production strategy.

1. Introduction

1.1. Objectives

The objective of this deliverable is to provide guidelines for assessing the fertilization needs on the investigated pilot sites (Cairo Montenotte [IT], Dél-Alföld [HU], Ormoz [SI] and Békés [HU]) and a recommendation of possible soil amendments which support the immobilization of heavy metals to tolerable levels for non-food agriculture.

1.2. Scope

Heavy metal contamination in soils comprises serious risks for the environment and human health. Therefore, methods that are able to reduce negative effects by immobilization are needed. This deliverable provides recommendations about soil amendments which could be introduced into the soil to support the immobilization of heavy metals. Non-food agriculture includes a lower risk on human health, since the grown plants, which potentially can take up contaminants from the soil, are not consumed as food. Still, fertilization management is also key in non-food agriculture to provide high yields on the one hand and minimize environmental impacts via overfertilization. This deliverable also summarizes current practices in fertilization management in central European countries and provides recommendations to assess the fertilization needs for non-food agriculture. Furthermore, it gives an overview of methods which are commonly used to assess nutrient status in soil for N, P and K, which allow more sophisticated and precise fertilizer management.

1.3. Relations to other documents

A short description of how this document relates to other documents developed within the project. In the PoLaRecCE project, this Deliverable 2.1.3 is linked to Activity 2.2, which includes all activities for the development of toolboxes for environmental site assessment (D 2.1.1, D 2.1.2 and D 2.1.3).

1.4. Intended Audience

This document is intended for local and regional administration, advisors and policymakers involved in soil management, farmers and land owners.

1.5. Usage guidelines

As a training material for end-users, this document has been written in an easy-to-understand language, supported by explanatory schemes. However, proper references are provided to allow those interested to further explore the topic.

2. Assessment of the fertilisation needs

2.1. Overview about the current recommendations to assess the fertlisation needs and methodologies to assess the nutrient status

The fertilization management for agricultural fields is based on the nutrient needs, which depend on both the plant species and variety, as well as the yield potential of the location. Nutrient sources also include soil reserves, which are available either immediately or through mineralization processes of organic matter. The link between nutrient needs and the nutrient supply from the soil forms the basis for determining additional nutrient requirements and planning fertilization management. Nitrogen (N), Phosphorous (P) and Potassium (K) are the most important plant-growth promoting nutrients. Therefore, we are mainly focussing on these three within this deliverable.

2.1.1. Nitrogen (N)

For environmental protection, especially groundwater, N-application thresholds are to be satisfied on national and EU level. The EU Nitrates Directive (91/676/EEC) [1] stipulates that no more than 170 kg of manure N ha^{-1} y^{-1} shall be applied. Further, it prohibits fertilizer application during times when the risk of nitrate leaching is high. Within the EU Framework for Protected Areas the primary legal instruments are the EU Habitats Directive (92/43/EEC) and the Birds Directive (2009/147/EC) [2], which establish the Natura 2000 network of protected areas which can further limit the N application on a specific area.

Most Central European countries use a N mass balance method at the field scale which is based on the difference between crop nutrient requirements and soil nutrient supply to determine fertilisation needs. National guidelines normally provide recommendations about the amount of N applied depending on the crop, and the yield potential of the location. The yield potential is determined retrospectively by calculating the mean yield from the last growing seasons (e.g., the Austrian guidelines for considered fertilization in agriculture and grassland [3] recommends using the last 5 years). Tables are used to classify yield levels based on these multi-year averages.

For further precision of determining the N-fertilization need, N_{min} can be measured. N_{min} determines the plant available mineral fraction of N in the soil, i.e., nitrate (NO_3^-) and ammonium (NH_4^+). If N stocks in 60 – 90 cm soil depth are above 40 kg N ha^{-1}, the amount of N applied can be reduced by the difference between N_{min} and 40 kg N ha^{-1} [3]. The sampling and analysis of N_{min} takes place before planting (i.e., normally early spring). There are many methods to measure N contents in soils. Table 1 lists the established extraction methods used to measure the soil N status in soils. The potassium chloride extraction is the most widely used extractant for measuring N_{min}. Alternatively, potassium sulphate (K_2SO_4) is used, especially for nitrate and nitrite, or when chloride (Cl^-) causes measurement issues with the used analytical technique. As a very mild extraction method $CaCl_2$ or distilled water can be used. Hot Water Extractable Organic Nitrogen (HWEON) is a method to estimate the potentially mineralizable organic N, which can become plant available over time. The Illinois Soil Nitrogen Test (ISNT) estimates the amount of plant-available nitrogen that can be mineralized from soil organic matter.

Table 1: Extraction methods to assess the plant available N content

Method	used reagents	Target N forms	Typical use	References
Potassium chloride	1M or 2M KCl	NH_4^+, NO_3^-, NO_2^-	Standard soil testing	Stevens et al. (1995) [4]
Potassium sulphate	0.5 M $KHSO_4$	NH_4^+, NO_3^-, NO_2^-	Alternative to KCl	Hood-Nowotny et al. (2010) [5]
Calcium chloride	0.0125 M $CaCl_2 \bullet 2H_2O$	NH_4^+, NO_3^-	Alternative to KCl, also possible for P and K	Simonis & Seataou (1995) [6]
Water extraction	-	NH_4^+, NO_3^-	Rapid/field assessment	Wada et al. (2006) [7]
Hot water extractable organic nitrogen (HWEON)	KCl $CaCl_2$	Potentially mineralizable organic N	Estimates future N supply	Curtin et al. (2006) [8]
Illinois Soil Nitrogen Test (ISNT)	NaOH H_3BO_3 H_2SO_4	Potentially available organic N	N mineralization potential	Khan et al. (2001) [9]

To measure the relevant N content in soils, many options exist. Table 2 shows the most important techniques to measure N in soils.

Aside from the N_{min} forms (NH_4^+, NO_3^-, NO_2^-) there is also a fraction of N called soluble organic N (SON) or Extractable Organic N (EON) which defines soil N that can be extracted from soil by water or other standard extractants or via electro-ultrafiltration (EUF) [10]. The EUF technique involves applying an electric field across a soil suspension, causing ions and molecules to migrate and be separated through an ultrafilter. This allows for the extraction and quantification of readily available nutrient fractions in soils which can also include easily extractable organic N (EUF-N_{org}) [11,12]. Besides the EUF-N_{org} also anaerobic N-mineralization or humus content can indicate the mineralization potential of a given soil [3]. For soils with higher mineralization potential, N fertilization may be reduced. However, in this report we are focusing on N_{min} determination only to assess the fertilization needs.

Table 2: Analytical techniques to measure N_{min} in soils

Method	Target N forms	Description	Reference
Colorimetric	NH_4^+, NO_3^-, NO_2^-	Colour reactions with the target N-form and analysis at certain wavelength with a spectrophotometer	Hood-Nowotny et al. (2010) [5]
Kjeldahl method	Total N	The classic method for determining total N; involves wet digestion, distillation and titration or colorimetric detection	FAO (2021) [13]
Photometric/ Spectrophotometric	Total N	Used for total N or specific N forms (e.g., nitrate, ammonium) after extraction and/or digestion.	Koistinen et al. (2019) [14]
Potentiometric	Easily extractable organic N	Measures NH_4^+ and NO_3^- directly in soil extracts; allows fast measurements, also in the field	Baumbauer et al. (2022) [15]
Combustion Method	Total N	Total N is measured by combusting soil samples and detecting released N gases; a thermal conductivity detector or an IR detector is used	Gautam et al. (2023) [16]

2.1.2. Phosphorous (P) and Potassium (K)

For phosphorus (P) and potassium (K) fertilization recommendations, soil analysis values serve as the basis. Targeted accurate applications are important, especially for P since it is a limited resource and a major factor of water body eutrophication. Reductions in P applications are often possible without yield reductions but reducing environmental impact and sparing resources [17].

There are several methods available to assess the plant available P and K in the soil. The most common ones are listed in Table 3.

Table 3: Extraction methods to assess the plant available P and K content

Method	used reagents	P	K	Mainly used	Suitable for	References
Calcium-acetate-lactate (CAL)	calcium acetate [$(CH_3COO)_2Ca \cdot x\ H_2O$] calcium lactate [$C_6H_{10}CaO_6 \cdot 5\ H_2O$] acetic acid [$CH_3COOH$]	✓	✓	Germany, Austria, Central Europe	most soils	Schüller (1969) [18], ÖNORM L 1087 [19]
Double-lactate (DL)	calcium lactate [$C_6H_{10}CaO_6 \cdot 5\ H_2O$] hydrochloric acid [$HCl$]	✓	✓	Scandinavia, Eastern Europe	neutral to acidic soils	Riehm (1943) [20]
Mehlich-3	acetic acid [CH_3COOH] ammonium nitrate [NH_4NO_3] ammonium fluoride [NH_4F] nitric acid [HNO_3] EDTA [a chelating agent]	✓	✓	United States, Canada	most soils	Mehlich 1984 [21]
Bray-1	ammonium fluoride [NH_4F] hydrochloric acid [HCl]	✓		widely used, less common in Europe	neutral to acidic soils	Bray & Kurtz (1945) [22]
Olsen	sodium bicarbonate [$NaHCO_3$] sodium hydroxide [$NaOH$] sulfuric acid [H_2SO_4] ammonium molybdate [$(NH_4)_6Mo_7O_{24} \cdot 4H_2O$] Potassium antimony tartrate [$KSbOC_4H_4O_6 \cdot 1/2\ H_2O$] ascorbic acid [$C_6H_8O_6$]	✓		Widely used in calcareous soils	neutral to alkaline soils	Olsen et al. (1954) [23] FAO 2021 [24]
Morgan/ modified Morgan	ammonium acetate [$NH_4CH_3CO_2$] or sodium acetate [CH_3COONa] acetic acid [CH_3COOH]	✓	✓	United States United Kingdom	neutral to acidic soils	Morgan (1941) [25]
Calcium chloride	0.0125 M $CaCl_2 \bullet 2H_2O$	✓	✓	Europe, Asia	neutral to acidic soils	Simonis & Seataou (1995) [6]

A wide range of extraction methods developed over the last decades whose use is also influenced by its historical development. The calcium-acetate-lactate method was firstly developed by Schüller 1969 [18] and is widely used in standard protocols in Central Europe, especially in Germany and Austria [26]. It is suitable for most soils with different pH, suitable for both P and K, and used in the ÖNORM L1087 [19]. Therefore, we are recommending this method for soil extraction to assess the nutrient status of P and K.

After soil extraction, P and K concentrations need to be measured. For this, also several methods developed. Table 4 shows analytical techniques to measure P in soil extracts. In general, there are two principles used: photometry where a colour reaction is determined by measuring the absorbance at a specific wavelength and emission spectroscopy which measures the emission of light from excited phosphorus atoms in the plasma.

Table 4: Analytical techniques to measure P in soils

Method	Principle	Description	Reference
Murphy-Riley (Molybdenum Blue)	colorimetric	Phosphate reacts with ammonium molybdate under acidic conditions to form a phosphomolybdate complex, which is then reduced to form a blue-coloured complex; measurement of absorbance at 880 nm or at 660 nm with a spectrophotometer	Murphy & Riley (1962) [27] Angelova (2022) [28] ÖNORM L 1087 [19]
Vanadate-Molybdate method	colorimetric	Forms a stable yellow phosphovanadomolybdate complex whose absorbance is measured at 470 nm; less sensitive to timing and reagent stability but also less accurate than the Molybdenum Blue method	Misson (1908) [29] Buzetzky et al. (2023) [30] EN ISO 6878:2004 [31] ÖNORM L 1087 [19]
Fiske-Subbarow Method	colorimetric	An early and still referenced method where phosphate reacts with ammonium molybdate and is reduced by 1-amino-2-naphthol-4-sulfonic acid (or other agents) to form a blue colour; measurement of absorbance at 660 nm	Fiske & Subbarow (1925) [32] Yuen & Pollard (1951) [33]
Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES)	emission spectroscopy	soil extract is introduced into the IPC-OES instrument where it is atomized in a plasma torch. Excited phosphorus atoms emit light at characteristic wavelengths (commonly 213.617 nm)	Yang (2018) [34]

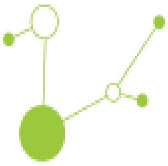
Colorimetric techniques are in general simple and cost effective, however, they can only measure inorganic P (orthophosphate). Although inorganic P is normally the dominant proportion of P in soil extracts, substantial amounts of organic P can be present [35]. This can lead to significant underestimations in the P nutrient status of the soil resulting in overfertilization. To analyse total P within the soil extract, a digestion of the organic P would be necessary. Several established methods are available. The use of potassium persulfate is commonly used as an oxidation reagent to transform organic P forms into orthophosphate which can be measured colorimetrically [36]. Alternatively, the use of Inductively Coupled Plasma-Optical Emission

Spectroscopy (ICP-OES) also allows the determination of the total P is soil extracts. ICP-OES is a modern and robust analytical technique offering advantages over colorimetric methods. The soil extract is introduced into the ICP-OES instrument where it is atomized in a plasma torch. Excited phosphorus atoms emit light at characteristic wavelengths, and the intensity of this emission is proportional to the P concentration. It also allows to measure K and other plant nutrients and elements. It is less suitable for N, since N is very abundant in the atmosphere which creates a high background noise during measurement.

For potassium also several analytical techniques have been developed. Table 5 lists well established methods to determine the K content in soil extracts. An ammonium acetate extraction followed by Atomic Absorption (AAS) or ICP-OES is considered as the gold standard for laboratory measurement of soil K. Photometric methods and ion-selective electrodes (ISE) provide fast field-based alternatives with moderate sensitivity. NIR spectroscopy offers real-time, non-destructive analysis.

Table 5: Analytical techniques to measure K in soils

Method	Principle	Description	Reference
Flame photometry	Emission of light by K ions in flame	Intensity of light emitted by potassium ions in a flame is measured	Chavan et al. (2024) [37]
Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES)	emission of light in plasma	Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES)	Yang et al. (2018) [34]
Atomic Absorption Spectroscopy (AAS)	Absorption of light by K atoms	Potassium is measured by detecting the absorption of light at a specific wavelength as it passes through a vaporized sample	Temperli 1969 [38] Liang (2020) [39]
Ion-Selective Electrode (ISE)	electrochemically	Portable potassium ion meters use ion-selective electrodes to directly measure K^+ concentration in soil extracts.	Sethuramasamyraja et al. (2007) [40]
NIR Spectroscopy	Absorption of NIR light	Emerging technique for real-time, non-destructive analysis of soil K, often combined with data mining for calibration	Du et al. (2025) [41]
Photometry/ Spectrophotometry	colorimetric	Uses test kits, simple method which can be used in the field	e.g., Thongkam & Hemavibool (2022) [42]



2.2. Recommended methods to assess the nutrient status and fertilization

Fertilization management is crucial for successful (non-food) agriculture to provide high yields and minimize pollution of water bodies through leaching and emissions of harmful gases (N_2O, NH_3). As a straightforward procedure we propose the assessment of the N-nutrient status via the KCl or $CaCl_2$ extraction and measurement of the N_{min} with a colorimetric method. Section 2.2.1 describes the established method mainly used at the University of Natural Resources and Life Sciences, Vienna (BOKU). To also account for organic forms of N and their potential long-term fertilization via mineralization we recommend the EUF-N_{org} Method. For P and K we recommend the CAL-extraction method based on the ÖNORM L1087 which is described in section 2.2.2.

These recommendations for fertilization are based on the Austrian guidelines for considered fertilization in agriculture and grassland [3] which is well established for agricultural practices and extensively used as a standard procedure. Other central European countries might deviate slightly from these recommendations and guidelines. In case of uncertainty, we refer to the national/regional available guidelines.

2.2.1. Nitrogen

Table 6 lists the recommended yearly N fertilisation for medium yield potential for different crops based on the Austrian guidelines for considered fertilization in agriculture and grassland.

Table 6: Nitrogen needs for medium yield potential for different crops [3] (translated)

	culture	kg N ha^{-1}
cereals	wheat, durum	110 - 130
	rye	80 - 100
	spelt	80 - 100
	winter feed barley	100 - 120
	winter brewing barley	70 - 90
	triticale	90 - 110
	spring feed barley	80 - 100
	spring brewing barley	50 - 70
	oat	70 - 90
root crops	maize	120 - 140
	silage maize	140 - 160
	sugar beet	110 - 140

	fodder beet	120 -140
	table potatoes	130 - 150
	early potatoes/seed potatoes	90 - 110
	grain millet/-sorghum	120 - 140
	silage millet/-sorghum	140 - 160
oleiferous plants and legumes	field pea/field bean	0 - 60
	soybean	0 - 60
	canola	120 - 140
	sunflower	40 - 60
	oil pumpkin	60 - 80
Cover crops/ forage	without legumes	40 - 80
	with legumes	0 - 40
Special cultures	poppy	50 - 80
	caraway (planting year/harvest year)	30 - 80/90 - 120
	grapevine (planting / harvest year)	0-30 / 40-70

Established method at the University of Natural Resources and Life Sciences, Vienna (BOKU) to measure N_{min} contents in soils

For N_{min} 50 g of fresh soil was extracted with 200 ml 0.0125 M calcium-chloride dihydrate ($CaCl_2 \bullet 2H_2O$) solution and shook with a rotating-shaker for 30 minutes at 20 rpm and then the soil-suspensions are filtered. For the ammonium (NH_4^+) determination deionized water, 0.3 M NaOH solution and 8.5 g Sodium salicylate + 0.06 g sodium nitroprusside dihydrate in 50 ml are mixed at a ratio of 1:1:1 to make up the color reagent. For the oxidation reagent 0.05 g of dichloroisocyanuric acid is dissolved in 50 ml. The 100 µl of soil extract is pipetted in 96 well microtiter plates followed by 50 µl of color reagent and 40 µl oxidation reagent. After 30 min at room temperature (25°C) the absorbance is measured colorimetrically with a Tecan Infinite Pro plate reader at 660 nm wavelength. For Nitrate determination a Vanadium(III)-chloride solution is made up by dissolving 400 mg Vanadium(III)-chloride in 50 ml of 1 M HCl. Secondly, 50 mg of N-(1-Naphthyl)ethylenediamine dihydrochloride is dissolved in 250 ml of deionized water. Thirdly, 5 g of sulfanilic acid is dissolved in 500 ml deionized water. For the color reaction 100 µl of soil extract is pipetted into a 96 well microtiter plates followed by 100 µl Vanadium(III)-chloride solution, 50 µl N-(1-Naphthyl)ethylenediamine dihydrochloride solution and 50 µl Sulfanilic acid solution. After incubation at 37°C for 30 minutes, the absorbance can be measured at 540 nm. With a calibration curve, the concentrations of NH_4^+ and NO_3^- can be calculated from the absorbance values. The N_{min} content is then calculated as the sum of NH_4^+-N and NO_3^--N.

1.1.1. Phosphorus and Potassium

The Austrian guidelines for considered fertilization in agriculture and grassland [3] define content classes of P and K contents. These classifications are shown in Table 7 and Table 8.

In Table 9 fertilization needs for different crops/agricultural practices are shown for fields with content class C. For other content classes correction factors from Table 10 are applied.

Table 7: content classes for P [3] (translated)

Content class	Nutrient supply	Agriculture [mg P kg^{-1}]	Grassland [mg P kg^{-1}]
A	very low	< 26	< 26
B	low	26 - 46	26 - 46
C	adequate	47 - 111	47 - 68
D	high	112 - 174	69 - 174
E	very high	> 174	> 174

Table 8: content classes for K [3] (translated)

Content class	Nutrient supply	Agriculture [mg K kg^{-1} y^{-1}] clay content [%]			Grassland [mg K kg^{-1} y^{-1}]
		Light (<15)	medium (15-25)	heavy (>25)	[mg P kg^{-1}]
A	very low	< 50	> 66	> 83	< 26
B	low	50 - 87	66 - 112	83 - 137	26 - 46
C	adequate	88 - 178	113 - 212	138 - 245	47 - 68
D	high	179 - 291	213 - 332	246 - 374	69 - 174
E	very high	> 291	> 332	> 374	> 174

Table 9: Fertilization needs of P and K for content class C [3] (translated)

	culture	P_2O_5 [kg ha^{-1} y^{-1}]	K_2O [kg ha^{-1} y^{-1}]
cereals	wheat, durum, rye, spelt, winter barley, spring barley, triticale, oat	55	80

root crops	maize	85	200
	silage maize	90	225
	sugar beet	85	320
	fodder beet	85	320
	table potatoes	65	200
	early potatoes/seed potatoes	60	180
	grain millet/-sorghum	85	210
	silage millet/-sorghum	95	375
oleiferous plants and legumes	field pea/field bean	65	100
	soybean	65	120
	canola	65	90
	sunflower	75	200
	oil pumpkin	65	200
Cover crops/ forage	without legumes	50	180
	with legumes	25	80
Special cultures	poppy	55	100
	caraway	60	80
	grapevine	20	60

Table 10: correction factors for the numbers in Table 9 above for different content classes [3] (translated)

		P_2O_5 [kg ha^{-1} y^{-1}]				K_2O [kg ha^{-1} y^{-1}]
content class	specification	correction factor			specification	correction factor
A		1.5				1.5
B		1.25				1.25
C1		1				1
C2	90 – 110 mg/kg P	0.5	cereals, potatoes	clay < 15 %	148 – 178 mg/kg K	0.5
				clay 15 – 25 %	177 – 212 mg/kg K	
				clay > 25 %	205 – 245 mg/kg K	
			other cultures	clay < 15 %	148 – 178 mg/kg K	0.75
				clay 15 – 25 %	177 – 212 mg/kg K	
				clay > 25 %	205 – 245 mg/kg K	
D1	clay < 15 %*	0.5				0.5

D2	cereals	0
E		0

*… P fertilization as subsurface banding

The CAL method to measure P and K contents in soils (ÖNORM L 1087)

Preparations of the solutions:

- Stock solution:

77 g of calcium lactate and 39.5 g of calcium acetate are to be dissolved in hot water. Then, 89.5 ml of acetic acid are to be added, the solution is to be cooled, and subsequently filled up with water to a total volume of 1000 ml. The stock solution must always be checked for the formation of precipitates. These can be re-dissolved by heating the entire stock volume.

- Working solution:

One volume part of the stock solution is to be diluted with water to five volume parts. The pH value is to be adjusted to pH 4.1 using acetic acid.

Implementation:

5.0 g of air-dried fine soil (<2mm) are to be weighed into a shaking vessel, mixed with 100 ml of the working solution, and swirled manually in such a way that the soil is completely moistened and does not stick to the walls of the vessel. The vessel is then to be shaken for two hours. Good mixing of the soil and extraction solution must be ensured. In the case of calcareous soils, care must be taken not to seal the shaking vessels immediately due to the development of CO_2.

After shaking, filtration is to be carried out using a folded filter, discarding the first portion of the filtrate. The remaining filtrate is to be collected and used for analysis.

Correction of the phosphorus content:

For soils with pH < 6, a correction of the phosphorus content is required. The calculation for soils with a pH < 6 must be carried out according to:

$$P_{corr} = P_{CAL} * 0.98 + 9.2$$

With:

P_{corr}	Calculated "plant-available" phosphorus content for soils with pH < 6

P_{CAL} Phosphorus content determined in the CAL extract, given in mg P / 100 g

At pH values measured in calcium chloride the "plant-available" phosphorus from apatites cannot be fully determined. In acidic soils, the "plant-available" phosphorus is sufficiently accurately calculated using the phosphorus value obtained from the CAL extract and the correction factor.

Analysis

Preferably P and K can be measured by ICP-OES or AAS. P can also be determined colorimetrically by the Molybdenum Blue or Vanadate-Molybdate method. However, for colorimetic analysis, meta-, pyro- or polyphosphates cannot be transferred completely to orthophosphates.

3. Methods to support immobilization of trace elements

3.1. Environmental and human health challenges of contaminated soils

Soil pollution by trace elements like mercury (Hg), lead (Pb), cadmium (Cd), arsenic (As), zinc (Zn), nickel (Ni), copper (Cu), selenium (Se) and vanadium (V) drastically increased over the last decades. This severely affects the environment and human health. Within Europe 694 000 sites are identified as contaminated sites, registered in national/regional inventories, where polluting activities take/took place [43]. However, it is estimated that around 2.8 million sites exist within the EU-28 where polluting activities took/are taking place [43]. A wide range of potential sources are identified such as industrial effluents, coal burning, lead-containing gasoline, mining activities, application of animal manure or sewage sludge into soil municipal waste/landfills and pesticides. High efforts are undertaken to remediate such sites, often at high economic cost. Therefore, developments in improving and innovating remediation techniques are of utmost priority for environmental and human health protection.

3.2. Recommendations for innovative soil amendments for in-situ immoblization of trace elements

Traditional remediation techniques include soil washing, excavation and landfilling. However, those measures only relocate the contamination. Alternatively, the use of in-situ immobilization has emerged as a promising way to target soil contamination issues. The principle of in-situ immobilization is to add amendments to the soil which are capable of sorbing the pollutants present in the soil to a degree that minimizes pollution of other sites through water bodies and erosion and ideally to provide ecosystem services. Non-food agriculture includes a broad range of practices which provide value for humankind. It includes e.g., biofuels and bioenergy, building and construction materials, fibres and plants which are used to produce chemicals/renewable biopolymers. For those purposes the risk harming human health is lower compared to food production.

There are several sorbing materials which can act as a pollutant adsorbent. Numerous materials have been investigated such as different natural minerals (e.g., limestone, magnetite, zeolite, hematite, feldspar and clay minerals), industrial by-products (e.g., coal fly ash, red mud), filter materials (e.g., activated carbon, hydrous zirconium oxide) and biochar. Within this deliverable we are focussing on three promising materials for in situ immobilisation of trace elements: biochar, zeolite and chitosan.

3.2.1. Biochar

The use of biochar has gained significant attention as an adsorbent for trace elements [44,45]. Biochar is a solid, carbon-rich material which is obtained by the thermochemical conversion of biomass under oxygen-limited conditions [46]. Figure 1 shows a picture of biochar made from a mixture of wood clippings and crop residues. Due to its microporous/mesoporous structure, organic mineral species and the variety of functional groups at their surface, biochar exhibits great potential as an adsorbent material [47]. Compared to other trace element sorbing materials, it is relatively inexpensive. Beyond that, it possesses the potential of long-term carbon storage since it is very recalcitrant in soils [48] which makes it a negative emission technology (NET). In principle many feedstocks which are rich in organic carbon are suitable for pyrolysis ranging from crop residues over nutshells to wood/wood clippings. A global meta-analysis from Rehmann et al. (2021) [49]showed that biochar can decrease the bioavailability of potential toxic metals (PTMs) by 40% and 22% in plants. However, this can vary substantially among the different heavy metals. They also showed that the PTM availability is strongly dependent on physico-chemical properties of the biochar. Effective biochars had surface areas of >100 m^2 g^{-1}, neutral to alkaline pH and were pyrolyzed at temperatures >500°C. Regarding the application rate, best results were observed at 1.1-3%. Rehman et al. (2021) [49] also stated that biochar’s potential to reduce metal toxicity effects is more driven by soil properties than the plant system.

Figure 1: Biochar from wood clippings and crop residues

3.2.2. Zeolite

Zeolite is a group of crystalline, microporous aluminosilicate minerals composed mainly of silicon, aluminium and oxygen. Their porous structure gives them a high surface and an excellent ion exchange capacity which makes them a valuable material for the adsorption of pollutants. Natural zeolite is primarily formed through the alteration of volcanic glass or ash by pore water under low-grade metamorphic or hydrothermal conditions [50]. Major deposits are typically found in regions with high volcanic activity (e.g., USA, China, Japan, Italy, Hungary). In recent years zeolite gained significant attention as a potential pollutant adsorbent for soil remediation [51]. Based on their chemical composition and structure, natural zeolites have a high affinity for cations, which makes it suitable to sorb many commonly problematic heavy metals in contaminated soils. Natural zeolites are often chemically or physically modified to increase their cation exchange capacity (CEC) [52,53]. E.g., the modification of zeolite with acid solution or salt solution implies the replacement of other cations by H^+ (acidic solution) or Na^+ (salt solution).

Compared to other existing adsorbent materials, zeolite is inexpensive [54] and available in large quantities. Natural zeolites possess many advantages but also some limitations. The key advantages include a large internal surface area, low density, low hardness, high crystallinity, and applicability with minimal processing steps. Limitations include variability in these properties due to natural heterogeneity, a primary affinity for cations (with anionic pollutants being less effectively sorbed), and the potential presence of impurities, which may also encompass pollutants.

Many experimental studies were already conducted to assess the degree of immobilization of heavy metals by zeolite. Clinoptilolite is the most used natural zeolite and therefore often used in scientific experiments. Ye et al. (2021) [55] observed reductions of bioavailable heavy metals of 31% (Cu), 6.5% (Zn) and 38.5% (Pb) at a zeolite concentration of 5%. Moeen et al. (2020) [56] reported reductions of 5.5% (Cd), 28.4% (Zn), 23.2% (Pb) and 35.6% (Cu), also at a zeolite concentration of 5%.

There are several ways to treat natural zeolites to improve their performance. Thermal treatment allows the removal of impurities and improvements in structural, morphological and physicochemical properties. The structure of the zeolite is very responsive to water-vapor pressure and temperature changes which implies changes in cell size, geometry and cations from the framework channels [57]. Acid treatment is the most commonly used treatment option for natural zeolites. It leaches the exchangeable cations with H^+ ions and raises porosity by removal of impurities [58], which both improve the adsorption capacity. Alkaline treatment disrupts covalent bonds between O and H of the hydroxyl functional groups (-OH). H^+ is replaced by Na^+ which creates an electronegative bond between O and Na [58]. Studies have shown that the adsorption capacity was increased by 10 – 20 % by alkaline treatment of natural zeolites [59,60]. Furthermore, a modification with surfactants is possible. This method has been extensively explored for immobilization of organic pollutants mainly [61].

3.2.3. Chitosan

Chitosan is a natural biopolymer derived from chitin, commonly sourced from shellfish waste. However, it can also be produced synthetically by fungi cultures [62]. Its unique structure, rich in amine and hydroxyl groups, makes it an effective and environmentally friendly agent for immobilizing heavy metals in contaminated soils. Its ability to adsorb a wide range of pollutants at a high rate makes it a promising method to remediate soil and water [63]. As derivative from living organisms, chitosan is biodegradable in soils [64]. This is, on the one hand, beneficial since it cannot cause contamination by itself for the soil. On the other hand, immobilized pollutants by chitosan are remobilized or taken up by soil microorganisms during degradation. This might not be a problem for water remediation, since it adsorbing material can be removed, however for in situ soil remediation a combination of adsorbents is necessary for long term immobilization. Comparative analyses have shown that chitosan modified biochar, zeolite and manganese dioxide can be an effective combination to immobilize heavy metals [65]. Especially the combination with biochar shows promising results [66–68].

3.3. Conclusion

Biochar, zeolite and chitosan are promising materials for the remediation of contaminated soils. There is a broad variety of properties and treatment options which allows improvements in their capacity to immobilize trace elements. On-site assessments of the contamination and pedo-climatic conditions are crucial for effective use of these methods. This allows an improved decision making on which material or material-combination is best for successful in-situ remediation.

Glossary

A list of notions/terms specific to this document with short explanations

Notion	Description
AAS	Atomic Absorption
CEC	cation exchange capacity
EUF	Electro-ultrafiltration
ICP-OES	Inductively Coupled Plasma-Optical Emission Spectroscopy
K	potassium
N	nitrogen
NET	negative emission technology
NIR	near infrared
P	phosphorous
PTMs	Potentially toxic metals
TE	trace elements

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