



TESIS DOCTORAL

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TECNOSUELOS REALIZADOS CON RESIDUOS Y SU APLICACIÓN PARA LA MEJORA DE LOS SERVICIOS AMBIENTALES

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Programa de Doctorado en Medio Ambiente y Sostenibilidad

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El Dr. D. Jose Navarro Pedreño, director, y el Dr. D. Ignacio Gómez Lucas, codirector de la tesis doctoral titulada **“Tecnosuelos realizados con residuos y su aplicación para la mejora de los servicios ambientales”**,

INFORMAN

Que Dña. M^a Teresa Rodríguez Espinosa ha realizado bajo nuestra supervisión el trabajo titulado **“Tecnosuelos realizados con residuos y su aplicación para la mejora de los servicios ambientales”** conforme a los términos y condiciones definidos en su Plan de Investigación y de acuerdo al Código de Buenas Prácticas de la Universidad Miguel Hernández de Elche, cumpliendo los objetivos previstos de forma satisfactoria para su defensa pública como tesis doctoral.

Lo que firmamos para los efectos oportunos en Elche.

Director de la tesis

Codirector de la tesis

Dr. D. Jose Navarro Pedreño

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El Dr. D. Jose Navarro Pedreño, Coordinador del Programa de Doctorado en Sostenibilidad y Medio Ambiente,

INFORMA

Que Dña. M^a Teresa Rodríguez Espinosa ha realizado bajo la supervisión de nuestro Programa de Doctorado el trabajo titulado **“Tecnosuelos realizados con residuos y su aplicación para la mejora de los servicios ambientales”** conforme a los términos y condiciones definidos en su Plan de Investigación y de acuerdo al Código de Buenas Prácticas de la Universidad Miguel Hernández de Elche, cumpliendo los objetivos previstos de forma satisfactoria para su defensa pública como tesis doctoral.

Lo que firmo para los efectos oportunos en Elche

Coordinador del Programa de Doctorado en Medio Ambiente y Sostenibilidad

Prof. Dr. D. Jose Navarro Pedreño

A Teresa e Inés.

«A lo largo de los siglos, hubo hombres que dieron los primeros pasos por nuevos caminos, sin más pertrechos que su propia imaginación... Lucharon, sufrieron y lo pagaron. Pero ganaron... Su verdad era su única motivación; su propia verdad y su propio trabajo para lograrlo a su propia manera»

Ayn Rand (El Manantial)

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RESUMEN

La esperada tendencia de crecimiento de la población y de los asentamientos urbanos a lo largo de todo el mundo, implica un aumento de la tasa de ocupación del suelo, que principalmente afecta a los suelos con mayor potencial agrícola. Actualmente, la situación de los suelos en Europa no es halagüeña, debido a que los suelos son un recurso no renovable y a que entre el 60 y 70 % de los suelos europeos están degradados. Esto conlleva un detrimento en la provisión de servicios ambientales de los suelos, afectando a su capacidad de producir alimentos y a la disponibilidad de nutrientes para los cultivos, entre otros, implicando la aparición de deficiencias en la ingesta de micronutrientes en la población mundial, debido a que los alimentos contienen menor concentración de nutrientes. Asimismo, el aumento de la población mundial implicará un incremento de la demanda de alimentos, comprometiendo la

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seguridad alimentaria. Para atender esta creciente necesidad de alimentos, se espera un aumento en la producción vegetal, acarreado también, un incremento en las tasas de generación de residuos agrícolas.

Ante estos retos, la Unión Europea ha lanzado una serie de estrategias enmarcadas dentro del *European Green Deal*, entre las que es prioritaria la preservación de los ecosistemas y sus servicios asociados, la recuperación de los suelos degradados, el aprovechamiento de los residuos de forma circular y la reducción de la pérdida de nutrientes en los suelos. Sin embargo, para cumplir con dichos objetivos, se requiere disponer de suelos con alta calidad agrícola. Las referencias bibliográficas consideran que la formulación de suelos técnicos a la carta (tecnosuelos o *technosols*) a partir de residuos agrícolas puede ser una opción válida que contribuya a atender todas estas necesidades.

Por lo tanto, el propósito de esta tesis es ampliar el conocimiento sobre las propiedades de los residuos agrícolas que puedan contribuir al aporte de nutrientes y a su mineralización efectiva, así como a identificar los riesgos asociados a la presencia de dichos nutrientes, principalmente los también considerados como pertenecientes al grupo de los metales pesados y elementos traza. De este modo, se facilitará la elección de los residuos más adecuados para la formulación de tecnosuelos que puedan potenciar el uso sostenible de los recursos, para auspiciar la implantación de las estrategias que emanan del *European Green Deal*, para acrecentar la provisión de servicios ambientales, y, por ende, para asegurar la salud de los ecosistemas y las personas. El aporte del trabajo de investigación se sustenta en la hoja de ruta trazada con los siguientes objetivos específicos: (i) conocer el estado del arte sobre los tecnosuelos; de tal forma que permita el estudio del conocimiento acumulado del concepto tecnosuelos (*technosols*), sobre el interés que suscita entre la comunidad científica, sobre los ámbitos de aplicación, así como los posibles beneficios ambientales (ecosistémicos) que pueden reportar su uso; (ii) exponer la viabilidad de recuperar y reconvertir suelos sellados en suelos funcionales para la producción agrícola, dilucidando el papel que pueden desempeñar los tecnosuelos en esta transformación; (iii) evaluar las propiedades físicas y químicas, la composición elemental y la solubilidad

de los nutrientes disponibles en los residuos de poda y recolección seleccionados, para conocer su potencial para elaborar tecnosuelos como sustrato agrícola, sobre la base del suministro de nutrientes y la capacidad de mineralización del nitrógeno; (iv) identificar la composición elemental y el contenido de elementos traza en los residuos orgánicos, para determinar si existe un riesgo ambiental para su uso como sustrato agrícola; (v) valorar la aplicación de soluciones basadas en la naturaleza, utilizando residuos como material adsorbente y de intercambio en biorreactores, para comprobar el potencial de mejora de las propiedades fisicoquímicas de las aguas marginales y de baja calidad que se usan para riego y los efectos en la concentración de nitrógeno, como medida para prevenir los procesos de eutrofización.

Para ello realizamos una revisión bibliográfica sobre los tecnosuelos, y analizamos las propiedades fisicoquímicas, la composición elemental, y el contenido de nutrientes solubles (Na, K, Ca, Mg, Fe, Mn, Cu, Zn, Cd, Cr, Ni y Pb) de los siguientes residuos de poda y recolección: poda de almendro, turba comercial, paja de heno, restos de poda de olivo, corteza (piel) de granada, acículas de pino, hoja de palmera, compost de lodo de depuradora y restos de poda de vid (**Capítulo 3**). Además, determinamos la concentración de nitrógeno orgánico y amoniacal (N) de los residuos y su relación C/N.

Las referencias previas consultadas indican que los suelos técnicos elaborados con residuos, podrían ser incluidos y clasificados como *Technosols* utilizando la base mundial de referencia del recurso suelo, *World Reference Base for soil resource WRB* (**Capítulo 4**). La elaboración de tecnosuelos está siendo estudiada con mayor interés, especialmente a partir del año 2013, principalmente en el ámbito de la restauración de espacios mineros y urbanos. Sin embargo, debido a su gran potencial para proveer servicios ambientales y su capacidad para funcionar como un suelo natural, son un firme candidato para atender la necesidad de suelos agrícolas fértiles que requiere la implantación de las estrategias del *European Green Deal* y el incremento de la productividad agrícola.

Los suelos que se encuentran degradados, ya sea por la presencia de una capa sellante (suelos sellados), por procesos de compactación o de contaminación, no son

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funcionales para la provisión de servicios ecosistémicos tan importantes como la producción de alimentos, e incluso pueden llegar a generar servicios negativos. De tal forma, los resultados obtenidos en el **Capítulo 5**, muestran que los tecnosuelos pueden facilitar la recuperación de los espacios degradados, evitando incorporar suelo fértil extraído de otras zonas. Tras eliminar la capa sellante, remediar la contaminación y la compactación, los suelos pueden recuperar su funcionalidad ecosistémica y el aporte de residuos puede facilitar la transformación hacia su utilidad agrícola.

Los resultados alcanzados en el **Capítulo 6** indican que los residuos de poda y recolección analizados presentan propiedades fisicoquímicas adecuadas (p. ej. un alto porcentaje de materia orgánica) y un elevado contenido de nutrientes en su composición elemental (Na, K, Ca, Mg, Fe, Mn, Cu y Zn), lo que sugiere que pueden ser interesantes para potenciar la producción agrícola tras su utilización en la formulación de tecnosuelos. Además, estos residuos orgánicos son, de los estudiados, los que muestran mayores concentraciones de nutrientes rápidamente solubles con altos índices de solubilidad. Por el contrario (**Capítulo 7**), obtienen concentraciones de nitrógeno soluble reducidas, asociado a una alta relación C/N, por lo que para que se produzca la mineralización de la materia orgánica, las bacterias requerirán disponer de fuentes de nitrógeno adicionales, bien del suelo o de fertilizantes. De tal forma, consideramos que, para la mineralización efectiva de los residuos de poda, se requiere combinar su aplicación en el suelo con fertilizantes. Con los datos obtenidos, podremos seleccionar el plan de fertilización más adecuado, el residuo que más nos interesa aportar al suelo sobre la base de su contenido en nutrientes y su relación C/N.

Abordando los riesgos asociados a la incorporación de residuos de poda al suelo (**Capítulo 8**), todos los residuos estudiados cumplen con los límites estipulados por la normativa reguladora de los sustratos de cultivo, enmiendas y fertilizantes. Además, en cuanto a la normativa que regula los límites de metales pesados en los suelos agrícolas, cabría prestar atención al compost de lodo de depuradora si se aplica sobre suelos ácidos, no así para los residuos de poda y recolección. Por lo tanto, hay residuos cuya aplicación no presenta restricciones en cuanto a los límites establecidos, sin embargo, para otros residuos conviene ser cauteloso.

Con la intención de estudiar el potencial de los residuos para la provisión de servicios ambientales, tan importantes como la depuración de aguas de excedentes de riego, se construyeron plantas piloto de biorreactores anaerobios (**Capítulo 9**). Se combinaron dos tipos de diseño (flujo de agua horizontal y vertical) y dos tipos de residuos (orgánico e inorgánico). Los resultados de los análisis del agua de riego tratada indicaron que estos tratamientos son efectivos para la reducción de la mayoría de los parámetros fisicoquímicos estudiados, principalmente en el caso de la concentración de N. Se alcanzó la reducción del 100% de N, posiblemente gracias a la relación C/N del residuo orgánico. Por lo que estos tratamientos podrían contribuir a la prevención de los procesos de eutrofización de las aguas.

Se requiere seguir investigando en el futuro sobre la formulación de tecnosuelos a partir de residuos orgánicos, dado la amplia variedad de residuos, factores y condiciones, sobre todo en el ámbito de la experimentación en campo, para potenciar la provisión de servicios ecosistémicos.

SUMMARY

The expected trend of population and urban settlements growth throughout the world implies an increase in the rate of land occupation, which mainly affects soils with the highest agricultural potential. Currently, the soil situation in Europe is not promising because soils are a non-renewable resource and 60-70% of European soils are degraded. This leads to a detriment in the provision of environmental services of soils, affecting their capacity to produce food and the availability of nutrients for crops, among others, implying the appearance of deficiencies in the intake of micronutrients in the world's population since food contains lower concentrations of nutrients. Furthermore, the increase in the world's population will lead to an increase in the demand for food, compromising food security. To meet this growing need for food, an increase in crop

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production is expected, also leading to an increase in agricultural waste generation rates.

Faced with these challenges, the European Union has launched a series of strategies within the framework of the European Green Deal, among which the preservation of ecosystems and their associated services, the recovery of degraded soils, the use of waste in a circular way and the reduction of nutrient loss in soils are priorities. However, to meet these objectives high agricultural quality soils are required. References in the literature consider that the formulation of technical soils (technosols) from agricultural residues can be a valid option to help meet all these needs.

Therefore, the purpose of this thesis is to broaden the knowledge on the properties of agricultural residues that can contribute to the supply of nutrients and their effective mineralization, as well as to identify the risks associated with the presence of these nutrients, mainly those also considered as belonging to the group of heavy metals and trace elements. In this way, to facilitate the choice of the most suitable residues for the formulation of technosols that can enhance the sustainable use of resources, to support the implementation of the strategies emanating from the European Green Deal, to increase the provision of environmental services, and thus to ensure the health of ecosystems and people. The contribution of the research work is based on the roadmap drawn up with the following specific objectives: (i) to know the state of the art of technosols; so as to study the accumulated knowledge of the technosols concept, the interest it arouses among the scientific community, the fields of application, as well as the possible environmental (ecosystem) benefits that its use can bring; (ii) to expose the feasibility of recovering and reconverting sealed soils into functional soils for agricultural production. To elucidate the role that technosols can play in this transformation; (iii) to assess the physical and chemical properties, elemental composition and solubility of available nutrients in selected pruning and harvesting residues for their potential to produce technosols as agricultural substrates based on nutrient supply and nitrogen mineralization capacity; (iv) identify the elemental composition and trace element content of organic waste to determine whether there is an environmental risk for its use as an agricultural substrate; (v) application of nature-based solutions, using waste as

adsorbent and exchange material in bioreactors, to test the potential for improving the physico-chemical properties of marginal and low quality waters used for irrigation and the effects on nitrogen concentration, as a measure to prevent eutrophication processes.

For this purpose, we conducted a literature review on technosols, and analyzed the physicochemical properties, elemental composition, and soluble nutrient content (Na, K, Ca, Mg, Fe, Mn, Cu, Zn, Cd, Cr, Ni and Pb) of the following pruning and harvesting residues: almond pruning, commercial peat, hay straw, olive pruning, pomegranate peel, pine needles, palm leaf, sewage sludge compost and vine pruning (**Chapter 3**). In addition, we obtained its concentration of organic and ammoniacal nitrogen (N) and the relation C/N.

Previous references indicate that technical soils made from waste could be included and classified as Technosols using the World Reference Base for soil resource WRB (**Chapter 4**). The development of technosols is being studied with increased interest, especially since 2013, mainly in the field of restoration of mining and urban areas. However, due to their great potential to provide environmental services and their ability to function as a natural soil, they are a strong candidate to address the need for fertile agricultural soils required for the implementation of the European Green Deal strategies and the increase of agricultural productivity.

Soils that are degraded either by the presence of a sealing layer (sealed soils), compaction or contamination processes are not functional for the provision of ecosystem services as important as food production and can even generate negative services. Thus, the results obtained in **Chapter 5** show that technosols can facilitate the recovery of degraded areas by avoiding the incorporation of fertile soil extracted from other areas. After removing the sealing layer, remediating contamination and compaction, soils can recover their ecosystem functionality and the contribution of residues can facilitate the transformation to agricultural use.

The results achieved in **Chapter 6** indicate that the pruning and harvesting residues analyzed show suitable physicochemical properties (e.g. a high percentage of organic

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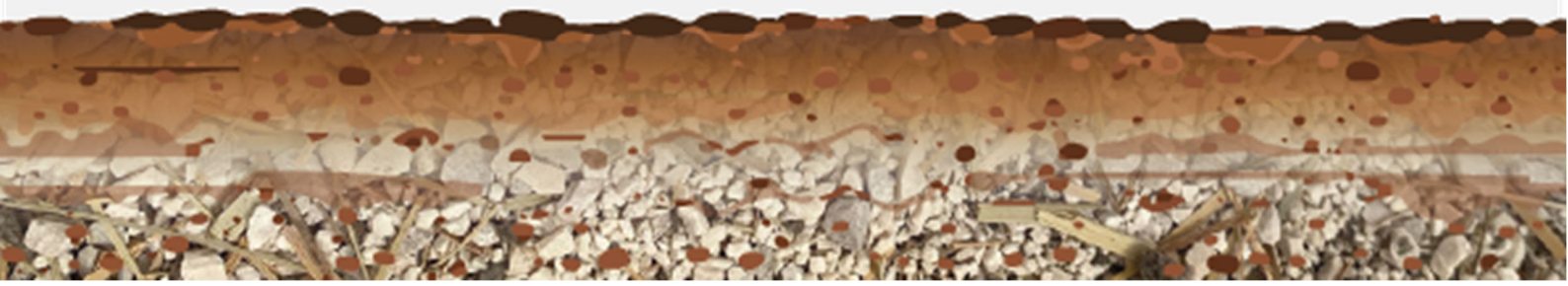
matter) and a high content of nutrients in their elemental composition (Na, K, Ca, Mg, Fe, Mn, Cu and Zn), suggesting that they may be of interest for enhancing agricultural production after their use in the formulation of technosols. In addition, these organic wastes are, among those studied, those that show the highest concentrations of rapidly soluble nutrients with high solubility indices. On the other hand (**Chapter 7**), they obtain reduced concentrations of soluble nitrogen, associated with a high C/N ratio, so that for the mineralization of organic matter to occur, the bacteria will require additional sources of nitrogen, either from the soil or from fertilisers. Thus, we consider that for the effective mineralization of pruning residues, it is necessary to combine their application to the soil with fertilizers. With the data obtained, we will be able to select the most suitable fertilization plan, the residue we are most interested in adding to the soil based on its nutrient content and C/N ratio.

Addressing the risks associated with the incorporation of pruning residues into the soil (**Chapter 8**), all the residues studied comply with the limits stipulated by the regulations governing cultivation substrates, amendments and fertilizers. Furthermore, with regard to the regulations governing the limits for heavy metals in agricultural soils, attention should be paid to sewage sludge compost if it is applied on acid soils, but not to pruning and harvesting residues. Therefore, there are some wastes for which there are no restrictions in terms of limits, but for other wastes caution should be exercised.

In order to study the potential of waste for the provision of environmental services, as important as the purification of irrigation surplus water, anaerobic bioreactor pilot plants were constructed (**Chapter 9**). Two types of design (horizontal and vertical water flow) and two types of waste (organic and inorganic) were combined. The results of the analyses of the treated irrigation water indicated that these treatments were effective for the reduction of most of the physicochemical parameters studied, mainly in the case of N concentration. 100% N reduction was achieved, possibly thanks to the C/N ratio of the organic residue. Therefore, these treatments could contribute to the prevention of water eutrophication processes.

Further research is needed in the future on the formulation of technosols from organic residues, given the wide variety of residues, factors and conditions, especially in field trials, for enhancing ecosystem services provision.

CAPÍTULO 1: INTRODUCCIÓN



1.1. El recurso suelo

El suelo es un recurso no renovable a corto plazo ya que, en la actualidad, su tasa de degradación es mayor que la de su capacidad de regeneración natural. La cantidad de suelo fértil disponible se reduce anualmente, tanto es así que se estima que en 60 años se habrá agotado (FAO, 2022a). Dado que el 95% de los alimentos requiere un suelo fértil como soporte, la producción agrícola puede verse comprometida. Actualmente, entre el 60 y 70% de los suelos en Europa se encuentran degradados. En términos cuantitativos, afecta en torno a 2,5 millones de km² requiriendo una inversión de 50 mil millones de euros para su recuperación (EC, 2020a). Aunque se están aunando esfuerzos para revertir la degradación de los suelos, diversos retos permanecen pendientes de solución. Entre las principales amenazas que deben hacer frente los suelos en Europa destacan la contaminación debido al desarrollo de las actividades humanas y la

INTRODUCCIÓN

producción agrícola (por el uso de pesticidas y fertilizantes que también conllevan la eutrofización de las aguas), así como la degradación por su sellado y compactación (Cachada *et al.*, 2012; Li *et al.*, 2018; EC, 2020a).

De la misma manera que un suelo degradado puede ser un factor de riesgo para la salud; un suelo sano puede ser un componente de bienestar. Por lo tanto, los suelos velan por nuestra salud de diversas formas: ofrecen protección contra los daños de las tormentas y las inundaciones, permiten el desarrollo de los ciclos bioquímicos, controlan la erosión (Lehmann, 2006; Macías y Camps Arbestain, 2010), favorecen la descontaminación mediante la retención, fitorremediación y biorremediación microbiana (Lehmann, 2006; Yap y Peng, 2019), reducen el efecto “isla de calor” de los centros urbanos (Lehmann, 2006; Bokaie *et al.*, 2016), controlan la población de patógenos y proveen de antibióticos y medicinas (Wall *et al.*, 2015). Además, aportan valores culturales, estéticos y forman parte de los paisajes tradicionales (Constantini y Lorenzetti, 2013) que implican un potencial turístico favoreciendo el desarrollo económico de las poblaciones (Tobias *et al.*, 2018). En las construcciones que disponen de un jardín vertical o cubierta vegetal, se mejora la eficiencia energética de las viviendas, se previene el daño por la lluvia ácida, se reduce la contaminación acústica y se potencia la retención de contaminantes mejorando la calidad del aire (Cascone, 2019). Sin duda, uno de sus mayores beneficios es que pueden paliar los efectos del cambio climático y contribuir a alcanzar la neutralidad de emisiones, ya que son un gran reservorio de carbono orgánico (Falkowski *et al.*, 2000; Lehmann, 2006; Edmondson *et al.*, 2012; Brevik *et al.*, 2018; Montanarella y Panagos, 2021; Navarro-Pedreño *et al.*, 2021).

Todos estos beneficios son definidos como servicios ambientales, ya que tienen en cuenta la naturaleza antropogénica de su origen, independientemente de si se producen intencionadamente o no. FAO (2023) considera que, aunque a veces el término servicios ecosistémicos se utiliza indistintamente junto con el de servicios ambientales, hay matices que los diferencian: los servicios ecosistémicos aluden exclusivamente a los beneficios reportados por los entornos naturales, y para valorar el pago de los servicios

prestados por las actividades humanas se mencionan como servicios ambientales (Derissen y Latacz-Lohmann, 2013).

Por el contrario, si un suelo está degradado, su funcionalidad ecosistémica se reduce y puede afectar a la salud humana por exposición directa a los contaminantes presentes en el suelo (vía digestiva, dérmica o por inhalación) o indirecta (Rodríguez-Eugenio *et al.*, 2018). Debido a que las ciudades son los entornos con más densidad de población, también son los lugares en los que mayor número de personas están expuestas a la presencia de contaminación. De hecho, las ciudades europeas albergan entre 2.001 y 5.000 residentes por kilómetro cuadrado (EC, 2018). Asimismo, la salud de los suelos urbanos es un tema de gran interés para la comunidad científica, prueba de ello es la prolífica variedad de referencias bibliográficas disponibles al respecto (Constantini y Lorenzetti, 2013; Abel *et al.*, 2015; Charzýnski *et al.*, 2017; Tresch *et al.*, 2018; Quéneá *et al.*, 2019; Baragaño *et al.*, 2020; Paradelo *et al.*, 2020; Guillén *et al.*, 2021).

1.2. Desarrollo urbano y consecuencias para el suelo

La evolución de las tasas de población mundial y su preferencia de asentamiento son un factor relevante para poder predecir, reducir y mitigar los impactos asociados con el uso del suelo. La población mundial en 2020 alcanzó los 7.700 millones de personas, y se espera que continúe aumentando hasta 9.800 millones en 2050 (PRB, 2020). A nivel de continentes, todos experimentarán un incremento de sus índices de población excepto Europa que hacia 2050 aquejará un leve descenso. En 2020 el 56% de la población (4.353 millones) escogió desarrollar sus vidas en entornos urbanos (PRB, 2020). Se estima que el número de asentamientos urbanos (superior a 300.000 habitantes) aumente desde 1.934 en 2020 hasta 2.363 en 2035, albergando una población de 5.555 millones de personas en 2035 (UN-HABITAT, 2020a; UN-HABITAT, 2020b), siendo un fenómeno común a todos los continentes y a todos los tamaños de urbes.

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Ya que las consecuencias derivadas de la expansión territorial de los entornos urbanizados pueden ser diversas, resaltamos alguna de ellas. La ocupación del suelo en la Unión Europea, entre 2012 y 2018, afectó a 539 km² año⁻¹, principalmente asociado a terrenos de zonas periurbanas (Aksoy *et al.*, 2017) que son los que mayor potencial agrícola tienen (Schiavina *et al.*, 2019; UN-HABITAT, 2020). De tal forma, más del 78% de los terrenos ocupados, entre el 2000 y 2018, correspondían a áreas agrícolas (EEA, 2021). Una consecuencia directa de este proceso de reconversión del uso del suelo, es la reducción en la capacidad de producción agrícola para atender la creciente demanda de alimentos por parte de la población mundial (Gardi *et al.*, 2015; Aksoy *et al.*, 2017; Marquard *et al.*, 2020).

Asimismo, el 99.5% del suelo ocupado en la Unión Europea, entre 2012 y 2018, se destinó a usos que requerían el sellado o la retirada de la capa fértil del suelo (EEA, 2021). El recubrimiento del suelo con materiales impermeables conlleva que el suelo queda aislado y no puede realizar sus beneficiosas funciones ambientales. Esto no solo implica la pérdida de funcionalidad, sino también la generación de servicios ecosistémicos negativos como son el aumento del efecto “isla de calor” y del riesgo de inundaciones, la reducción de la infiltración de agua para la recarga de los acuíferos, la negativa afección a la biodiversidad y al ciclo del carbono (Gardi *et al.*, 2015; Bokaie *et al.*, 2016; Tobias *et al.*, 2018; Correa *et al.*, 2021; Hardaker *et al.*, 2021; Sobocká *et al.*, 2021).

Por ende, los núcleos urbanos cada vez más poblados requerirán garantizar la seguridad y salud de sus habitantes. Sin embargo, los entornos urbanos y periurbanos son la principal fuente de impactos ambientales globales, emitiendo más del 70% de las emisiones globales de CO₂ y consumiendo entre el 60 y 80% de la energía producida (Gurney *et al.*, 2015). Se estima que serán los entornos que, de forma general, más van a sufrir las consecuencias del cambio climático y curiosamente, son los que menos preparados están para hacerles frente.

De la misma manera, las ciudades tendrán que aumentar la provisión de recursos (agua, suelo fértil, energía), así como el desarrollo de infraestructuras y otras

instalaciones (González-Méndez y Chávez-García, 2020). Para 2050 se espera que la demanda global de agua aumente un 55% (FAO, 2017b; UNESCO, 2020; Altés *et al.*, 2023). Sin embargo, se considera que en 2050 el 60% de la población mundial sufrirá escasez de agua, no solo por la carencia física del recurso, sino también por la progresiva degradación de la calidad del agua, ya que se reduce la cantidad de agua que es segura para su uso (Qadir *et al.*, 2007; FAO, 2017c; Elbehiry *et al.*, 2020). Durante el periodo que comprende los años 2016 a 2019 las aguas europeas clasificadas como eutróficas supusieron un 81% de aguas marinas, un 31% de aguas costeras, un 36 % de ríos y un 32% de lagos (EC, 2021b).

Por lo tanto, las ciudades intensificarán su huella ambiental al aumentar la producción de residuos, emisiones y vertidos (Filho *et al.*, 2019; Zambon *et al.*, 2019; Losco y Biase, 2021), requiriendo mayores esfuerzos en políticas que potencien la autosuficiencia, la economía circular, el reciclado y valorización de residuos, la depuración de aguas y la reducción de emisiones, particularmente los gases de efecto invernadero.

1.3. Producción de residuos agrícolas

Se espera que la generación de residuos a nivel global alcance la cifra de 3.400 millones de toneladas en 2050 (The World Bank, 2018). En 2018 las ciudades europeas produjeron 492 kg per cápita de residuos municipales, de los cuales el 47% entraron en procesos de reciclado (Eurostat, 2020). En el ámbito de los residuos asociados a la producción agrícola, actualmente en Europa se generan aproximadamente 700 millones de toneladas al año, suponiendo entre un 10 y un 12% de las emisiones de gases de efecto invernadero (Fortunati *et al.*, 2020). Además, la producción de residuos agrícolas aumenta anualmente en un 7,5% (Wang *et al.*, 2015). Estos datos implican un reto y una oportunidad para la gestión sostenible, a nivel ambiental y económica, de las corporaciones agrícolas, para seguir avanzando hacia el uso de los residuos sobre la base de los principios de la economía circular (Diacono *et al.*, 2019; Fortunati *et al.*, 2020).

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Desde tiempos inmemoriales, los residuos de los sistemas agroforestales se consideraban una materia prima valiosa por su contenido en materia orgánica y nutrientes, siendo utilizados como fertilizantes en la propia explotación agrícola. La aparición de los fertilizantes químicos relegó su papel desde la valorización a la eliminación. Actualmente la quema de los restos de poda es una práctica extendida, implicando un aumento del riesgo de incendios, de las emisiones de gases y contaminantes a la atmósfera, y una pérdida de carbono secuestrado y de los elementos y nutrientes que los componen (Repullo *et al.*, 2012; Gómez-Muñoz *et al.*, 2016; Anguria *et al.*, 2017). Sin embargo, los estados miembros de la Unión Europea están llamados a regular y evitar la quema de rastrojos, excepto por razones fitosanitarias, para la mitigación del cambio climático y el mantenimiento de la materia orgánica (EU 2021/2115).

1.4. Presencia de nutrientes en los alimentos y en los suelos

Una dieta adecuada para las personas implica la incorporación de al menos 25 elementos minerales, que proceden principalmente de la ingesta de vegetales (White y Brown, 2010). 13 de estos elementos (N, P, K, Ca, Mg, S, Fe, Mn, B, Mo, Cu, Zn, y Cl, aparte de O, C y H) son considerados esenciales para el desarrollo de los cultivos (Blaya y García, 2003; Oueriemmi *et al.*, 2021). Sin embargo, a nivel mundial, más de 2.000 millones de personas sufren deficiencias en la ingesta de micronutrientes (Fe, Mn, B, Mo, Cu, Zn y Cl), ya que, durante los últimos 70 años, el contenido en vitaminas y nutrientes en los alimentos ha descendido drásticamente (FAO, 2022a). Esto afecta tanto a países desarrollados debido a la sobreexplotación de cultivos, como en vías de desarrollo debido a la presencia de suelos poco fértiles (FAO *et al.*, 2021b).

La liberación de nutrientes en los suelos procede de la solubilización de la roca madre o de los sedimentos, así como de la mineralización de la materia orgánica. Hossain *et al.*, (2017) y muchas prácticas de agricultura ecológica, destacan la importancia de

incorporar los residuos orgánicos al suelo para potenciar la productividad de los cultivos, la biodisponibilidad de los nutrientes y la absorción de macronutrientes por parte de las plantas. Sin embargo, Foereid (2019) puntualiza que no todos los nutrientes que proceden de fertilizantes orgánicos están inmediatamente disponibles, ni tampoco cuándo pueden llegar a estarlo.

Aunque los beneficios de los fertilizantes orgánicos son incuestionables, ya que mejoran las propiedades físicas de los suelos, la actividad microbiana, el suministro de nutrientes, la biodiversidad y la provisión de servicios ecosistémicos, el almacenamiento de carbono, entre otros (Anwar *et al.*, 2015; Cole *et al.*, 2016; Rico Hernández *et al.*, 2016; Hossain, 2017; Cavalli *et al.*, 2018; Diacono *et al.*, 2019; FAO, 2022a), de acuerdo con FAO, no son “*risk-free*”, es decir, no están libres de riesgos, principalmente por el material del que procedan (FAO, 2022b). Por añadidura, un exceso o deficiencia de nutrientes puede conllevar problemas para la salud humana (p.ej.: malnutrición, enfermedades), para el crecimiento de los cultivos (p.ej.: inseguridad alimentaria, costes añadidos) y para la sostenibilidad de los ecosistemas (Jiwan y Ajay, 2011; Oueriemmi *et al.*, 2021; FAO, 2022b). En la Unión Europea se estima que 137.000 km² (6,24% de suelo agrícola) registran concentraciones de metales pesados por encima de los límites establecidos por las disposiciones legales (Tóth *et al.*, 2016).

1.5. *European Green Deal*

La UE, consciente de los retos mencionados anteriormente, lanza el Pacto Verde Europeo, también conocido como *European Green Deal*, para proteger los recursos naturales, la salud y el bienestar de los ciudadanos (EC, 2019). Para lograrlo, la Comisión Europea ha desarrollado varias estrategias, en las que la gestión sostenible de los recursos naturales (suelos, aguas y residuos) es el eje principal.

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Comenzamos destacando la Estrategia de la Biodiversidad 2030, cuya misión es volver a acercar la naturaleza a nuestras vidas, protegiendo y revertiendo la degradación de los ecosistemas (EC, 2020b). Para ello, estipula la necesidad de plantar como mínimo 3.000 millones de árboles y requiere a las ciudades que desarrollen planes urbanos verdes. Los esfuerzos en las ciudades deben encaminarse a aumentar los ecosistemas verdes urbanos y a reducir la contaminación (en suelos, agua y aire), empleando infraestructuras verdes y soluciones basadas en la naturaleza.

La estrategia *Farm to Fork* 2020 pretende diseñar un sistema productivo alimentario que sea saludable y respetuoso con el medio ambiente (EC, 2020c), procurando que al menos el 10% de las áreas agrícolas presenten características paisajísticas de alta diversidad. Otro de los pilares fundamentales es la promoción de las prácticas de agricultura ecológica para 2030, aplicándose en el 25% del suelo agrícola y potenciando que se reciclen los residuos orgánicos como fertilizantes. De tal forma, este objetivo se refuerza con la estrategia de Economía Circular, lanzada para que los residuos sean considerados como materia prima y puedan tener mayor aprovechamiento (EC, 2020d). Además, aboga por aumentar el reciclado, la reducción del sellado del suelo y la rehabilitación de zonas selladas abandonadas.

La Directiva Marco del Agua (EC, 2000) trata de asegurar el uso sostenible y la calidad de los recursos hídricos para 2027. Los materiales en suspensión, las sustancias que contribuyen a la eutrofización y las sustancias que tienen una influencia negativa sobre el balance de oxígeno, entre otras, son una de las principales preocupaciones.

La estrategia 2030 para el suelo, define la hoja de ruta para proteger y restaurar los suelos europeos (EC, 2021a). Entre los objetivos propuestos para ello, establece: reducir a cero la ocupación neta del suelo para 2050, lograr un buen estado ecológico y químico en las aguas superficiales y un buen estado químico y cuantitativo en las aguas subterráneas de aquí a 2027, reducir las pérdidas de nutrientes en un 50 % como mínimo, que dará lugar a la reducción del uso de fertilizantes en al menos un 20 %, por ejemplo, empleando residuos orgánicos de forma segura. En definitiva, pretende

conseguir una sociedad resiliente frente al cambio climático, plenamente adaptada a sus inevitables efectos de aquí a 2050.

1.6. Recursos requeridos para desarrollar el *European Green Deal*

Como ha sido abordado anteriormente, los suelos europeos afrontan diversas amenazas que restringen su salud y adecuada funcionalidad. Esto no quiere decir que todos los suelos urbanos estén degradados o contaminados, según reflejan los resultados obtenidos por Paradelo *et al.*, (2020). Sin embargo, para cumplir con las estrategias del pacto verde las ciudades europeas tendrán que implementar ambiciosas actuaciones sostenibles evitando comprometer recursos como la ocupación del suelo, y la calidad del agua y el suelo.

Resulta complicado medir la superficie urbana con potencial para ser convertida en zona verde. Un estudio realizado en la ciudad de Viena (Austria), estimó que disponía de 12.000 ha de fachadas y 1.800 ha de tejados que podrían albergar vegetación (Stangl *et al.*, 2019). Por lo general, se estima que los tejados ocupan entre el 20 y 30% del área total de una ciudad (González-Méndez y Chávez-García, 2020) y algunos países como Alemania, muestran una clara tendencia de crecimiento de tejados convertidos en cubiertas verdes (Cascone, 2019). Además, para la ampliación de zonas verdes urbanas también pueden aprovecharse los solares o áreas industriales abandonadas (Tobias *et al.*, 2018), evitando así la ocupación de más suelo y asegurando su conexión ecológica (Losco y Biase, 2021).

Las futuras necesidades de agua de las ciudades sobre la base del nuevo paradigma verde, han sido estudiadas por Ruíz-Pérez *et al.* (2020), concretamente para la ciudad de Sevilla (España), concluyendo que los volúmenes hídricos fluctúan dependiendo de las especies introducidas. Los matorrales autóctonos requieren la menor cantidad de agua de lluvia (desde 0,13 a 0,14 m³ m⁻²) y con el menor aporte de agua subterránea o

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de riego (desde 0,05 a 0,08 m³ m⁻²). Por el contrario, los parterres con rosales requieren la mayor cantidad de agua tanto de origen pluviométrico (0,31 m³ m⁻²) como por aporte extra de riego (0,46 m³ m⁻²). En definitiva, la cantidad y calidad de agua necesaria para albergar el nuevo paisaje natural urbano depende de su zona climática, de las necesidades nutricionales de cada especie, así como de las funciones sistémicas que tienen que ser recuperadas o potenciadas.

Análogamente, estos nuevos entornos urbanos verdes requerirán de un suelo fértil, que pueda albergar la vegetación y permita la provisión de servicios ambientales. De acuerdo a González-Méndez y Chávez García (2020), el sustrato más usado para las infraestructuras verdes es el suelo natural. Conclusiones que concuerdan con las obtenidas por Rokia *et al.*, (2014), señalando que los suelos principalmente proceden de áreas circundantes. Así estimaron que anualmente en Francia se extraen 3 millones de metros cúbicos de suelo fértil de los alrededores para atender la demanda de suelo en las ciudades. En suma, con la loable intención de restaurar o vegetar las áreas urbanas, debemos evitar la extracción de suelo fértil de otras zonas, ya que generaremos problemas añadidos.

En cuanto a los sistemas agrarios, para la reducción de los impactos ambientales asociados, la agricultura sostenible se postula como una opción cada vez más extendida y demandada por los consumidores, ya que también vela por la prevención de la salud. Uno de los principales pilares de la agricultura ecológica es la gestión sostenible del suelo, puesto que su calidad y salud son decisivas para la producción agrícola, la nutrición y salud humana y la biodiversidad de los ecosistemas agrícolas (El Chami *et al.*, 2020; FAO, 2022a). FAO (2017a) resalta que los principales retos de la gestión sostenible del suelo, para asegurar la provisión de servicios ecosistémicos, son minimizar la erosión, aumentar el contenido en materia orgánica, fomentar el equilibrio y los ciclos de nutrientes, prevenir, minimizar y mitigar la salinización, alcalinización y acidificación, preservar y potenciar la biodiversidad del suelo, mejorar la gestión del agua del suelo, prevenir y mitigar la compactación del suelo y restaurar los suelos sellados. Para ello, FAO (2017a) propone varias opciones, pero de entre ellas solo hay una que puede contribuir a todos estos problemas y es la cobertura del suelo con residuos orgánicos,

siempre y cuando se asegure su inocuidad. Esto se debe a que la aplicación de residuos orgánicos en el suelo aumenta la biodiversidad del ecosistema agrícola, el secuestro y almacenamiento de CO₂, el suministro de nutrientes a los cultivos, así como potencia la nutrición humana (Rabary *et al.*, 2008; Cole *et al.*, 2016; Anguria *et al.*, 2017; Cavalli *et al.*, 2018; Diacono *et al.*, 2019; Rocchi *et al.*, 2020; FAO, 2022a).

Es más, numerosos estudios consideran que la aplicación de residuos orgánicos como sustrato para los cultivos, también favorece el suministro de nutrientes (El-Ramady *et al.*, 2014; Diacono *et al.*, 2019; Amoriello *et al.*, 2020; Greco *et al.*, 2020; Zipori *et al.*, 2020). Afortunadamente, su utilización para formular suelos técnicos adecuados para la producción agrícola comienza a ser estudiada, y diversos autores concluyen que pueden contribuir a la seguridad alimentaria (Rokia *et al.*, 2014; Anwar *et al.*, 2015; Oliver y Gregory, 2015; Hossain *et al.*, 2017; Coull *et al.*, 2021). De forma generalizada, los suelos disfuncionales, contaminados o infértiles pueden mejorar con la aplicación de residuos y su transformación en suelos técnicos, ya que se estimula la actividad microbiana y las propiedades del suelo (Rabary *et al.*, 2008; Rico Hernández *et al.*, 2016; Hossain *et al.*, 2017). Debido a que los suelos son un componente fundamental para la infraestructura verde (Deeb *et al.*, 2018), algunos autores defienden que los residuos pueden ser utilizados para generar tecnosuelos, que aplicados en zonas urbanas puedan contribuir al desarrollo del *European Green Deal* (Li *et al.*, 2018; Deeb *et al.*, 2020; Pruvost *et al.*, 2020).

Además, otros autores (Rokia *et al.*, 2014; Fourvel *et al.*, 2019; Rees *et al.*, 2019; Barredo *et al.*, 2020; Deeb *et al.*, 2020; González-Méndez y Chávez-García, 2020; Ugolini *et al.*, 2020) consideran que los tecnosuelos también pueden diseñarse para recuperar los servicios ambientales de ecosistemas acuáticos degradados. De hecho, los tecnosuelos se han utilizado con éxito para mejorar la calidad del agua de escorrentía superficial en restauraciones mineras, pluvial urbana y residual (Deeb *et al.*, 2018; Elbehiry *et al.*, 2020). Sin embargo, su capacidad para mejorar la calidad del agua de riego no ha sido tan estudiada, especialmente cuando no se incorporan macrófitos.

1.7. Suelos con influencia humana

Las actividades humanas se desarrollan sobre los suelos, por lo que inevitablemente indican en ellos. Tanto es así, que estos suelos con fuerte influencia humana han sido incluidos en la base de referencia mundial del recurso suelo conocida como WRB (IUSS, 2015), perteneciendo a dos grupos de referencia de suelos: *Anthrosols* (intensivo uso agrícola) y *Technosols* (contienen cantidad significativa de artefactos, materiales ajenos a los originados por la formación de suelos de manera natural). Los *Anthrosols* son “suelos que han sido modificados profundamente por actividades humanas, tales como la adición de materia orgánica o mineral, carbón vegetal o residuos domésticos, o el riego y la labranza”. Los *Technosols* comprenden “suelos cuyas propiedades y edafogénesis están dominadas por su origen técnico. Contienen una cantidad significativa de artefactos (> 20% en volumen, peso ponderado, de artefactos en los 100 cm superiores de la superficie del suelo o hasta roca continua), siendo los artefactos algo en el suelo reconociblemente hecho o fuertemente alterado por el hombre o extraído de profundidades mayores; o están sellados por material duro técnico (material duro creado por los seres humanos que tiene propiedades diferentes de la roca natural) o contienen una geomembrana. Incluyen suelos de desechos (vertederos, lodos, escorias, desechos o escombros de minas y cenizas), pavimentos con sus materiales subyacentes no consolidados, suelos con geomembrana y suelos construidos artificialmente” (IUSS, 2015).

En definitiva, se reconoce en la actualidad, tanto en los sistemas de clasificación de suelos como en los diferentes documentos y estrategias promovidas por las administraciones, que el suelo está afectado por una serie de problemas derivados de la acción humana y que estos alteran y generan nuevos suelos que pueden ser disfuncionales. Para recuperar la funcionalidad, se plantea la estrategia de crear suelos técnicos, es decir, que no obedecen al desarrollo normal bajo los factores formadores de los suelos de la zona en concreto, sino que son creados expresamente para poder dar respuesta a los problemas existentes. Para conocer realmente si se consigue tal objetivo,

la recuperación de los servicios ambientales, es necesario conocer y valorar los materiales que pueden constituir los tecnosuelos, su comportamiento y propiedades aislados y en conjunto, formando nuevos medios edáficos.

CAPÍTULO 2: FINALIDAD Y OBJETIVOS



2.1. Finalidad y objetivos

Los desafíos recientemente enunciados nos exponen la necesidad de indagar sobre cómo podemos abordar un desarrollo sostenible, en el que los suelos sean conservados y restaurados. Frente a la escasez y degradación del suelo, estudios precedentes, inician y enfocan la discusión hacia la generación de suelos “a la carta” empleando residuos como materia prima.

A pesar del gran potencial que puede conllevar la formulación de suelos técnicos a partir de residuos, para su uso como sustrato agrícola, urbano o para recuperar suelos degradados (o generarlos donde han desaparecido), existen ciertas limitaciones, como la necesidad de ampliar el conocimiento científico y la inexistencia de un marco normativo que regule su uso.

FINALIDAD Y OBJETIVOS

En consecuencia, la finalidad básica de esta tesis es la de enriquecer el conocimiento sobre las propiedades de materiales empleados para la formulación de tecnosuelos, como los residuos de poda o recolección, que puedan contribuir al aporte de nutrientes, por ejemplo, mediante la solubilización o su mineralización efectiva, así como a identificar los riesgos asociados a la presencia de contaminantes.

Esto permitiría facilitar la elección de los residuos más adecuados para la formulación de suelos, tomando como base la intención de potenciar el uso sostenible de los recursos, para auspiciar la implantación de las estrategias que emanan del *European Green Deal*, para acrecentar la provisión de servicios ecosistémicos, y, por ende, para asegurar la salud de los ecosistemas y las personas.

El aporte del trabajo de investigación se sustenta en la hoja de ruta trazada considerando los siguientes objetivos específicos:

- 1) Conocer el estado del conocimiento actual sobre los tecnosuelos y sobre el interés que suscita entre la comunidad científica, sobre los ámbitos de aplicación, así como los posibles beneficios ecosistémicos que pueden reportar su uso. Se aborda en el **Capítulo 4** denominado "*Urban areas, human health and Technosols for the Green Deal*".
- 2) Exponer la viabilidad de recuperar y convertir suelos degradados en suelos funcionales para la producción agrícola, dilucidando el papel que pueden desempeñar los tecnosuelos en esta transformación. Se acomete en el **Capítulo 5** titulado "*Land recycling, food security and Technosols*".
- 3) Evaluar las propiedades físicas y químicas, la composición elemental y la solubilidad de los nutrientes disponibles en los residuos de poda y recolección seleccionados, para conocer su potencial para formular tecnosuelos como sustrato agrícola, sobre la base del suministro de nutrientes y la capacidad de mineralización del nitrógeno. Para ello aportamos los **Capítulos 6 y 7**, que incluyen los artículos "*Soluble elements released from organic wastes to increase available nutrients for soil and crops*" y

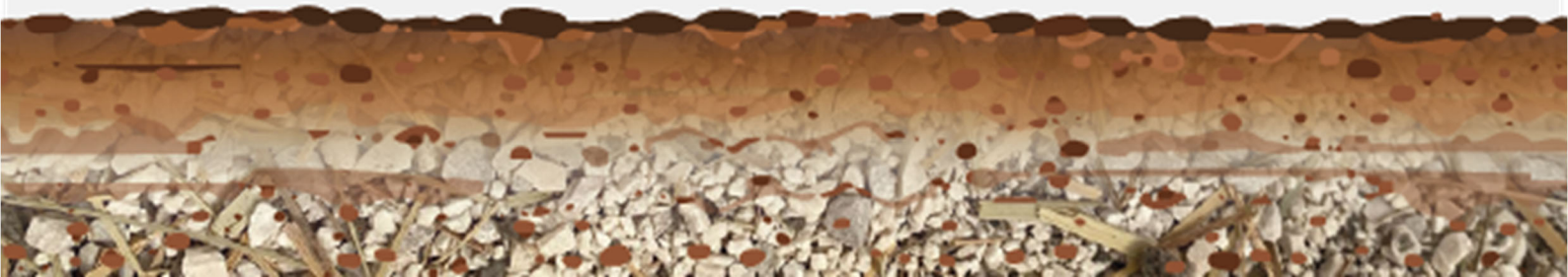
“Nitrogen management in farming systems under the use of agricultural wastes and circular economy”.

- 4) Identificar la composición elemental y el contenido de metales pesados solubles en los residuos orgánicos, para determinar si existe un riesgo de contaminación ambiental y para su uso como sustrato agrícola. El **Capítulo 8** *“Environmental risk from organic residues”* se ocupa de este objetivo.
- 5) Aplicación de soluciones basadas en la naturaleza, utilizando residuos como material adsorbente y de intercambio en biorreactores, para comprobar el potencial de mejora de las propiedades fisicoquímicas de las aguas marginales y de baja calidad que se usan para riego y los efectos en la concentración de nitrógeno, como medida para prevenir los procesos de eutrofización. El **Capítulo 9** titulado *“Low-quality irrigation water treated using waste biofilters”* abarca este objetivo.

La consecución del propósito de esta tesis, de la disertación conjunta de los capítulos que la conforman, será comentada y contrastada en los **Capítulos 10 y 11** sobre discusión y conclusiones.

Los artículos de esta tesis doctoral presentada por compendio de publicaciones, han sido transcritos tal y como figuran en dichas publicaciones.

CAPÍTULO 3: MATERIALES Y MÉTODOS



3.1. Revisión bibliográfica

Para abordar el estudio bibliográfico sobre los tecnosuelos, se comenzó realizando un análisis de la literatura existente al respecto. Para ello se utilizaron motores de búsqueda de internet y consultamos las bases de datos de referencias científicas: Scopus y la plataforma de investigación y colaboración científica ResearchGate.

Se realizó la búsqueda utilizando palabras clave relacionadas con el ámbito de interés. De tal forma, diversas variantes del término *technosols* fueron empleadas para estudiar el concepto, campo de aplicación y relevancia (**Capítulo 4**).

Este método también fue empleado en el **Capítulo 5**, con el fin de averiguar si los suelos sellados pueden ser recuperados para uso agrícola con su transformación en nuevos tecnosuelos. Posteriormente, los datos obtenidos fueron contrastados y

complementados con informes recabados en los sitios web de las instituciones oficiales referenciadas en la bibliografía.

A lo largo de toda la tesis, hemos mantenido un hilo conductor de aspectos a abordar, que mostramos en el siguiente mapa conceptual (Figura 1).

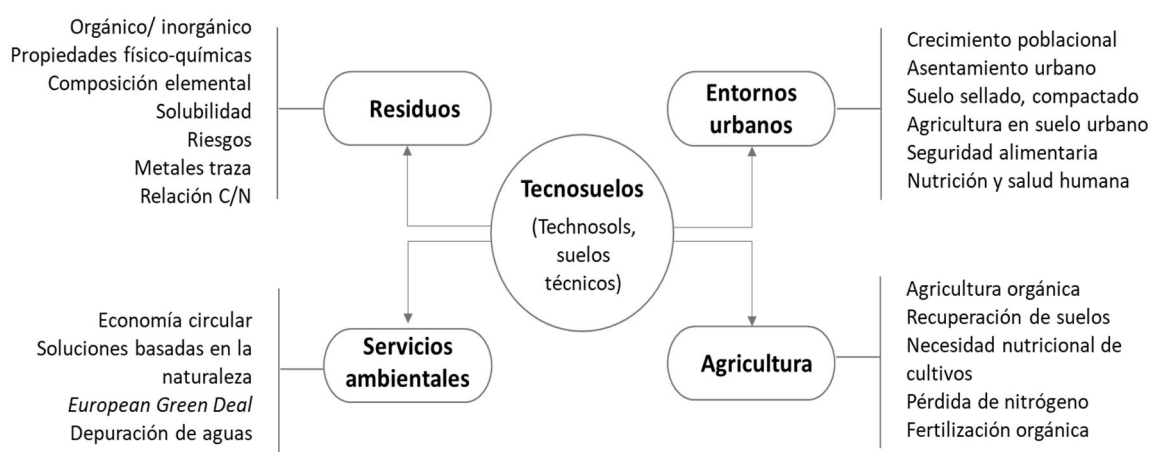


Figura 1. Mapa conceptual de la tesis. Fuente: Elaboración propia.

3.2. Los residuos utilizados

Diversos residuos han sido objeto de estudio a lo largo de la tesis que nos ocupa. Los criterios para la selección de los residuos fueron los siguientes: a) disponibilidad y proximidad (basándonos en las estrategias de economía circular y residuo cero); b) facilidad de manejo y acondicionamiento previo; c) propiedades organolépticas relacionadas con las molestias asociadas a su gestión y manejo; d) y el potencial esperable para formular tecnosuelos.

De tal forma los residuos empleados fueron (**Capítulos 6-9**):

- Restos de poda de almendro (*Prunus dulcis*)
- Turba comercial
- Paja de heno
- Restos de poda de olivo (*Olea europaea* L.)
- Pericarpio, corteza o piel de granada (*Punica granatum* L.)
- Acículas de pino (*Pinus halepensis*)
- Restos de poda de palmera, concretamente las hojas (*Phoenix dactylifera* L.)
- Compost de lodo de depuradora
- Restos de poda de sarmiento de vid (*Vitis vinifera*)
- Inorgánico (grava)

Los residuos de poda y las acículas de pino (depositadas en el suelo tras su caída de los árboles), fueron recogidos de áreas agrícolas o forestales próximas a Elche (Alicante, España). El compost procede de la estación depuradora de aguas residuales (EDAR) de Aspe (Alicante, España), habiendo sido estabilizado mediante un proceso de compostaje.

3.3. Acondicionamiento de los residuos

Todos los residuos orgánicos fueron sometidos a un secado a temperatura ambiente forzada en el interior de invernadero cerrado (ubicado en la Universidad Miguel Hernández de Elche, España), alcanzando, durante más de un mes, temperaturas por encima de 40°C. Posteriormente, los residuos orgánicos también fueron cortados y triturados a 5 cm para su aplicación con una biotrituradora (Tritone One 2030, Machine Agricole).

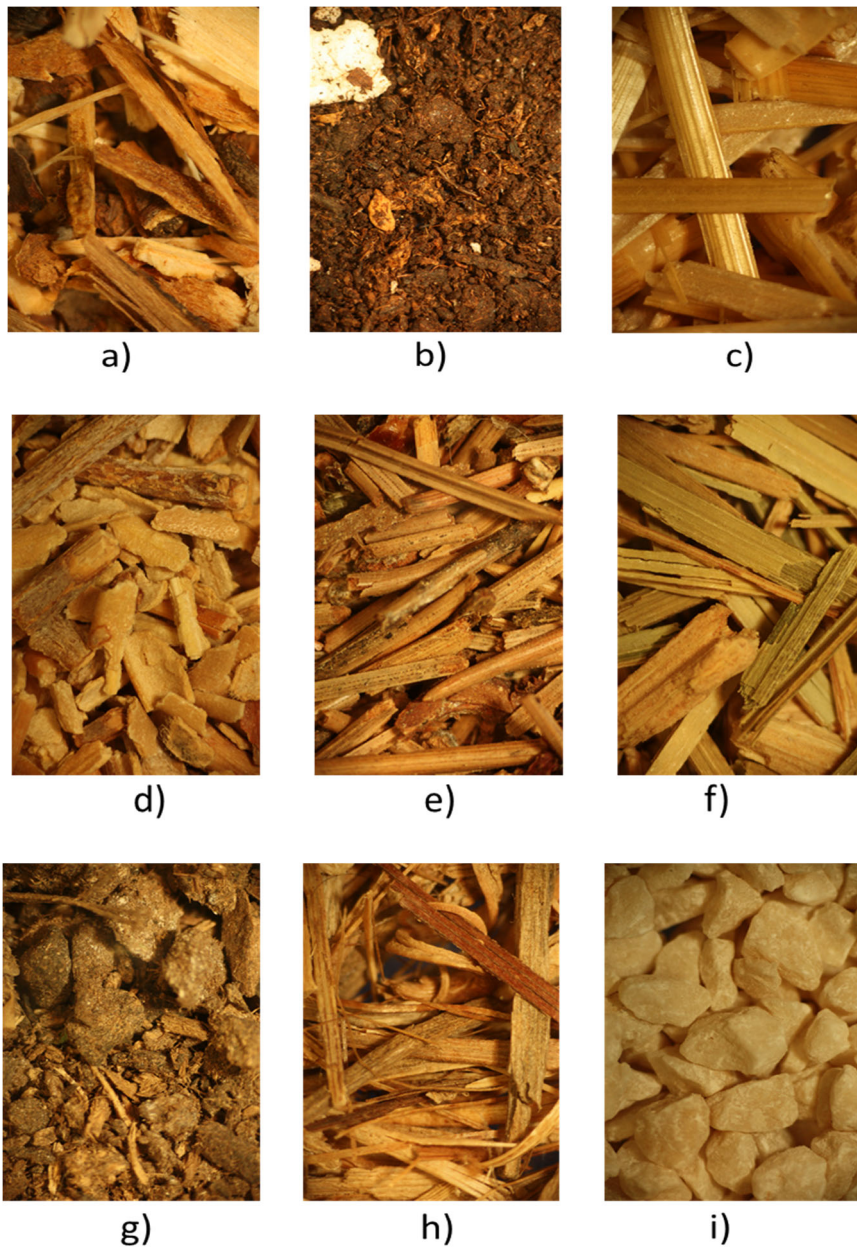


Figura 2. Imágenes obtenidas con lupa binocular de los residuos tras su acondicionamiento: a) restos de poda de almendro; b) turba comercial; c) paja de heno; d) restos de poda de olivo; e) acículas de pino; f) restos de poda de palmera; g) compost de lodo de depuradora; h) restos de poda de sarmiento de vid; i) grava.

Fuente: Elaboración propia.

Se aplicaron acondicionamientos posteriores que incluían el triturado de los mismos a fracciones más finas en función del tipo de análisis fisicoquímico requerido. En la Figura 2 se muestran las imágenes (40 aumentos) obtenidas con lupa binocular, de algunos residuos estudiados tras su acondicionamiento.

3.4 Caracterización de los residuos

Los residuos fueron analizados en laboratorio para determinar:

- Las propiedades fisicoquímicas (**Capítulos 6-9**): densidad aparente (ρ_b) calculada volumétricamente como ratio entre la masa del residuo y el volumen, así como también la porosidad (AENOR, UNE-EN 13041, 2012); el contenido en materia orgánica (MO) determinado como la pérdida por combustión (*Loss on ignition* - LOI) en un horno mufla a 450 °C tras haber sido secado en horno (105 °C) (AENOR, UNE-EN 13039, 2001); contenido en humedad con horno a 105 °C (MC) (AENOR, UNE-EN 13040, 2008); el contenido en carbono orgánico total (CO) se obtiene por oxidación (Iglesias y Pérez, 1992; Puyuelo *et al.*, 2011); análisis del contenido en nitrógeno total (N) mediante el método Kjeldahl (AENOR, UNE-EN 13342, 2001; AENOR, UNE-EN 13654-1, 2002; Jones, 2001; FAO, 2021a; Doyeni *et al.*, 2022). La relación C/N se calcula con los datos CO y N obtenidos. Además, se calcula el porcentaje de N mineralizado en dos escenarios de mineralización de la materia orgánica (10% y 15%) para un ciclo de cultivo (aproximadamente 6 meses) (Jat *et al.*, 2018) y la cantidad de residuo orgánico necesaria para suplir la demanda de N de diversos cultivos, asumiendo las tasas de mineralización y que todo el nitrógeno es suministrado por los residuos orgánicos.
- La composición elemental se determinó para conocer el contenido en nutrientes y metales pesados (Na, K, Ca, Mg, Fe, Mn, Cu, Zn, Cd, Cr, Ni y Pb) (**Capítulos 6 y**

- 8).** Se obtiene mediante espectrofotómetro de absorción atómica (AAS) después de realizar una digestión ácida (ácido nítrico 69% + H₂O₂) de las muestras (0,2 g) en un microondas (Moral *et al.*, 1996).
- El contenido de elementos solubles se determinó en extracto acuoso y a partir de ahí el índice de solubilidad (**Capítulos 6 y 8**). Para obtener el extracto acuoso, se empleó la relación peso de residuos y volumen de agua 1/10. Para cada extracto acuoso obtenido se determinó adicionalmente el pH (AENOR, UNE-EN 13037, 2012) y la conductividad eléctrica (CE) (AENOR, UNE-EN 13038, 2012), midiendo el contenido en nutrientes y elementos traza (Na, K, Ca, Mg, Fe, Mn, Cu, Zn, Cd, Cr, Ni y Pb) mediante espectrofotometría de absorción-emisión atómica. Además, el índice de solubilidad de cada elemento se obtiene como el porcentaje del contenido de un elemento en el extracto acuoso respecto al contenido del elemento en la composición elemental (Jamroz *et al.*, 2020).

3.5 Planta piloto de biorreactores

Inspirándonos en el funcionamiento de las soluciones basadas en la naturaleza, se construyeron plantas piloto experimentales de depuración de aguas de riego, a modo de biorreactores, utilizando residuos como material filtrante (**Capítulo 9**).

Las aguas de esta experimentación se tomaron directamente de la Acequia Mayor del Pantano de Elche, antes de su paso junto al Convento de Santa Clara, entre el Camino de la Fábrica de Ferrández y el Paseo de Santa Clara (coordenadas geográficas UTM X: 701.170,5 m; Y: 4.239.112,38 m). Con una frecuencia semanal y siendo la duración total de 20 semanas.

Se diseñaron dos tipos de filtros verdes pasivos anaerobios con lámina de agua no superficial (Figura 3), unos con flujo de agua horizontal y otros con flujo vertical. Ambos

prototipos son realizados por duplicado. Se ubicaron dentro del invernadero de la Universidad Miguel Hernández de Elche.

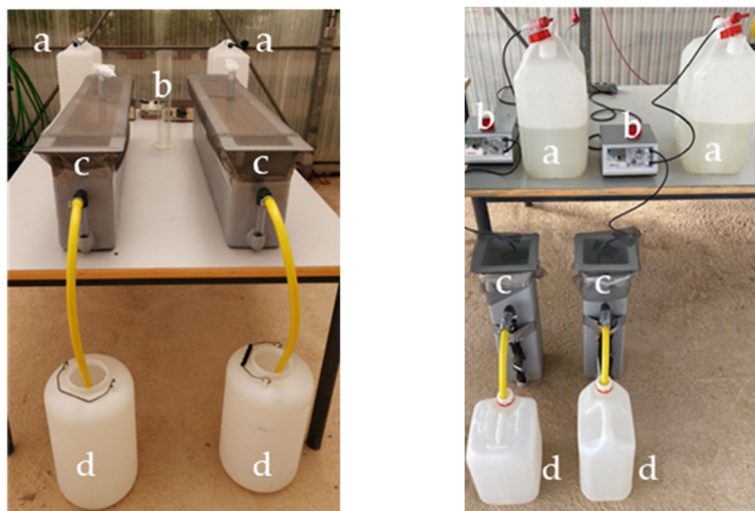


Figura 3. Biorreactores. A la izquierda: biorreactores anaerobios con flujo de agua horizontal. A la derecha: biorreactores anaerobios con flujo de agua vertical. (a) depósitos de polietileno con el agua de riego; (b) bombas peristálticas; (c) biofiltro; (d) efluentes recuperados en depósitos de polietileno. Fuente: Elaboración propia.

El influente (agua de riego) ubicado en los depósitos de polietileno (Figura 3a) era remplazado semanalmente para evitar la degradación del agua. El suministro constante de agua de riego a los biorreactores se realizó empleando bombas peristálticas (Figura 3b), con el mismo caudal de entrada en los cuatro prototipos (caudal estimado de $2,3 \text{ l día}^{-1}$ y tiempo de retención del agua en el biorreactor en torno a 4 días). Para reducir al máximo posible la evaporación, el acceso a insectos y la germinación espontánea de semillas, los biorreactores se cubrieron con una malla de 1mm situada unos 8 cm por encima de la superficie. Las dimensiones y detalles de diseño de los biorreactores se facilitan en el **Capítulo 9**.

MATERIALES Y MÉTODOS

Se utilizaron dos residuos, uno de carácter inorgánico, procedente de actividades extractivas de yacimientos calizos (grava, G). El otro residuo es orgánico, procedente de restos de poda de almendro (A). La grava utilizada fue la fracción de tamaño de grano comprendida entre de 2-3 mm, consistente en su práctica totalidad en carbonato de calcio y en menor medida de magnesio.

De tal forma, combinando los residuos y el diseño de los biorreactores, experimentamos con cuatro tipos de biorreactores:

- Flujo horizontal con grava (HG).
- Flujo horizontal con grava+poda de almendro (HA).
- Flujo vertical con grava (VG).
- Flujo vertical con grava+poda de almendro (VA).

3.6 Caracterización de las aguas

El influente (I) y los efluentes (E) -EHG, EHA, EVG y EVA- obtenidos tras la depuración con cada tratamiento fueron analizados semanalmente.

Los análisis de agua se realizaron siguiendo las directrices de los métodos de estandarización APHA (2012). De tal forma, se obtuvo el pH (método 4500-H+ y 2580), la CE (método 2510), los sólidos en suspensión (SS) (método 2540D), la demanda química de oxígeno (DQO) usando el kit de digestión con viales de HANNA (método 5220), la alcalinidad total, el contenido en bicarbonatos y carbonatos (método 4500-CO₂ y 2320D). Además, se obtuvo el contenido en nitrógeno total (N) utilizando un kit HANNA (HI94767), donde el persulfato determina el nitrógeno total por oxidación de todos los compuestos nitrogenados a nitrato.

Los cambios semanales de las concentraciones de cada uno de los parámetros, se calcularon como el porcentaje de variación según la ecuación 1 (Namaldi y Azgin, 2023):

$$\text{Variación (\%)} = (1 - (C_e / C_i)) \times 100 \quad (1)$$

Donde C_e es el valor del parámetro analizado en el efluente y C_i el del influente. Cuando el resultado de la variación es positivo hay una reducción de la concentración, por el contrario, si el negativo se produce un incremento.

3.7 Análisis estadístico

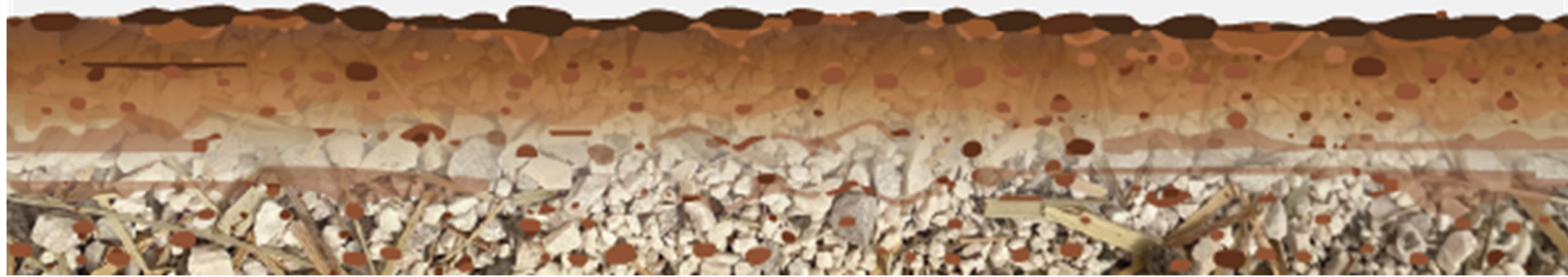
Se utilizaron diversas metodologías para conocer el valor estadístico de los resultados obtenidos. En primer lugar, se usaron estadísticas descriptivas para calcular la media y desviación estándar.

Para valorar las diferencias entre tratamientos, se empleó el análisis de varianza (ANOVA) y el test de comparación múltiple de Tukey, utilizando como herramienta informática el programa SPSS Statistics (IBM SPSS Statistics en Windows, versión 26.0. Armonk, NY, USA: IBM Corp.)

CAPÍTULO 4: Urban areas, human health and Technosols for the Green Deal.

Este capítulo corresponde con el trabajo:

Rodríguez-Espinosa, T., Navarro-Pedreño, J., Gómez, I., Jordán Vidal, M.M., Bech Borrás, J., Zorpas, A.A., 2021. Urban areas, human health and Technosols for the Green Deal. *Environmental Geochemistry and Health*, 43, 5065–5086. DOI: <https://doi.org/10.1007/s10653-021-00953-8>



ABSTRACT

Authors aim to carry out a bibliographic review as an initial approach to state of the art related to the quality of urban soils, as well as its possible link with human health. This concern arises from the need to highlight the consequences that soil could face, derived from the growth and aging of the population, as well as its predicted preference for urban settlement. Urban development may pose a challenge to the health of urban soils, due to degradative processes that it entails, such as land take, sealing, contamination, or compaction. A healthy soil is the one which maintains the capacity to support ecosystem services, so it can provide numerous benefits to human health and well-being (carbon sequestration, protection against flooding, retention and immobilization of pollutants and a growth media for vegetation and food production). This article addresses threats facing urban soils, the strategies put forward by the European Union to deal with them, as well as the issues that require further attention. Greening cities could be a consensual solution, so authors analyse whether soils of cities are ready for that challenge and what resources need to maintain soil ecosystem functions. This review proposes to use made by waste Technosols for a sustainable green city. Despite the use of Technosols as a type of soil is very recent, the interest of the scientific community in this field continues to grow.

Introduction

The consequences of climate change pose a growing threat to safety of cities and their inhabitants (Filho et al., 2019). This review has the intention to study the level of vulnerability of cities from the prism of soils and its relationship with human health.

Soils are a non-renewable resource (EC, 2020a), as it is not replenished with enough speed at which it is consumed. Further, the optimal functioning of soils is of great importance to provide ecosystem services (Brevik et al., 2018).

Soil current situation in Europe indicates that 60-70% of soils are unhealthy (EC, 2020a), implying more than 2,539,953 km² affected. Mainly due to management practices, and to a lesser extent, to air pollution and climate change (EC, 2020a). To contextualize the subject and content, authors provide specific data on the difficulties faced by soils (Table 1), and focus on the most directly linked with urban or peri-urban areas.

Table 1 Soil threats in Europe

Soil disturbance	Share of affected soil (EC, 2020a)
Contaminated sites	2.8 million potentially (but only 24% are inventoried)
Soil sealed	2.4 %
Compaction	23%
Losing carbon	cropland: 0.5% per year petlands: 50%
Residual pesticides	83% (21% of agricultural soils with cadmium concentrations above the limit for drinking water; and 6% with heavy metal content potentially unsafe for food production)
Eutrophication	65-75% of agricultural soils.
Water erosion	24%
Desertification	25% at high or very high risk

These soil degradation processes in Europe generates total annual costs of 50 billion € (EC, 2020a). Most of Table 1 issues are associated with the development of human activities, so authors take into account demographic and settlement trends.

The worldwide population in 2019, was 7.7 billion, and it's expected to grow to 10.8 billion in 2100 (United Nations, 2019). All regions will grow in total population, except Europe, which will suffer a decrease by 2100. The aging of the world population is a fact, and in some regions, like Europe, will be a more pressing phenomenon, where the share of elderly will arise near 30% by 2100, and there will be more than a half million centenarians by 2050 (Eurostat, 2019).

Between 1975 and 2015, about 92% of worldwide urban centers population has grown, and has doubled in 46% of cities. In 2015, 141 cities reached high population densities (above 20,000 people/km²). In European cities, the density is approximately between 2,001 and 5,000 residents per km², with predominantly mid-sized rather than large cities (EC, 2018). Focused on European older people (aged 65 years or more) in 2018, the 42% were living in urban regions, a 38% in intermediate regions, and only a 20% in rural regions (Eurostat, 2019).

Despite the fact that urban centers occupy less than 1% (EC, 2018), and grey infrastructure (buildings, roads and other sealed surfaces) cover approximately 3% (Edmondson et al., 2012) of the Earth's surface, they are one of the main sources of global environmental impacts, as well as being, possible the least prepared to face them (Filho et al., 2019).

The increase in urban population implies ensuring the supply of necessary resources (González-Méndez and Chávez-García, 2020), their health and well-being, the development of productive activities, transport, among others. This translates into an intensification in the ecological footprint of cities (Zambon et al., 2019), due to generation of waste and emissions (Losco and Biase, 2021), loss of greenness and biodiversity, and soil occupation (Filho et al., 2019). According to Gurney et al. (2015), cities are the main driver of climate change, emitting more than 70% of global fossil-fuel CO₂, and account for between 60 and 80% of energy consumption (UN-HABITAT, 2017).

The world consumption of biomass, fossil fuels, metals and minerals, is estimated to double and the recycling sector is projected to triple in size from 2017 to 2060 (OECD, 2019), but only 12% of the materials used in Europe in 2017 come from recycling (Eurostat, 2020a). By 2050, waste generation across the world is expected to reach 3.40 billion tones, and only 19% of waste is recovery (The World Bank, 2018). In 2018, European cities generated 492 kg of municipal waste per capita, which 47% was recycled and composted (Eurostat, 2020b).

In order to carry out the state of the art of urban soils conditions and its association with human health, we applied a methodology focused on exploring ad hoc publications on Official Institutions websites, internet search engines as well as scientific reference databases. Based on this, we explore the use of Technosols in urban and peri-urban environments in literature as a possible strategy to achieve the objectives of the European Green Deal and Sustainable Developments Goals proposed by United Nations.

Results and discussion

Urban health

The World Health Organization (WHO) defined a “healthy city as one that is continually creating and improving those physical and social environments and expanding those community resources which enable people to mutually support each other in performing all the functions of life and in developing to their maximum potential” (WHO, 1998). In 2008, WHO expressly indicated direct relationship between the health of cities and the health of their citizens (WHO, 2008).

Analyzing the health of cities is a complex purpose (Webster and Sanderson, 2012), and WHO can be the reference framework in this area. WHO considers that the city environment has a double effect on the health of citizens and on their own perception of health (WHO, 1994). Galea and Vlahov (2005) indicate physical environment of a city encompasses air, water, green areas, geological and climate conditions.

WHO (1994) developed its European Healthy Cities Network, with the aim of measuring the health of cities, and being the starting point for establishing improvement strategies. This requires the use of multisector indicators (health status, health services, lifestyle, infrastructures, environmental and socioeconomic indicators), due to the various connotations of health, and may vary depending on the source consulted (Table 2).

Table 2 Environmental quality indicators for healthy cities.

Environmental quality indicators	Reference
Air quality, water quality, water and sewage services, noise pollution, radiation, open spaces, infestations and food quality.	WHO (1994)
Derelict industrial sites, pedestrianization, sport and leisure facilities.	Webster and Sanderson (2012)
Land contamination, local food growing, flood risk, overheating, biodiversity.	London Healthy Urban Development Unit (2014)
Residential density, land use, urban sprawl and urban heat.	Prasad et al. (2016)
Physical, chemical, biological indicators. Presence of metals.	Tresch et al. (2018b)
Land use and urban design, food environment.	Pineo et al. (2018)
Soil quality index.	Zambon et al. (2019)
Concentration PM _{2.5} , emission of nitrogen oxides, municipal waste and recycling rate, ground water of good chemical status, CO ₂ emissions, Natura 2000 area in good quality, urban green areas, soil sealing and surface water of good ecological status.	Lafortune et al. (2019)
Soil health to fight rural poverty, for sustainable agriculture and forestry, for healthy and sustainable diets and urban environments, for education. Soil health and landscapes for water, supporting bioenergy production, city greening and urban agriculture, circular bioeconomy. Soil health for climate change mitigation and adaptation, supporting biodiversity and soil health supported by an enabling environment.	EC (2020a)

Few references include direct indicators of soil quality to evaluate urban health. For instance, Zambon et al. (2019) chose soil quality index to analyze urban footprint of land consumption. Recently the European Commission propose a list of soil health indicators for achieving the Sustainable Development Goals (SDGs) (EC, 2020a). The European Environmental Agency (EEA) currently use several indicators to answer key policy questions, and there are a set about land and soil (EEA, 2019). One of the indicators

included in this scope is the progress of management of contaminated sites, and concludes that in 2011 the main sources of soil contamination in Europe were waste disposal and treatment (38.1%), and industrial and commercial activities, that usually take place in urban or peri-urban settings. The most common soil pollutants in Europe are heavy metals (34.8%) and mineral oils (23.8), both possible associated with industrial development.

On this basis, European cities are making efforts to analyze their level of sustainability and implementing improvement strategies, proof of this is the variety of urban rankings index available, such as European Soot-free City Ranking, European Green City Index, Europe Quality of Life Index, European Smart Cities Ranking, Smart Sustainable Cities Ranking. Akande et al. (2019) compare these urban assessment systems, highlighting the variability of the results, due to the level of definition of the ranking scope, the lack of a type of reference city, the source of the data and its weighting methodology. Analyzing the top3 sustainable cities that appears in the comparison made by Akande et al. (2019), we observe that two of the mentioned urban sustainability evaluation programs, chose Stockholm, Copenhagen and Zurich.

The interest of European cities to be an example in sustainability, encourages cities to set ambitious goals, such as Copenhagen, plans to be the world's first carbon-neutral capital city by 2025, and Stockholm, purposes to achieve 100% renewable energy by 2040 (Lafortune et al., 2019).

Analyzing more references to know the health status of European cities, the SDGs Index, shows the degree of compliance with the 17 SDGs on the Agenda 2030 of 45 capital cities and large metropolitan areas. The top3 cities in that Index are Oslo, Stockholm and Helsinki. However, performance data suggest that Europe will not meet the SDGs by 2030. Possibly, because great challenges remain to be achieved in the objectives more related to the environmental field: SGD11 Sustainable cities and communities, SDG 12 Responsible Consumption and Production, SDG 13 Climate Action, SDG 14 Life Below Water and SDG 15 Life on Land (where urban green areas and soil sealing are evaluated). The results of the indicators and compliance with the SDG 3 Good Health and Well-being show that nine cities have reached the objective, but the majority present challenges remain (Lafortune et al., 2019).

Currently it is possible to know the degree of sustainable performance of the main cities of countries such as The United States of America, Italy and Spain (Lafortune et al., 2019). The analysis of the SGDs performance in 100 Spanish cities could help to face the challenges of urban clustering, since Spain is one of the European countries with the largest urban population share (Sánchez de Madariaga et al., 2018).

To assess the health of cities based on indicators that do not use a specific methodology or focus on a specific city, the environmental quality of the urban ecosystem, could be a suitable option, due to their undeniable connection (Oliver and Gregory, 2015). The EEA warns about environmental status in Europe (air pollution, climate change, exposure to chemicals and less ratio of green areas access), which represents a detriment to the health and quality of life of citizens, being the cause 13% of deaths in the European Union. What's more, EEA considers we could avoid these deaths if we focus on improving environmental quality. In fact, the COVID-19 pandemic illustrates it, probably been attributed to ecosystem degradation due to zoonosis processes, and one of the potential anthropic actions that accelerate it is urbanization (because of the land use change and the unsustainable consumption of natural resources) (EEA, 2020a).

Further, the climate change not only poses serious threats to the health of citizens, indeed is a severe source of stress to urban infrastructure and entire urban system (The World Bank, 2010), due to greater exposure and lower adaptation capacity (Filho et al., 2019). The vulnerability of cities, and therefore the well-being of their inhabitants, is most highly correlated with their degree of dependence on natural resources and ecosystem services, which in turn, the ecosystem services are linked to the level of impact and the ability to adapt to climate change (Barnett and Adger, 2007). Maybe, the battlefields against the causes and consequences of climate change are our urban areas; therefore, it is key to propose a sustainable city model.

Healthy soil

Continuing with the relevance that ecosystem services represent on human welfare, authors consider convenient to list them (UN-HABITAT and WHO, 2020):

- Supporting (nutrient cycling, soil formation, primary production and vegetation medium).
- Provisioning (natural resources, water and food).
- Regulating (climate, pollution buffering, disease regulation and water purification).
- Cultural (aesthetic, spiritual, educational and recreational).

Most of these services develop directly on the soil and influence by its conditions. Soil health is “the continued capacity of soils to support ecosystem services” (EC, 2020a). Defining this concept is not an easy task, and will need more discussion (Ling Ng and Zhang, 2019) meanwhile authors want to add that soil health could be associated with soil ability to contribute to human health. Consideration that may be in accordance with its importance in safe warding human health (Montanarella and Panagos, 2021).

Recently, the European Commission agree on 8 indicators to measure soil health (EC, 2020a): “presence of soil pollutants, excess nutrients and salts, soil organic carbon stock, soil structure including soil bulk density and absence of soil sealing and erosion, soil biodiversity, soil nutrients and acidity (pH), vegetation cover, landscape heterogeneity and forest cover”.

Human activities can compromise the health of soil because of the presence of polluting substances (Cachada et al., 2012) for example, emissions or discharges from industries, emissions from road traffic, agricultural fertilizers and pesticides, among others. As well, human development, can decrease soil physical, chemical or biological functionality, for example, due to the urbanization process (Li et al., 2012), which causes compaction and sealing (Li et al., 2018), and reduces their capacity for food production, pollution attenuation, hydrological cycling and energy balance (Munafò et al., 2013).

Soil pollutants can affect human health through the following pathways of exposure: digestive route by consuming food that has accumulated pollutants from soils, dermal exposure, or by inhalation of vaporized pollutants. There is also the possibility of secondary contamination from soils, by coming into contact with contaminated water or by deposition of atmospheric pollutants (Rodríguez-Eugenio et al., 2018). Although it may seem otherwise, citizens are also in close contact with soil, not only due to their food intake, but also due to the development of their professional, sports and leisure activities, during their travels, even next to their homes. Urban soil surrounds us, and are present in parks, along roads, sports fields, urban rivers, peripheral areas, near buildings and infrastructures (Li et al., 2018), as well as public or private gardens, playgrounds, beaches, brownfield sites, even in urban orchard-gardens, rooftops and vertical gardens, which are increasing their presence in our cities.

Table 3 References related to urban soil pollution in Europe.

Study area	Urban soil quality assessment	Reference
Italy land uses (included urban areas)	Soil organic matter content and bulk density in Italy	Constantini and Lorenzetti (2013)
Topsoil, rubble soils, and natural soils in Berlin (Germany)	Heavy metals and benzo[a]pirene	Abel et al. (2015)
Sealed soil with asphalt or concrete, semipermeable and non-sealed soils in Torun (Poland)	Heavy metals and soil sealing	Charzyński et al. (2017)
Urban garden (allotment and home gardens) in Zurich (Switzerland)	Physical, chemical, biological and heavy metals content	Tresch et al. (2018b)
Roadside linden trees soil, in Paris (France)	Physical and chemical parameters. Trace elements.	Quénéa et al. (2019)
Lawn, forest, urban agriculture, green roof and peri-urban agriculture soils, in Santiago de Compostela (Spain)	Physical and chemical parameters	Paradelo et al. (2020)
Periurban area soil, designed for residential use, in Madrid (Spain)	As concentration	Baragaño et al. (2020)
Urban and peri-urban areas (included parks, open spaces, salt marshes, agricultural lands and industrial areas), in Huelva (Spain)	Potentially toxic elements (PTEs)	Guillén et al. (2021)

The interactions between soil and health are complex, because the heterogeneity of urban soils and anthropic activities. Further, citizens expose to several types of pollutants, and the level of exposure and our autoimmune capacity can vary throughout our lives. So, cities can be areas of generation of pollution, as well as, which could be where most people are exposed (Table 3).

Table 3 analyze urban quality pollution versus several land uses. In such way, topsoil and rubble subsoils in Berlin (Germany) show elevated concentrations of heavy metals and benzo[a]pirene (Abel et al., 2015), while artificial soils in Torun (Poland) are little altered by heavy metals (Charzyński et al., 2017). A recent research of lawn, forest, urban agriculture, green roof and peripheral agriculture soils in Santiago de Compostela (Spain), concludes that soils preserve from the negative consequences of urbanization processes, since they are in a similar state to natural soils. Despite this, collected values of pH, salinity, Ca and Mg content, in urban gardens, surpass those of the peri-urban agricultural soils, mainly due to more intensive fertilization practices on urban gardens (Paradelo et al., 2020). The need to apply sustainable management is also manifested in the study of urban gardens in Zurich and considered crucial for the urban ecosystem (Tresch et al., 2018a). In turn, the high contamination data in the soils of Huelva (Spain) show how relevant is to know the health risk that soils may entail, with the intention of planning the land uses to preserve the health of people (Guillén et al., 2021).

Li et al. (2018) maintain that analyzing potential risk to health requires evaluating the level of exposure to the pollutant, and the severity of the damage it may cause (Li et al., 2018). Guillén et al. (2021) carry out research to assess the risk to adult or children health related to site-specific relative bio-accessibility of toxics elements present in urban soil. Although the results show that children are the segment of the population with the highest total carcinogenic risk, in many analyzed samples the carcinogenic risk levels exceeded limits proposed by the regulations, affecting both adults and children. A peripheral green and recreational area reached extremely risk, which in turn are the areas with the highest probability of residential development in its vicinity.

Directly related to the urbanization process, Charzyński et al. (2017) highlight soil sealing consequences for citizens well-being. Soil sealing is one of the greatest threats mentioned in the Soil Thematic Strategy (EC, 2006), as a syndrome of land degradation

(Tobias et al., 2018), and for developing its functions (Munafò et al., 2013). It consequently increases the risk of potential floods and water scarcity, endangers biodiversity, and leads to environmental change on a larger scale (EC, 2018). In addition, supposes the increase of urban heat island effects (EC, 2012).

Although efforts are being made to reverse soil degradation, some challenges remain to be faced. The sealed surface in Europe reaches 2,4% (Table 1) and only 13% of urban land recycled (EEA, 2020a). In some cases, it is considered that soil sealing is not reversible (Constantini and Lorenzetti, 2013). In addition, 2.323 contaminated sites remedied (EEA, 2020a), compared to 2.8 million potentially contaminated sites (Table 1).

Further, the presence of bacteria resistant to antibiotics has been detected in soils strongly affected by human presence (Popowska et al., 2011). Soil biodiversity is greatly affected in urban environments and the presence of human derived microorganisms can alter the soil ecosystem.

Healthy soil and health benefits

Therefore, as previously stated, due to degradation and presence of pollutants, some unhealthy soils can be a source of risk to human health (Baragaño et al., 2020). In fact, many authors defend this interconnection (Brevik et al., 2020; Wu et al., 2015). Likewise, a degraded soil can be a risk factor for our health; a healthy soil can be a component of well-being. Authors consider how a healthy soil silently watches over our health (Table 4).

One of the most significant benefits of urban soils related to hazard prevention and environment quality for citizens are “protection against rainstorm damage and flooding events by allowing water infiltration, decomposition of organic contaminants, retention and immobilization of contaminant, sequestration of carbon, buffering of climate mainly through cooling by evaporation, and a media for vegetation growth” (Lehmann, 2006).

Table 4 Soil benefits for human health

Soil benefits	Reference
Protection against rainstorm damage and flooding. Media for vegetation growth.	Lehmann (2006)
Allow biochemical cycles.	Lehmann (2006) Macías and Camps Arbostain (2010)
Erosion control	Macías and Camps Arbostain (2010)
Reduce urban heat island effect.	Lehmann (2006) Bokaie et al. (2016)
Host biodiversity.	EC (2012)
Cultural value and traditional landscape.	Constantini and Lorenzetti (2013)
Control pathogens. Provide antibiotics and medicines.	Wall et al. (2015)
Urban agriculture for nutritional health and local economy. Personal wellness and community betterment.	Kumar and Hundal (2016)
Touristic potential and landscape connectivity.	Tobias et al. (2018)
Decontamination (retention, phytoremediation and microbial bioremediation).	Lehmann (2006) Yap and Peng (2019)
Energy conservation in buildings, preventing acid rain, reduce sound exposure and enhance aesthetic value (rooftop with soil).	Cascone (2019)
Circular economy (use of wastes)	Fourvel et al. (2019) Barredo et al. (2020) Ugolini et al. (2020)
Against climate change effects and to achieve emission neutrality (store organic carbon).	Falkowski et al. (2000) Lehmann (2006) Edmondson et al. (2012) Brevik et al. (2018) Navarro-Pedreño et al. (2021) Montanarella and Panagos (2021)

Soil ability to absorb and transmit heat, and its contribution to urban heat island effect, has been studied related to land use by Bokaie et al. (2016). The areas with vegetation cover are those with the lowest average temperature, however the areas with the highest average temperature surprisingly were the bare land, and in second place the asphalt-paved surfaces, with a difference between the highest and lowest average of 8°C. What is

more, they concluded the risk of respiratory and heart diseases increases in residential areas most affected by urban heat island consequences.

Parallel to that, the incorporation of soils in rooftops as a substrate for vegetation also contributes to improve air quality levels, to conserve energy in buildings, as well, to reduce sound exposure (Cascone, 2019). Vegetated rooftops and green urban areas, require healthy soil in order to ensure plant survival and improvement of aesthetic value (Cascone, 2019).

The protection of the aesthetic and cultural values of the soils and the characteristic landscapes that make up (Constantini and Lorenzetti, 2013), enhance tourism and generate economic benefits for the local population (Tobias et al., 2018). In turn, the security of having quality food, which in the case of those grown in urban orchard-gardens, promote local community betterment and self-sufficiency (Kumar and Hundal, 2016).

Soils (and of course, urban soils), play a main role in the greenhouse gases cycle and erosion control, so it will be essential to reach a soil optimal operating state, to be able to deploy all their purifying and regulating potential against the effects of climate change and to achieve emission neutrality (Montanarella and Panagos, 2021). The loss of soil due to erosion processes leads to the loss of stored organic carbon in the surface horizon, in Mediterranean dry climate areas, the amount of organic carbon stored can decrease from 1-3 t C ha⁻¹ cm⁻¹ to < 1 t C ha⁻¹ cm⁻¹ (Macías and Camps Arbestain, 2010). At the same time, waste management is a source of greenhouse gas emissions, when its destination is disposal or incineration, in addition the essential components are not reincorporated into biochemical cycles (Macías and Camps Arbestain, 2010). Greenhouse gases cycles (CO₂, CH₄ and N₂O) can be regulated by soils (Brevik et al., 2018). Soils are a key piece in the global carbon cycle (Navarro-Pedreño et al., 2021), in fact, the vegetation and soil carbon reservoir on Earth, is three times greater than the atmospheric pool (Falkowski et al., 2000). Therefore, some urban environments are a source of CO₂ emission, and at the same time, urban ecosystems can be carbon reservoirs due to the storage in vegetation and in urban soils. Cambou et al. (2021) consider urban area soil organic carbon stock mainly depends on whether the soil is sealed or not. Carbon entry into sealed soils is practically impossible (Cambou et al., 2021), although Cambou

et al. (2018) mention the importance of analyzing subsoil organic carbon storage, in urban sealed soils because total amount is relevant. In fact, approximately 69% of carbon storage in a citywide related to greenspace soil, 13% on sealed soil and 18% on vegetation (Edmondson et al., 2012). Hence, it is convenient to identify carbon storage controlling factors, in urban areas. For instance, in open urban soils, management practices (mulching or return of clipping) and land use (highest average soil organic carbon stock in garden public place and park and lowest in roadside) are crucial for soil organic carbon stock, among others (Cambou et al., 2021).

The compilation of numerous references on actions to mitigate and adapt to climate change in urban areas by Sharifi (2020), revealed that most of them are related to urban soils: land use, urban design (connections, ventilation, shading, orientation, water permeable surfaces and water harvesting), waste recycling and reuse, green roof, roof garden, green façade, network of parks, urban greenery and open spaces, urban nature protection (forests, green belt, protection of natural habitats), urban agriculture, xeriscaping and infill and brownfield development.

Soil can host at least one fourth of the Earth's biodiversity (EC, 2012). The biodiversity of microorganisms that soil host is crucial for the control of those that are pathogens for humans, for our stimulation immune system to control allergic diseases, for providing antibiotics and medicines (Wall et al., 2015), and as well as for the decontamination of soils through phytoremediation and microbial bioremediation (Yap and Peng, 2019).

It seems interesting to mention that the EEA (2020a), in its healthy environment-healthy lives report, refers to the Sustainable Development Goals (SDG), approved by the United Nations (UN), aims to reduce deaths related to environmental pollution, to reach a toxic free air, water and soil. Furthermore, contributes an environmental factor list that cause impact on human health, as environmental human health indicators ("air quality, noise, indoor air quality, extreme weather, heatwaves, floods and chemicals"), but the soil is not included. Since soil host of most of the ecosystem services on which people's health depends, authors propose to analyze soil health as a possible human health stressor too.

Europe Green Strategy

Europe has proposed to be the first emission-neutral continent in 2050, based on the document the European Green Deal (EGD) (EC, 2019), protecting natural capital, and the health and well-being of citizens from environmental risks and impacts. To reach it, the European Commissions has developed several strategies and regulations, in which the sustainable management of our natural resources (soil and waste as a resource) plays a main role:

- Biodiversity Strategy 2030 (for bringing nature back into our lives) designed for protecting at least 30% of the land and bringing back at least 10% of natural area under high-diversity landscape features (EC, 2020d). Related to urban areas, the Biodiversity Strategy focus on planting at least 3 billion additional trees (facilitating urban tree planting, as well) and requesting cities to develop ambitious Urban Greening Plans by the end of 2021. Efforts will direct towards protecting and increasing green urban ecosystem by using green infrastructure and nature-based solutions and reducing pollution to zero (soil, water and air). Further, addressing land take and restoring soil ecosystems (future Soil Thematic Strategy 2021), supporting the recovery of nature (at least 15% of degraded ecosystems, prioritizing ecosystem with the most potential to capture and store carbon), limiting soil sealing and urban sprawl, and tackling pollution and invasive alien species.
- European Climate Law with the aim of reducing CO₂ emissions and increase sink of soils (EC, 2020e).
- Farm to Fork Strategy 2020 for designing a healthy and environmentally friendly food system, bringing back at least 10% of agricultural area under high-diversity landscape features (EC, 2020b).
- Circular economy action plan, for increasing recycling, promoting initiatives to reduce soil sealing, rehabilitate abandoned or contaminated brownfields and increase the safe, sustainable and circular use of excavated soils (EC, 2020c).

Waiting to know the objectives stipulated by the Soil Thematic Strategic 2021, the Seventh Environment Action Program (7th EAP) promote no net land take in the European Union by 2050 (EU, 2013). Previously, the Thematic Strategy for Soil Protection launched on 2006 (EC, 2006), is considered as the precursor to soil protection initiative in Europe, for preventing and restoring soil degradation (Payá Pérez and Rodríguez Eugenio, 2018).

The EGD is a great challenge for our current model of life, alien to nature, and it will undoubtedly require great efforts. The urban environment faces ambitious and necessary objectives for our health and quality of life. The involvement of cities and the European Commission in promoting and rewarding these endeavors is evident with the Urban Agenda for the EU-Pact of Amsterdam (signed in 2016) and the following awards. The European Green Capital Award launched in 2008 requires indicators of sustainable land use and green growth, among others. The European Green Leaf Award launched in 2014, aims at smaller cities, and uses indicators of sustainable land use and circular economy, for instance (EC, 2021).

The EGD sets out to focus innovation and research efforts to achieve large-scale changes in adaptation to climate change, cities, soil, and oceans. The EGD considers that Europeans can reach their green commitment, by adopting Green Infrastructure (GI) methodology to support nature-based solutions (NBS). In accordance to the European Green Infrastructure Strategy (EC, 2013), GI defined as “strategically planned network of natural and semi-natural areas with other environmental features designed and managed to deliver a wide range of ecosystem services. GI is present in rural and urban settings”. Despite the wide spectrum of environments for which GI are applied, in practice it seems to be mainly in urban areas (Chatzimentor et al., 2020). Possibly because its primary objective is to reproduce natural ecosystems services and that is essential for soils and human health (Coutts and Hahn, 2015; EC, 2013) and because of less presence of green areas in urban areas.

Are urban soils prepared for The Green Deal?

As previously stated, European soils face several threats (Table 1), amongst them, authors underline urban soil pollution (Table 3). This is not to say that all urban soils are degraded or polluted, as reflected in the findings of Paradelo et al. (2020). However, some urban soils need to be restored (Abel et al., 2015; Guillén et al., 2021), with the aim that cities can be service-facilitating ecosystems for the health and safety of their inhabitants.

In accordance with the EGD (EC, 2019), authors consider GI and NBS as the best tool for remediation of contaminated urban sites (Li et al., 2018; Baragaño et al., 2020), for carbon sequestration (González-Méndez and Chávez-García, 2020) and for reducing flooding risk and biodiversity conservation (Demiroglu et al., 2014). GI are capable of regulating temperature due to soil insulating properties, as well as because soils are the substrate on which vegetation develops, generating protection against temperatures with its shade and evapotranspiration. In Mediterranean environments, green walls can reduce around 59% of energy consumption for cooling (González-Méndez and Chávez-García, 2020). Berndtsson (2010) studied the crucial role that green roofs plays retaining pollutants carried during rain runoff.

Thus, we are interested in knowing how green European cities are at present and what resources will need for their greening plans.

The concept of green spaces, can include “public green areas used predominantly for recreation such as gardens, zoos, parks, and suburban natural and forests, or green areas bordered by urban areas that are managed or used for recreational purposes” (WHO, 2016). Sometimes, research on urban green areas shows differences in the conclusions, perhaps due to the selection criteria of what is a green space or not. This is the case of the study carried out by Webster and Sanderson (2012) about healthy cities indicators, and the calculation of the surface area of urban green spaces, varies widely, from 0.31% in Arezzo (Italy) to 61.53% in Gothenburg (Sweden).

Searching for references that have measured green areas, authors found the following approaches:

- SDG15 fulfillment of 45 European capital cities and large metropolitan areas (Lafortune et al., 2019): the indicators to measure the achievement of the SDG15, are: Natura 2000 Area in good quality (%), urban green area (%), soil sealing (%) and surface water of good ecological status (%). Only two cities (Oslo and Ljubljana) have achieved SDG15. Authors calculate an average value of the green area percentage present in the 45 cities chosen, obtaining 19.82%. The urban green area percentage results vary greatly, authors provide the top3 (63.72 % Oslo, 55.18% Marseille and 42.42% Ljubljana) and bottom3 (4.83% Milan, 4.38% Amsterdam and 3.55% Porto).
- Proximity to green space (WHO, 2016): The generalized indicator in Europe is the accessibility to green areas, measured as the percentage of citizens living within 300 m from a public open area of minimum size 0.5 hectares from a distance of 15-minute walk. Only 44 % European citizens have access to a green area 300 meters away (Vandecasteele et al., 2019), maximum distance considered by WHO as adequate (EC, 2018).
- Criteria for the perception of citizen satisfaction (EC, 2020f): the percentage of total satisfaction with green area evaluated in selected cities. Concludes that 77% of residents are satisfied with green spaces. Differences are observed in the percentage of satisfaction between cities in northern European countries, where citizens are more satisfied (96% Malmö, 94% Munich or Helsinki 94%), while in southeastern European countries, satisfaction share is lower (29% Athens, 30% Naples or 31% Heraklion). It would not be appropriate to generalize that the geographical location of the countries can predefine satisfaction, since there are cities in southern Europe with high satisfaction rates (86% Bologna, 81% Turin or 83% Oviedo).

Authors compare data of green area percentage versus level of satisfaction (Table 5).

Table 5 Percentage comparison of green area and citizen satisfaction.

City	% urban green área (Lafortune et al., 2019)	% urban green area satisfaction (EC, 2020f)
Oslo	63.72 %	94 %
Helsinki	27.68 %	94 %
Bratislava	27.52 %	55 %
Munich	16.27 %	94 %
London	9.72 %	93 %
Valleta	7.00 %	44 %
Athens	6.90 %	29 %

Analyzing Table 5 seems that key factor in the field of satisfaction is not so much the amount of green space percentage, but its accessibility and distribution (could be the case of Oslo and Munich). For example, a city with a large number of green spaces, but far from areas with the highest population density, provides less accessibility. In addition, cities with the same accessibility to green areas can obtain different satisfaction rates, so the quality and maintenance of green areas can also influence (EC, 2020f). Consideration that is consistent with WHO (2016), in relation to planning of green areas, prioritizes the presence of small green areas close to areas with the highest population density, and large green areas in the surroundings, ensuring the adequate connection between the green areas. The relevant enquiry is that citizen could appreciate the views of green spaces from their own home, since it provides psychological benefits (WHO, 2016). As well as being able to spend time enjoying larger green spaces, to obtain more significant benefits for their health (a more active lifestyle, better environmental conditions, among others) (Ridgley et al., 2020; Lovell et al., 2014).

Furthermore, the size of green urban areas is a strong determinant in the soil organic carbon stock. Thus, larger green urban areas (≥ 5 ha) have higher averages of soil organic carbon stock (12.3 ± 3.5 kg C m⁻²), compared to averages (9.6 ± 4.0 kg C m⁻²) of smaller areas (≤ 5 ha) (Cambou et al., 2021).

Therefore, cities can decide to increase the average of green areas to comply with the SDG15, to meet the considerations of the EGD, to improve the health of their citizens, to compensate for the loss of ecosystem services or just to increase ecosystem services. At

this point, European cities will require options to develop their greening strategy, as sustainable as possible, without compromising resources as land use, water or soil.

The potentially green urban area is complicated to measure, a study of the stock of buildings in Vienna, estimated 12,000 ha of façades and 1,800 ha of roofs (Stangl et al., 2019). In fact, rooftops occupy 20-30% of the total area of a city (González-Méndez and Chávez-García, 2020), surface potentially suitable for revegetation.

Tobias et al. (2018) consider cities greening begins with brownfields regeneration, avoiding land take. Moreover, conclude that recycled brownfields provide ecosystem services especially if they are unsealed, soil restored, and not compacted. Some European countries are betting on greenings existing surfaces, for example, rooftop. In 2014, there were 86,000,000 m² of green roofs in Germany, with a clear annual growth trend (Cascone, 2019). In addition, to restore, expand and protect urban green areas (existing and potential), to achieve a fully functional urban ecosystem, they have to connect as an ecological network (Losco and Biase, 2021).

Authors found articles that quantify the water needs of the new green city paradigm (Ruíz-Pérez et al., 2020). This article estimates the water footprint of an urban green area in Sevilla (Spain), using various patterns of plant species. Conclusions indicate that green areas with autochthonous scrub require the least volume of rainfall water (from 0, 13 to 0, 14 m³ m⁻²), the least volume of groundwater or irrigation (from 0, 05 to 0, 08 m³ m⁻²) and allow maximum recharge of aquifers and runoff (from 0, 38 to 0, 42 m³ m⁻²). On the contrary, the choice of ornamental rosebush, requires the highest value for both rainwater input (0, 31 m³ m⁻²) and irrigation input (0, 46 m³ m⁻²) contributing the least amount of water to aquifers or runoff. To study the quantity and quality of water required to host the new urban-natural landscape, it is complicated, since it will depend on the type of climatic zone, the nutritional needs of the plant species and the systemic functions need to be recovered or enhanced.

The introduction of new green areas would lead to an increase in required water and soil resources for plant maintenance. With the laudable intention of bioremediation or revegetation, we can take in consideration not extracting soils from other areas, since we generate another problem. According to González-Méndez and Chávez-García (2020), the most used substrate for GI is natural soil. The amount of topsoil from the surrounding

areas imported to meet the land needs in urban areas estimated in 3 million of $\text{m}^3 \text{yr}^{-1}$ in France (Rokia et al., 2014). However, the search in the field of the soil footprint of city greening has not been so fruitful, being a possible new research area.

Technosols for the European Green Deal

Soils are a fundamental component of green infrastructure (Deeb et al., 2018), and a none common solution for the EGD urban needs (Deeb et al., 2020) could be use of wastes to construct new urban soils (Pruvost et al., 2020; Li et al., 2018), as Technosols. In fact, urban soils can be made of exogenous materials and due to disturbances of human activities; they have lost their natural functions, becoming Technosols (IUSS, 2015).

Based on the circular economy, we propose the use of waste from human activity for generating urban Technosols, avoiding new natural resource extractions and increasing valuation rates. Therefore, various references seek to verify whether these Technosols can be functional, testing capacity for plant growth, physico-chemical parameters, reaching the conclusion that Technosols made by urban wastes can be a great option for urban greening (Barredo et al., 2020; Fourvel et al., 2019; Ugolini et al., 2020). Technosols even can be designed to store more organic carbon than natural soils (Rees et al., 2019), for thermal and water management and for biodiversity increased (González-Méndez and Chávez-García, 2020), and for the reclamation of contaminated urban sites maintaining nutrient cycling functions (Hafeez et al., 2012). Technosols are an optimal solution that does not compromise environmental or human health (Herrán Fernández et al., 2016; Baragaño et al., 2020). A European regulatory framework that contemplates not only limitations but possible uses of waste and testing methodology to comply with would be very useful. Moreover, this will be act as an example for other regulations.

Therefore, designing and applying Technosols is a valid strategy to face climate change (Macías and Camps Arbestain, 2010), and achieve a sustainable city model.

The modification of soil due to human activity would be contemporaneous with our presence on Earth. Named as anthropogenic soils and defined as “soils that have been

modified, influenced, and/or altered by human activities” (Capra et al., 2015), they have been studied extensively, mainly since explosive urban development in the 2000s.

One of the first definitions that expressly indicated the concept of Technosols is “other soils dominated by technogenic soil materials (refers to all anthropo-geomorphic soil materials created as the result of technical processes) a depth of 100 cm or a lithic or paralithic contact, whichever is shallower” (Rossiter and Burghardt, 2003). Lehman (2006) highlights the close relationship of Technosols with urban soils: “having technic soil material with an arte-fact content by volume of more than 50% for a depth of at least 10 cm, starting within 10 cm from the soil surface”. Considering technic soil as “soil material showing evidence of urban, industrial and related activities, and evidence is visible by a content of arte-facts by volume equal to or more than 20%”.

More recently, Technosols definition indicates that “contain artefacts \geq 20% (by volume, weighted average) in the upper 100 cm of the soil surface or to continuous rock or technic hard material” (IUSS, 2015).

Technosols have been created unintentionally (Santos et al., 2016) by humans, associated with the manipulation of the soils where human activities take place. As discussed before, humans can formulate soils with a specific purpose, with a greater or lesser technical complexity, based on empirical checks on its functional capacity. This second option is quite recent, and the majority of articles analyze the characteristics of Technosols applied in mining activities, possibly due to the need to deposit waste in landfill sites and to decontaminate mine lands (Rivas-Pérez et al., 2016; Arránz-González, 2011).

As mention before, notwithstanding, several authors’ verified functional behavior of Technosols made by waste, this quality was not included in Technosols' own definition (Séré et al., 2008). This definition may be suitable for soils manipulated and altered by humans, for structural purposes (base for infrastructures, rubbles or waste landfills, or areas affected by a land movement), but for technically designed soils with a specific mission, a more detailed definition is needed. Most of the authors agree on its composition (artefacts, such as, wastes, materials, soils), and its human origin; however, the possible usefulness or the functional services Technosols provide are not mentioned. An initial approach to define Technosols in terms of their functional viability recently provided, in

which the need to be suitable for the development of vegetation is attributed (Deeb et al., 2020).

Although we consider this definition as one of the most appropriate, it is necessary to point out that Technosols are soils designed with the intention of providing ecosystem services equal to those offered by natural soils, or to enhance an ecosystem service therefore it would surpass natural soils, ensuring human and environmental health.

In such a way, after discerning the environmental status of cities and analyzing the programs related to the Europe Green Strategy in the previous introduction, we carry out a bibliographic analysis on the use of made by waste Technosols, for improving urban soils conditions and inhabitant's health, as both should be objectives of any political action associated to the EGD.

Technosols lexical form

Using the Scopus online database for searching the word "Technosols" authors found 333 references (search scope abstract, article title and key words), and 1,081 references expanding to all search fields. In order to carry out a more accurate and focused study on articles based on the development and application of Technosols, authors define the quest scope limited to abstract, article title and key words, as our representative population.

If we explore the term "Technosol", 321 references appear, so authors consider that its use in the plural form is more widespread, choosing it as our official designation for this article. Due to the possible variations in the denomination, we analyze the possible use of similar words such as "Technosoil" or "Technosoils", from which almost no references are obtained, 8 and 7 references respectively. The exam for the word "Tecnosol", yields scarce references, because it is translated into Spanish or Portuguese.

Mainly Russian, Polish and Bulgarian affiliation authors, appearing in just only 6% of the references, observe the use of the term "Technogenic soil" as a synonym for Technosol. It is not widespread use and it is confined to Eastern European countries,

probably because Technosols are recognized in the Russian Soil Classification System as Technogenic superficial formations (IUSS, 2015).

Technosols interest evolution

Observing the chronology of publications, the first reference that includes the word “Technosols” in its title dates from 2005. The second from 2006, possible because the term “Technosols” was first mentioned in 2003 (Rossiter and Burghardt, 2003) and later was considered the introduction of the Technosols to the International Soil Classification System WRB in 2006 (IUSS, 2006). Undoubtedly, the use of Technosols as a type of soil is very recent compared to the beginning of the study of soil by modern science. The search for the term “soil” in Scopus on-line database provides 1,049,826 references, and the first reference dates from the year 1842.

Analyzing the Technosols published references histogram (Fig.1) authors observe an upward trend in the number of publications, reaching its maximum in 2018 with 59 references. Authors highlight the most prolific period with a total of 290 references (this implies 88 % of the total), from 2013 to 2020. The average per year of the number of published references and citations is 21 and 186, respectively.

While we notice that the number of references is most likely to maintain growth dynamics, on the contrary, we cannot indicate the same in the area of the number of citations made per year (Fig.1). Since 2013, the number of mentions has shown a strong increase, reaching its maximum in 2017 with 358 citations, however, from this moment on its trend reversed towards a drastic slowdown, not knowing the causes.

Investigating the most prolific writers in the field of Technosols, authors focus on the top5, with France (Schwartz, C.; Morel, J.L.; Watteau, F.; Séré, G) and Spain (Macías, F.) being the leading countries in research on this topic, covering 22.52% of total publications. It is worth mentioning the relevance of Eastern European countries, as they follow in the affiliation of the authors with the most publications (Pietrzykowski, M.;

Charzynski, P.; Greinert, A.; Minkina, T.). The format of most references (87.99%) corresponds to article, being the journal, the source type chosen in 92.19%.

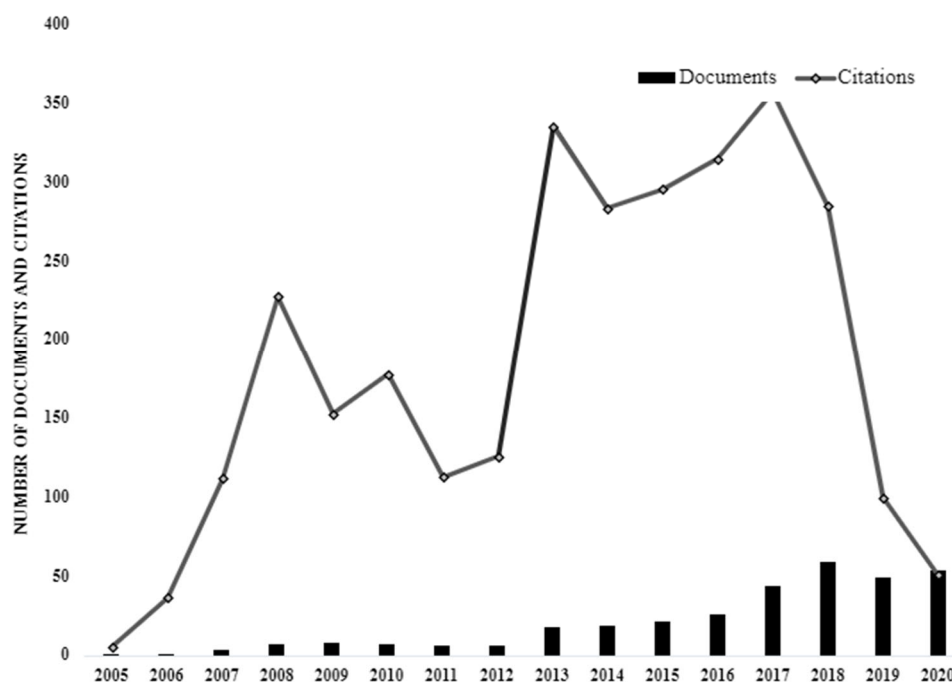


Fig.1 Number of documents and citations per year

Technosols fields of use

Almost half of the references (151 articles) are included in the ambit of “Mining and industrial activity” (Fig.2). Their main objective is to study anthropized soils due to the development of mining activities (Santos et al., 2019; Moreno-Barriga et al., 2017; Zornoza et al., 2017), in such way; many references analyze the evolution of soils over time, as well as studying the formulation of new Technosols to fill any deficiency or to amend the presence of polluting substances. In most cases, they are Technosols created with mining activity residues and will be applied in the mining operations themselves. In

the industrial field, authors found some articles related to the petrochemical, textile and ammunition industry (Thouin et al., 2019).

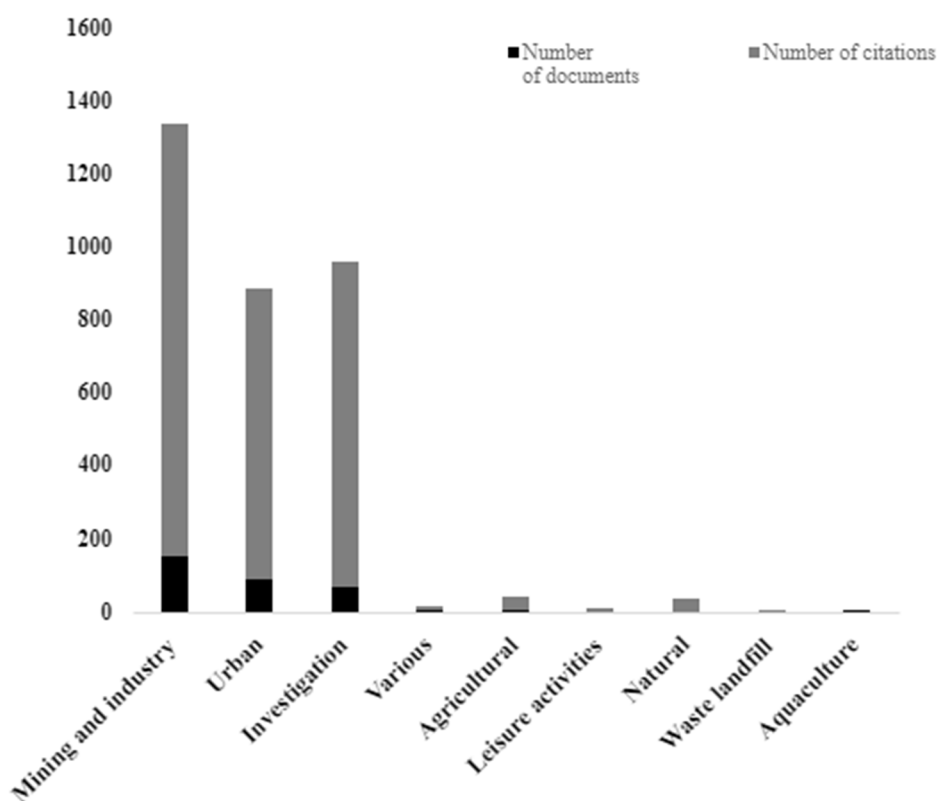


Fig.2 Number of documents and citations related to scope of use (from 2005 to 2020)

The next largest group (Fig.2), with 89 references, involves the use or study of Technosols in urban areas. Among issues addressed by authors (Baragaño et al., 2020; Rees et al., 2019; Charzyński et al., 2017) mainly, evaluate quality of urban soils (soil sealing or compaction, contamination and carbon sequestration). As well, formulate new Technosols for soil improvement by using municipal waste, for instance, (Barredo et al., 2020; Deeb et al., 2020; Ugolini et al., 2020), which can be used for city revegetation (rooftops, parks, brownfield reclamation).

The 70 articles included in the “Investigation” category (Fig.2) are documents that study pedogenesis, classification, formulation and analytical methods in general, without

detailing the use of Technosols for a specific purpose. The references classified as “Various” (only five articles), are investigations that compare the soils located in different settings.

Authors mention the existence of a minority of articles related to activities as diverse as agriculture (Rokia et al., 2014), recreational activities as golf courses (Obear et al., 2017), natural spaces, waste landfill (associated with municipal waste dumps), and aqua culture (Cortinhas et al., 2020), (Fig.2).

According to the data presented by Fig. 2, the references that arouse the most interest by the authors are mining and industry, followed by research references without a specific use, and thirdly those associated with urban areas.

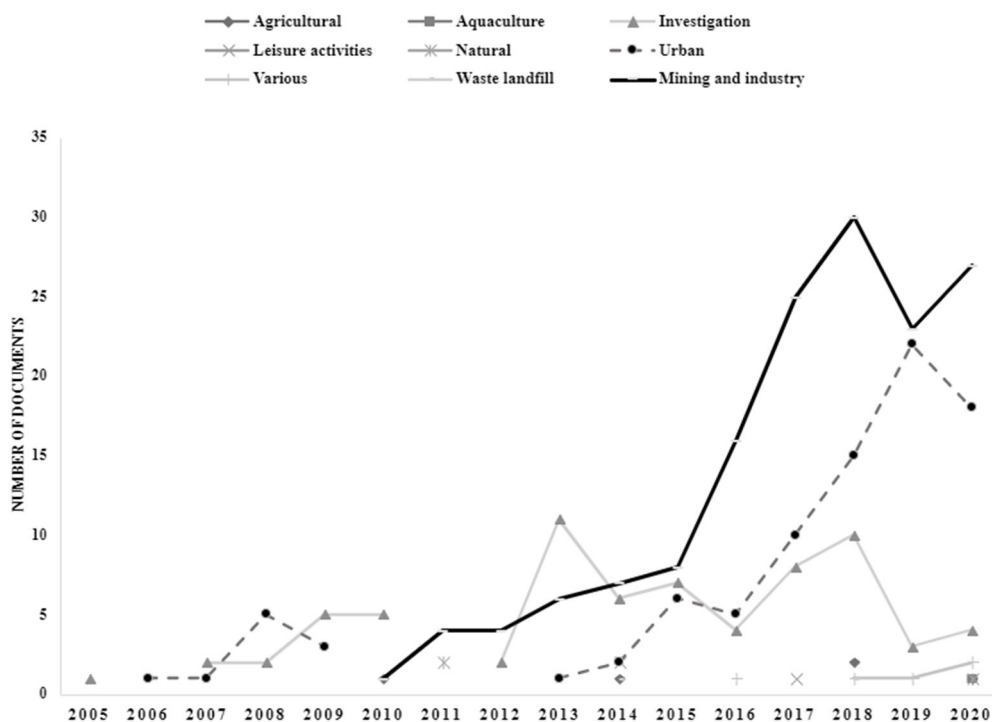


Fig.3 Evolution in the number of documents related to scope per use and year

Fig. 3 illustrates the evolution in the number of published references based on the use of Technosols. Mining and urban areas publications trend follow a growth pattern (more pronounced in the case of mining). Although it is interesting to comment that the first

publications cover the field of urban areas, a change occurs by the strong appearance of mining articles since 2010.

Health and Technosols association

Another indicator to consider within our data analysis are the key words selected by the authors. As mentioned before, the word “Technosol” is used as key word (39 times), but to a lesser extent than word “Technosols” (107 times). Authors were surprised by the diversity of key words used, with 160 terms, representing almost half the number of published references, but none of them was the word “health”. However, health-related terms are used, such as “heavy metals, soil pollutants, soil quality, carbon sequestration, phytoremediation, bioaccumulation or climate change”.

Further, the term “health” it is expressly mentioned only once in the title of a reference: “Effects of different in situ remediation strategies for an as-polluted soil on human health risk, soil properties, and vegetation “, (Baragaño et al., 2020). The scope of study is urban soils that are As-contaminated, and they experience adding organic wastes as an amendment, and evaluate the human risk.

Several publications include considerations on people's health during the development of research, principally those that analyze the incidence of polluting substances (mainly heavy metals) in Technosols (Tsolova et al., 2014). Despite being less common, there is also research focused on the health benefits of Technosols, as is the case of the interesting article developed by Ono et al. (2020). Their main intention is to study the capacity of the Technosols located in coastal zones to host trees that can reduce or avoid the devastating consequences of tsunamis on life and property.

Focusing on the articles on urban and peri-urban Technosols, we also find many references that, although they do not expressly mention health benefits, we consider that are closely related. The investigation of contaminated and degraded soils (soil sealing) with the intention of their regeneration covers most of the research articles in the field of urban Technosols. Some of them involve the use of constructed Technosols as amendments (Baragaño et al., 2020) and others analyze our cities underground

(Technosols) contamination degree (Moreno-Álvarez et al., 2020; Charzyński et al., 2017).

The second most prolific group involves the use of anthropogenic soils/Technosols as a substrate for GI development, by using municipal waste mostly for land reclamation (Barredo et al., 2020) and rooftops (Grard et al., 2020). Technosols benefit for climate change in the field of greenhouse gases management (Rees et al., 2019) also arouses interest in the scientific community and in the infiltration capacity for mitigation flood risk (Díaz-Sanz et al., 2020).

Fergusson (2017) establishes the relationship between the presence of pollutants in Technosols and the negative effect on human health and advises further research in this due to the wide variety of pollutants and their interactions.

Compilation of proposals

After reviewing the bibliography mentioned throughout this article, many authors agree that in the field of urban soils, many challenges remain to be faced. Consequently, this paper provides a compilation of their proposals:

- Strategies to enhance policy, sustainable soil management practices (Cambou et al., 2021; Montanarella and Panagos, 2021; Tresch et al., 2018b; Tresch et al., 2018a) and direct production processes towards sustainable models (EC, 2020a). In addition, seems to be a need for addressing the development of globalized regulations for soil protection, for using waste to formulate Technosols, and for standardizing assessment methods (Akande et al., 2019; Cambou et al., 2018).
- Authors agree on the requirement of expanding research on analyzing urban soil quality, to assess their level of ecosystem functioning as a service provider (Paradelo et al., 2020; Tresch et al., 2018a), and because additional studies can help to understand links between soils and health (Brevik et al., 2020; Fergusson, 2017). This purpose is not easy at all, due to the diversity of degradation processes and pollutants,

their interactions, and peculiarities of each urban settlement (Cambou et al., 2021). Authors suggest starting by evaluating areas with the greatest direct exposure of the most sensitive population (playgrounds, hospitals, schools) (Li et al., 2018), as well as soils with possible presence of contaminants with higher level of health hazard (industrial or polluting activities) and estimating bioavailability (Guillén et al., 2021).

- Another reasonable approach to tackle this issue could be to enlarge upon key issues, as improving soil organic carbon storage (Cambou et al., 2021; Montanarella and Panagos, 2021; Navarro-Pedreño, et al. 2021; Rees et al., 2019), sealed soils restoration (Tobias et al., 2018) and to achieve GI and NBS on the premise of resource sustainability (Bouzouidja et al., 2020).
- It is also worth monitoring pollution or degradation sources and establishing programs for reduction or elimination. At the same time, relating contamination causes with the risks for the health of inhabitants is a way of establishing priorities for action. Land use planning might be in accordance with soil quality, to avoid exposing population to health hazards (Guillén et al., 2021) and to achieve urban sustainability (Losco and Biase, 2021).
- Certainly, make even greater progress on protecting green areas, after checking whether the land requires any compensation measure, and expanding urban greening based on key parameters and required resources (Cambou et al., 2021; González-Méndez and Chávez-García, 2020; Ruíz-Pérez et al., 2020; Rokia et al., 2014). To this effect, seems convenient to carry out an inventory of potential areas to host vegetation (Cascone, 2019; Stangl et al., 2019; Tobias et al., 2018), and to connect it (Losco and Biase, 2021).
- For soils that need to be decontaminated or with functional deficiencies, it should be borne in mind that the application of amendments through the formulation of Technosols made by wastes (González-Méndez and Chávez-García, 2020; Rees et al., 2019; Hafeez et al., 2012; Macías and Camps Arbestain, 2010). In this way, planners could avoid using natural resources, reduce waste management impact and allow nutrients reincorporation to biochemical cycles of soil.

Conclusions

The present study addresses the state of the art of urban soils conditions, its links with urbanization and human health and contributes to the need of further research.

Despite, more than 60% of European soils are unhealthy, mainly because of the development of human activities, in reviewing the literature, no data found on how many of these soils correspond to urban areas. European trends reflect population growth and aging, as well; urban settlements expected to continue their expansion. This future perspective might increase ecological footprint of cities, and their contribution to climate change. Consequently, actions to mitigate its aftermaths are urgent in order to ensure urban soils capacity to provide ecosystem services and human wellbeing. Despite, European cities are making efforts to analyze and improve sustainability; existing data suggest that Europe will not meet SGDs by 2030. Possibly, because great challenges remain to be achieved related to environmental goals.

Therefore, more information on the needs of urban soils to provide ecosystem services would help to establish a greater degree of accuracy on this matter. One significant finding to emerge from this study is that healthy soils might preserve human health, and urban healthy soils may provide equal or more benefits than natural soils. In fact, amount of carbon stored by green urban areas seem to be associated mainly to their size. For greening plans and avoiding land take, consulted authors propose brownfield regeneration and greening existing surfaces, since they are able to provide ecosystem services as well. The introduction of new green areas might lead to an increase in required water and soil resources for plant maintenance. Further research might explore quantity and quality of water required to host the new urban-natural landscape.

Additionally, with the laudable intention of bioremediation or revegetation, we can take in consideration not extracting soils from other areas, since we generate another problem. Having found scarce references on the amount of soil required for the new city paradigm, it is a field of study to address. Based on the premises of the circular economy,

authors propose the use of waste from human activity for generating urban Technosols. The possibility of building Technosols with waste as a GI substrate could enhance the most required ecosystem functions for each area. It would be Technosols developed to increase the environmental performance of urban soils and human wellbeing.

After studying the references related to urban Technosols, authors found that even though it is recent, it arouses growing interest and they are applied in a wide variety of fields. Technosols definition maybe needs more discussion and authors provide one that includes its value as a provider of ecosystem services. It is relevant to underline ecosystem benefits of constructed Technosols are not expressly approached from the prism of human health.

Finally, authors provide a compilation of proposals and essentials highlighted by the authors of the aforementioned references, in relation to the improvement of urban soils as providers of ecosystem services as human health helpers.

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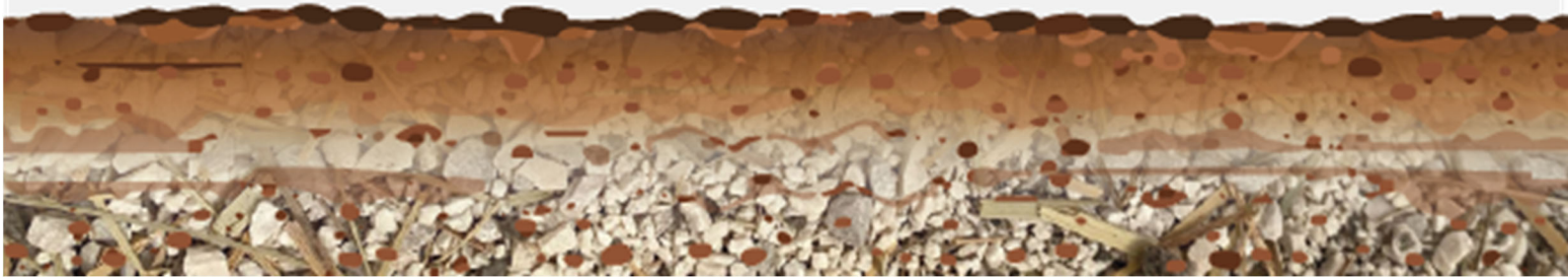
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CAPÍTULO 5: LAND RECYCLING, FOOD SECURITY AND TECHNOSOLS.

Este capítulo corresponde con el trabajo:

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ABSTRACT

The world population will grow up to 9.8 billion by 2050. The intensification in urban growth will occur on all continents and in all sizes of cities, especially in developing countries, experiencing a greater rising in urban agglomerations of 300,000 to 500,000 people, those of 500,000 to 1 million and those of 1 to 5 million, by 2035. In this way, the demand of soil to host human activities (land take) will increase, mainly affecting soils with greater agricultural potential close to cities, at the same time as the need for food will increase. Land rehabilitation can contribute to human food security, to enhance ecosystem services and, if made by waste Technosols, those are viable as substrate for urban agroforestry systems. Although the references for brownfield reclamation for urban agriculture, adding constructed Technosols and de-sealed soils can recover its ecosystem functions even food supply services and would be the solution in urban areas.

1. Introduction

Trend of rising population and number of urban settlements around the world increases pressure on land take ^[1-3]. Consequently, it is a challenge for coming decades, related to fertile soil conservation, provision of ecosystem services and biodiversity ^[1,2]. Mainly due to loss of fertile agricultural soils, compromising their role as biomass producers.

In addition, land take implies in most cases soil sealing for the expansion or development of new urban settlements ^[2]. Therefore, the loss of soil functionality and its ability to provide ecosystem services is further aggravated. To counteract these shortcomings, the EU promotes land recycling prior to land taking. Since this practice is currently a minority in Europe ^[1] and many other parts in the world, we analyze whether sealed soils or brownfields can become functionally valid even as biomass producer (urban forestry areas).

In this sense, it is important to consider that soil, a finite resource, is one of the most important stores of carbon to combat global warming and at the same time ^[4,5], basic for human health.

Therefore, the purpose of this work is to know if loss of ecosystem services (including food provision) associated with land take on agricultural land due to urban expansion, can be counterbalanced with land rehabilitation as a solution that can be applied in many countries but especially in developing countries and those with great percentage of soil sealed (i.e., in Europe). This rehabilitation can be of special interest in brownfields and by using made by wastes Technosols ^[5], and de-sealing soils.

2. Methodology

An analysis of literature related to consequences of population growth on arable land occupation, on ecosystem services provision and options to compensate this land take was done. This study is based on the need to determine if there is a qualitative relation

between people, urban and soil sealing and try to improve the interest of administrations and research community about the problems associated to soil sealing and the solutions that can be applied.

For this purpose, internet search engines and scientific reference databases were used. The analysis was based on looking for the following key words (in the first step): population growth, agricultural land take, soil sealing, unsealing, de-sealed, de-sealing, brownfield, land recycling, brownfield, orchard, allotment garden, community garden, urban agriculture, Technosols, germination crops, food security. After that, a detailed study of the results was done, literature selected and complemented with the reports on Official Institutions websites mentioned in the reference section.

Population and settlement data were collected and processed by using dynamic tables and graphs in Excel (Office, ©Microsoft) and IBM® SPSS Statistics.

3. Urban Growth and Soil Sealing

The world's population in 2020 reached 7.7 billion people, and it is expected to continue increasing to 8.9 billion in 2035 and 9.8 billion in 2050 ^[6]. Considering the continents, it is expected an increase for all except Europe, which will experience a slight decline towards 2050 (Figure 1).

Analyzing the settlement preferences of the world population in 2020, 56% choose urban environments for the development of their lives, which in quantitative terms is 4,353 million people. The urban population rate varies widely between continents and countries. Thus, in 2020, Asia is the continent with the largest urban population (2,359.26 million people), followed by America (815.2 million), Africa (575.34 million), Europe (560.25 million), and Oceania having the lowest number of urbanites (29.24 million people) ^[6]. The number of urban settlements also shows upward trends. In 2020 there are 1,934 registered cities around the world, and by 2035 it is estimated that they will increase to 2,363 ^[7], housing a population of 5,555 million people in 2035 (Figure 2) ^[8].

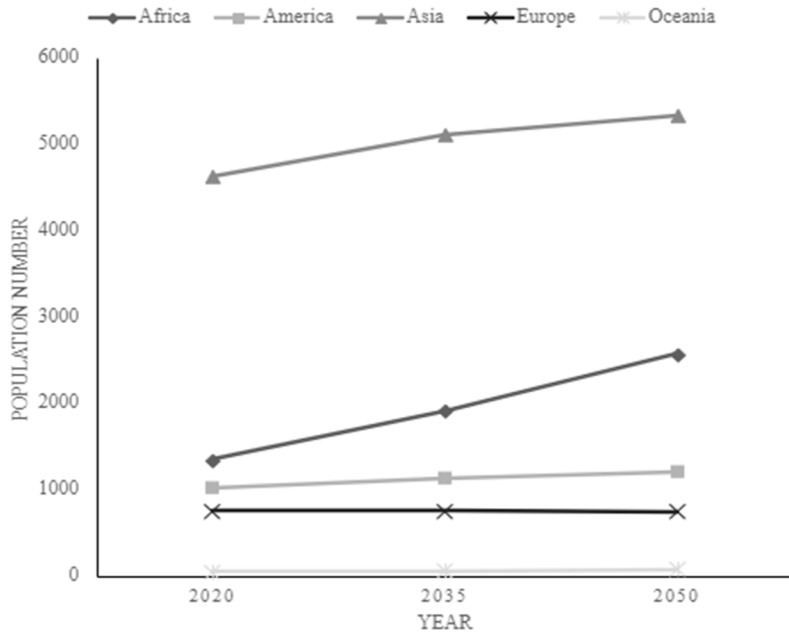


Figure 1. World population trends per continent expressed in millions of people (PRB, 2020).

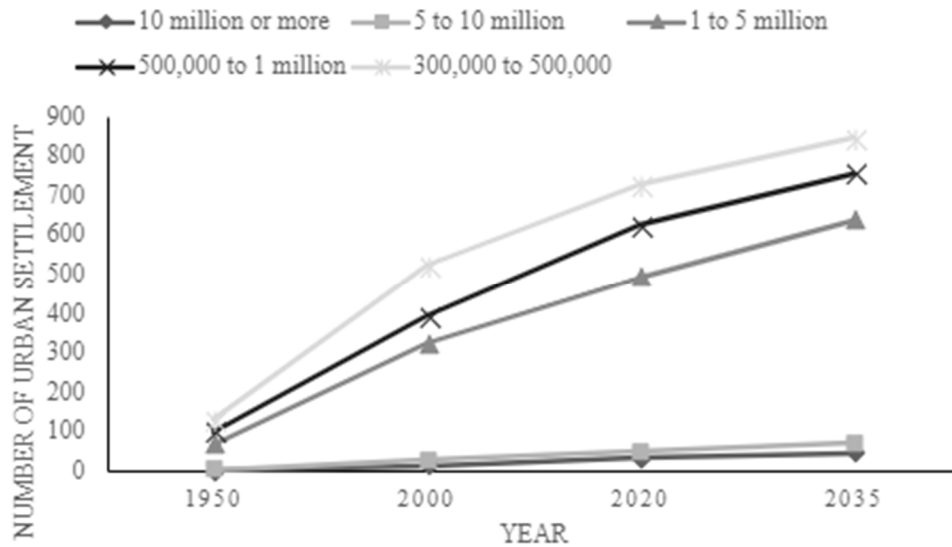


Figure 2. Number of world urban settlement trends (source: UN-HABITAT from UNDESA, 2020).

The intensification in urban agglomerations will occur on all continents and in all size of cities (Figure 3), although the increase in megacities (more than 10 million) is a phenomenon mainly associated with the Asian continent, which will increase from the current 21 megacities up to 32 megacities in 2035 [8].

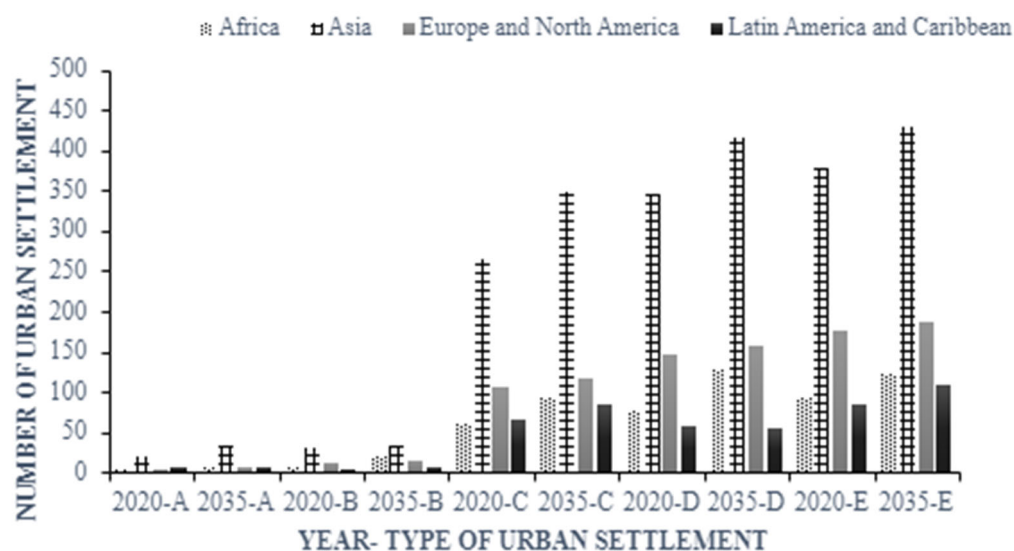


Figure 3. Continent type of urban settlement trends (2020-2035). In the figure, A: means urban settlement of 10 million people or more; B: 5 to 10 million; C: 1 to 5 million; D: 500,000 to 1 million and E: 300,000 to 500,000 urban people (source UN-HABITAT from UNDESA, 2020).

Extending the study to the data given by international organizations [6-8], 141 countries have an urban population rate $\geq 50\%$, reaching 3,257.16 million of urbanites. This is notorious in countries like China, USA and Brazil.

The expansion of urban population leads to land take and land cover changes, as a support for the development of human activities (housing, industrial or infrastructure construction) [3]. In Europe, from 1990 to 2015, population growth by 2.4% triggered built-up areas by more than 30% [9]. Land taking in EU28, between 2012 and 2018, amounted to 539 km²/year.

Land take, is a phenomenon that mainly takes place in peri-urban areas ^[2], areas that are associated with the highest quality soils for agricultural use ^[8,9] and the proximity food market. From 2000 to 2018 in EU28, more than 78% of occupied land affected agricultural areas, such as arable land and permanent crops (394.34 km²/year), pastures and mosaic farmland (212.44 km²/year) ^[12].

An immediate consequence of cropland decrease is the reduction in potential agricultural production capability to feed a growing population. In fact, Gardi et al. (2015) ^[3] estimated a loss of more than 6.2 tons of wheat (from 1990 to 2006) due to land take. This is a great concern in developing countries where it is more difficult to find accurate data of land take around the cities. In most of them, the immigration conditioned the increment of suburban areas with low health conditions and insufficient services and resources. This growth is directly associated to land take and soil sealing. Moreover, conditioned by an inexistent land planning and a disorderly occupation of the territory.

Moreover, as population and income levels increase, demand for food rise as well. Between 2000 and 2050, global demand for food crops projected to grow by 70- 85% ^[13]. Meeting rising food needs in terms of both quantity and quality, puts additional pressure on productive capacity of arable fields that last, requires transform forest, semi-natural or natural areas into new agricultural fields, or implies relying on non-local food supply, which could compromise food security ^[11-14].

It is worth mentioning that loss of arable land is counterbalanced to some extent by increasing in agricultural productivity, but in the long term it will be necessary to use soils from forest or natural areas, which may not be so fertile and be far away ^[3], and by increasing intensive land management. This can lead to environmental damage ^[15], which carries an associated impact on a more global scale. Increasing food production through expansion of agriculture, only provides food supply services, but in return, has negative effects on other ecosystem services, such as water availability and quality, carbon sequestration, flood control, ecotourism potential and regulating services ^[13].

Owing to this, Hardaker et al. (2021) ^[16] studied the best practices options to enhance ecosystem services provision on arable lands.

In addition, detriment of present and future ecosystem services could be aggravated if soil is sealed. For instance, the percentage of total land take EU28, for green urban areas, between 2012 and 2018, is only 0.52%, the rest allocated to host activities with greater or lesser need to seal or remove the existing fertile soil ^[12].

Soil sealing defined as "the permanent covering of an area of land and its soil by impermeable artificial material (asphalt or concrete, for instance)". The average of soil sealed related to population growth, was estimated in 200 m² per citizen (by 2006) ^[11]. Added to consequences previously stated related to land take, soil sealing upsets environmental balance, because soil ecosystem is isolated from others. Impervious soil not only implies a reduction in capacity to provide ecosystem services, but also supposes provision of negative services (disservices) such as intensification of the urban heat island effect, increase risk of flooding, reduce filtering water that drains into aquifers and evapotranspiration, and adversely affect biodiversity and carbon cycle ^[3,10,16-19]. Consequently, Sobocká et al. (2021) ^[18] concludes that urban centers are the "most environmentally sensitive area" due to high rates of soil sealing (more than 80%) and urban heat island effects, and lack of green areas.

4. Soil De-sealing and Technosols

In 2020, 2.4% of soil is sealed and only 13% urban development on recycled urban land in Europe. Therefore, the European Union launched the mission "Caring for soil is caring for life", to ensure 75% of soils are healthy by 2030 for food, people, nature and climate ^[20], in the same line that many programs from FAO. Among the objectives set, is no net soil sealing and increase to 50% re-use of urban soil, aligned with no net land take by 2050. The net land take concept "combines land take with land return to non-artificial land categories (re-cultivation)", from urban area to semi-natural land ^[12]. Accordingly, European Commission proposes direct actions to avoid soil sealing, by reducing land take or by land recycling ^[15], because land taking mainly for sealing soils without restoring brownfield is unsustainable ^[10]. Land recycling means "redevelopment of previously developed land (brownfield) for economic purpose, ecological upgrading of land for the

purpose of soft-use (green areas in the urban centers) and re-naturalisation of land (bringing it back to nature) by removing existing structures and/or de-sealing surfaces" [21]. Pytel et al. (2021) [22] proposed 8 possible transformation uses of brownfields, such as "cultural, didactic, natural, silvicultural, aquatic, economic, recreational and agricultural". In addition, we provide another option for brownfields reused, closely related to provision of ecosystem services, such as construction of wetlands or areas for water purification and run-off regulation [23]. All these new uses can be designed, to a greater or lesser extent, to host green urban areas with adequate ecosystem functionality, and a feasible option to avoid land occupation is to install on preserved constructions, green roofs and green walls. Land recycling for green spaces, can contribute to improve urban green infrastructure, and ecosystem services [10,11]. In fact, urban agriculture can develop on green roofs and walls [24], as well, on urban patches and plots of urban or suburban areas [25]. Nonetheless, in Europe brownfields restoration for green areas is a minority [10], which should be enhanced to compensate ecosystem services loss. Moreover, if reclaimed areas can be used for urban agriculture, it contributes to improvement of human health and food security [26,27].

Furthermore, Lal et al. (2021) [28] consider future land uses for sustainability of cities and megacities and for contributing to the fulfillment of Sustainable Development Goals (SDGs), are those related to urban garden, permaculture, vertical gardening and Technosols. Many cities use urban waste compost for urban agriculture [28], and consider viable incorporation of wastes as a substrate for plant species with agricultural utility [29,30].

Some constraints in the allocation of intended use are size of brownfields (areas between 1 and 20 hectares are suitable for green spaces) [22], soil state (contamination, fertility, among others) [23,31], and previous use mainly related to whether it has been sealed or not. Possibly this is due to the fact that brownfields of heavy industries show high rates of contaminated soils, so to avoid high costs of remediation, they are usually destined for secondary development [18]. Therefore, in the decision of the new use, economic criteria have priority over environmental or social ones [22,32]. Despite the fact that other interests prevail in the decision of the new use of brownfields, the relevance of the environmental benefits is unquestionable. Therefore, authors emphasize the

importance of urban agriculture in carbon sequestration. Feliciano et al. (2018) ^[33], indicates that second largest absolute mean change in soil carbon sequestration reached from the implementation of a home garden on an underutilized land. Carbon sequestration related to agroforestry systems (soil and above ground), depends on "plant species, system characteristics, management factors, agro-ecological conditions and soil characteristics". Among the management factors highlighted by Feliciano et al. (2018) ^[33], is the use of residues from agroforestry systems ^[5]. In fact, Lal et al. (2021) ^[28] indicate that development of agroforestry systems or biochar addition are the only two methods to increase carbon sequestration capacity of soils in the long term.

In other matters, Pytel et al. (2021) ^[22] provide the most common form of land use in Poland is green spaces, mainly in previous landfills or mine dumps, where there is not an impervious layer. Followed by secondary use mainly associated with post-industrial brownfields. Accordingly, Klenosky et al. (2017) ^[34] indicate it is common to create green areas on brownfields from landfills. The area occupied by derelict and urban vacant land in Scotland in 2019 is 10,936 hectares, and only 20% of it considered uneconomic to develop or viewed as suitable to reclaim for a 'soft 'use ^[35]. Consequently, Pytel et al. (2021) ^[22] consider that new use of recycled land tends to coincide with the use immediately prior to the one that ended up in disuse, as its reconversion is cheaper and easier. Still, in Scotland in 2019, 405 hectares of 10,936 urban vacant hectares previously used for agricultural purposes, and only 13 hectares brought back into agriculture use ^[35]. For urban agriculture, in addition to soil contamination factor ^[26,27], soil fertility is limiting. The development project of a children's museum, for the improvement of nutritional habits and production of food in gardens, needed fertile soil and organic compost to replace poor topsoil ^[36].

Sobocká et al. (2021) ^[18] consider brownfields that have hosted highly polluting activities should not be reclaimed for residential development or housing the most sensitive population, nor for green parks, without proceeding to cover contaminated soil with a layer of topsoil (at least 50 cm). As indicate by Pecina et al. (2021) ^[31], for agricultural use it would also be advisable to be cautious ^[37]. As healthy soils generate healthy crops, which is crucial to human health and agricultural productivity ^[28]. Moreover, Deeb et al. (2020) ^[37] contemplate that constructed Technosols show great

potential for brownfields restoration. De Sousa (2017) ^[32] indicates among remediation techniques for transformation of brownfields, the predominant is excavation, soil removal and backfill.

Therefore, at times, previous step to green land recycling is de-sealing soil. Which implies, according to the European Commission, "Removing asphalt or concrete and replacing them with topsoil on subsoil" ^[15]. At this point, we wonder if it is necessary to use topsoil from elsewhere to restore de-sealed soils, if de-sealed soils can achieve ecosystem services levels prior to sealing, and if so, if de-sealed soils can become biomass producers. Sealed soils experience an alteration of their properties, worse soil structure and organic matter, and moderate to high amount of trace elements, leading to a drastic reduction in microbial community, among others aftermaths ^[17,18]. In cases where it is completely necessary to add topsoil on de-sealed soils, an option to consider may be incorporation of Technosols made by wastes, to enhance ecosystem services ^[38]. It could be a new line of research, as authors have not found references in this context. Authors consider sealed soil is not a reversible process ^[39]. Maybe this needs more discussion, depending on removing impervious layer or not. In fact, Tobias et al. (2018) ^[10] consider all de-sealed brownfields have potential for providing ecosystem services if soil is restored. Recent references conclude de-sealed soils can restore their quality and fertility, by themselves, without adding topsoil ^[40]. De-sealed soils can even improve functional and biological levels, with shrub planting and irrigation.

As indicated by the aforementioned references, de-sealed soils can recover their ecosystem functions. However, would it also include the provision of food? Authors aim to discern if it is a feasible option to balance the loss of fertile soil for agricultural use, with de-sealed urban soil. The conclusions of Tobias et al. (2018) ^[10], establish sealed soils with agricultural potential can be reclaimed for food production, although at times the degree of soil compaction may be limiting. In addition, it would be convenient to know if de-sealed soils may need additional treatments and on what timescale, to become suitable for agricultural re-use. This paper ^[41], addressed this question, concluding de-sealed soils, without any additional treatment, only allowing colonization of spontaneous vegetation, improve their physical and chemical fertility. Even more, this can increase microbial biomass and biochemical activity, exceeding the values of agricultural soils.

Research is needed in this sense, because there were scarce references related to brownfield reclamation (sealed or not) for urban agriculture and using made by waste Technosols for improving soil properties and functions. Technosols and the use of wastes can be a solution, mostly of them that can be considered as bioresources coming for many activities (i.e., food waste) ^[42].

5. Conclusions

In 2020, the countries with more than half of their population in urban environments cover most of the habitable terrestrial territory. The expected increase in population will be associated with a rise in the number and size of cities worldwide (in Europe, the cities that will increase the most will be those with 500,000 to 1 million and those with 300,000 to 500,000 inhabitants), as well, with land take mainly affecting fertile soils. Consequently, it will be a challenge for food supply, food security and to provide ecosystem services.

Furthermore, most of the soil affected by land take is sealed, which implies provision of ecosystem disservices. To counteract it, the European Union, in addition to limiting land take, is promoting land recycling. Land recycling for green areas can enhance ecosystem services, an adding Technosols made by wastes, increase sustainability of cities and megacities, improve agricultural productivity and human health. Consequently, brownfield regeneration may go beyond constructing of new facilities that have an aesthetic, productive or recreational use, with the implementation of green areas.

At the same time, it would be advisable to avoid using natural soil to fill, bioremediate, or improve soil properties for urban agriculture, since the incorporation of Technosols as a substrate for crops, support of green areas and forest urban areas is a viable option. Besides, using de-sealed soils after rehabilitation for agricultural production seems to be a real possibility.

More information on land rehabilitation, Technosols and de-sealed soils for urban arable land uses would help us to establish a greater degree of accuracy on this matter.

So, new research and data supporting urban soil rehabilitation should be a target for local, regional and national administrations in order to improve our health and urban environments.

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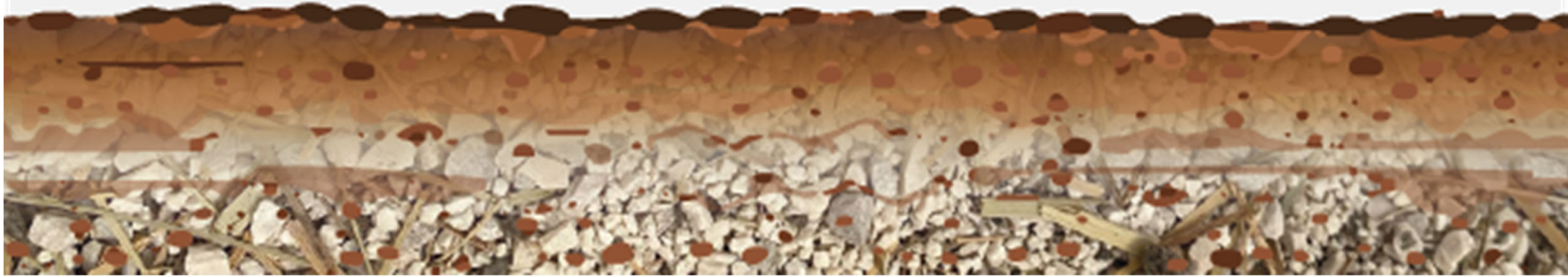
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CAPÍTULO 6: SOLUBLE ELEMENTS RELEASED FROM ORGANIC WASTES TO INCREASE AVAILABLE NUTRIENTS FOR SOIL AND CROPS.

Este capítulo corresponde con el trabajo:

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ABSTRACT

Member States of the European Union must ban burning arable stubble by 2023 and improve the recycling of organic waste into fertilizers and organic farming practices by 2030. The current lack of nutrients from soils and crops leads to food insecurity, human malnutrition and diseases. Consequently, innovative solutions are required, as technosols are constructed by waste. The objective of this paper is to educate on the nutrients that some pruning residues can provide. This work characterizes elemental composition, nutrients soluble fraction and physical and chemical properties of the following organic wastes: almond tree pruning, commercial peat substrate, olive tree pruning, pine needle, date palm leaf pruning, sewage sludge compost and vine pruning. The results show significant differences between macro (Na, K, Ca, Mg) and micronutrient (Fe, Mn, Cu, Zn) content and their solubility. Sewage sludge compost, olive pruning and pine needle are the three residues with the highest presence of nutrients in their elemental composition. Nevertheless, if a farmer applies pruning residues as a nutritional supplement for crops, it will be key to finding the short-term soluble nutrient rate and synchronizing the nutritional requirement curve of a plant's life cycle with its nutrient release. Consequently, organic waste (without composting treatment) obtains higher solubility rates, being date palm leaf residue the one with the greatest value. The solubility index of organic wastes can be significant in providing short-term nutrients to crops. Hence, our results can help in choosing the proper waste to enhance plant nutrient supply, mainly K, Ca, Mg and Na for crop nutrition, to ensure efficient biofertilization.

1. Introduction

The growing world population is expected to increase to 9.8 billion by 2050 [1], and occupation of land with superior agricultural potential for the expansion of cities will intensify pressure on the agricultural capacity to meet resulting agri-food demand [2,3]. With the intention of reducing the environmental impacts of agricultural systems, sustainable agriculture is postulated as an option that is increasingly widespread and demanded by consumers since it is also linked to health prevention. The FAO [4] defined sustainable agricultural development as “the management and conservation of the natural resource base, and the orientation of technological change in such a manner as to ensure the attainment of continued satisfaction of human needs for present and future generations. Sustainable agriculture conserves land, water, and plant and animal genetic resources, and is environmentally non-degrading, technically appropriate, economically viable and socially acceptable”. It is well known that although 95% of our food originates from the soil, it is a non-renewable resource, and food production is at risk. Fertile agricultural soil is decreasing yearly, so it is estimated to be depleted in 60 years [5].

One of the main pillars of sustainable agriculture is sustainable soil management since its quality and health are decisive for agricultural production, human nutrition and health, and agricultural ecosystem biodiversity [5,6]. The FAO [7] considers soil management sustainable “if the supporting, provisioning, regulating, and cultural services provided by soil are maintained or enhanced without significantly impairing either the soil functions that enable those services or biodiversity. The balance between the supporting and provisioning services for plant production and the regulating services the soil provides for water quality and availability and for atmospheric greenhouse gas composition is a particular concern”. The main challenges highlighted by the FAO [7] for sustainable soil management to ensure the provision of ecosystem services are minimizing soil erosion, enhancing soil organic matter content, fostering soil nutrient balance and cycles, preventing, minimizing and mitigating soil salinization, alkalization and acidification, preserving and enhancing soil biodiversity, improving soil water management and preventing and mitigating soil compaction and soil sealing restoration. To face them, the FAO [7] proposes several options, but there is only one that is common to all these problems: soil cover with organic residues such as mulching or organic amendments,

although it suggests preventing soil contamination by ensuring the safety of organic residues applied to the soil. Accordingly, El Chami et al. [6] indicated that sustainable agricultural practices are mostly related to the use of organic soil amendments and mulching. This is supported by Rabary et al. [8], who showed that no-tillage and permanent soil cover are key factors for improving soil properties. What is more, the use of organic and crop residues above ground is a valid option to increase the biodiversity of the agricultural ecosystem [9], CO₂ storage [8,10] and to improve nutrient supply [10–13] and human nutrition [5] and its application as a substrate is also considered for crop nutrient supply [10,14–17]. Its use to formulate suitable soil for agricultural production is one of the possible applications that have not been studied enough [18], especially from the point of view of the nutrient source.

Huge amounts of organic residues associated with agri-food production are generated annually. Currently, the European agricultural system generates about 700 million tons of agri-food waste, and it is estimated that between 10 to 12% of global emissions are associated with agricultural production [19]. This represents a challenge and an opportunity for environmentally and economically sustainable management of agricultural holdings to continue advancing in the use of its wastes according to principles of the circular economy [10,19]. Each type of agricultural production involves co-products, by-products and specific residues. Notwithstanding, one activity that is common to all farms is pruning. The resulting material is included in the category of waste since their production does not entail an economic benefit, even implying an expense associated with their management. Burning is a widespread practice for pruning remains management, which implies fire hazard [20], emission of greenhouse gases into the atmosphere, assuming a reduction in carbon sequestration, as well as loss of elements and nutrients that compose them [13,21]. Moreover, the Member States of the European Union have to ban burning arable stubble by 2023 in order to preserve the organic matter of soil [22]. Consequently, farmers need to know the nutrients that their pruning residues can provide to crops to match them with the plant's requirements.

Nevertheless, biowaste application to improve productivity and fertility of agricultural soils has been a common practice used since immemorial time, lately overshadowed by inorganic fertilizer [23]. Currently, Farm to Fork UE Strategy aims to recycle organic

waste into renewable fertilizer and increase organic farming by 2030 [24]. Organic residues have a great advantage over chemical fertilizers since they can improve the physical properties of soil and microbial activity, functionality and ecosystem services [14,25–27]. In addition, by choosing the best management practices based on their possible nutrient contribution, the rate of chemical fertilizers could be reduced or eliminated [23], with its consequent benefit for the health of ecosystems and people [28]. In fact, Zipori et al. [16] consider that the rate of inorganic fertilizer added is usually higher than necessary.

Against this background, due to it being essential for humans, animals and plant health, and the impossibility, for example, of synthesizing trace elements [29], new options are emerging for the use of pruning and crop residues, such as obtaining biochemical and enzymatic compounds, recycling bioplastics, civil engineering or energy [30–32]. Furthermore, an alternative use, since it allows the direct reincorporation of nutrients and elements into natural cycles and which does not require an industrial transformation process, is the soil application as mulching or as part of a functional substrate called technosols [33,34]. Therefore, dysfunctional, contaminated or not fertile soil may require it to stimulate microbial activity and soil properties [8,25,26] and to ensure food security [25,27,29]. To prepare anthropogenic soils, it is necessary to know their components, specifically those that will constitute the organic fraction and present hazardous substances.

Malnutrition is, globally and, more specifically, in developing countries, an essential issue that affects a number of people, and it continues to rise. After remaining almost unchanged from 2014 to 2019, in 2020, between 720 and 811 million people worldwide suffered from hunger, 161 million more than in 2019. It is possible that effects of the COVID-19 pandemic have had an impact on this issue, which complicates the challenge of meeting the goal of zero hunger from Sustainable Development Goals (SDGs) by 2030 [35]. Asia and Africa are the most affected continents [35]; in addition, they usually have poorly fertile soils, as many international aid programs show. Therefore, affordable, sustainable and manageable practices that provide nutrients are required in these areas [13]. As we know, an adequate human diet implies the incorporation of at least 25 mineral elements, whose food reservoir is mainly through plants [36]. Plants are composed of 20

basic elements: C, H, O, N, P, K, Ca, Mg, S, Fe, Mn, B, Mo, Cu, Zn, Cl, Na, Si, Co, and Ni that are provided from soil solution (except for C and O) [37]. Thirteen of these elements (N, P, K, Ca, Mg, S, Fe, Mn, B, Mo, Cu, Zn, and Cl), apart from oxygen, carbon and hydrogen, are considered essential for the growth of all crops [28,38]. In addition, Na, Se, Co, Al, Ni and Si are beneficial for plant growth and Na, Se, and Co are essential for mammals [29]. White and Broadley [39] consider Fe, Zn, I, Se, Ca, Mg and Cu the mineral elements that are most lacking in human nutrition. In addition, worldwide, over 2 billion people are suffering from micronutrient deficiencies, and over the last 70 years, nutrients and vitamins in food have drastically decreased [5]. It also happens in developing countries due to over-cultivation on soils with reduced phyto-availability of essential elements to human nutrition.

The release of nutrients in soil occurs from the solubilization of the parent rock or sediments and from the mineralization of organic matter. To benefit crop yield, the soil nutrients available and absorbed by plants must be presented in soluble forms in the soil solution [36]. The speed of waste decomposition and nutrient release is important for sustainable crop management practices, mainly influenced by climatic conditions (temperature and humidity), soil quality (properties, microbiological activity and aeration rate), residue composition (for instance: biochemical composition, nutrient concentration and type of structure: lignified or not), and the application method (more or less direct contact of residue with soil, above or underground), as well as recycling treatment (drying, composting, pyrolysis among others), and residue size and storage method [11,13,20,23,27,40,41]. Moreover, Zipori et al. [16] found that seasonality (in which residues are applied) is important, especially in Mediterranean climates, to take advantage of the leaching effect of nutrients from rainfall at the end of winter and spring.

The decomposition of organic matter occurs in two phases, an initial one characterized by the washing of soluble compounds and nutrients and by decomposing of labile materials (sugars, phenols, starch and protein), followed by decomposing of recalcitrant materials (cellulose, hemicellulose, tannins and lignin) [20,42]. Although Hossain et al. [25] highlight the importance of organic residues to increase crop productivity, the bioavailability of micronutrients in soil, as well as macronutrients absorption by plants, Foereid [41] contemplates that not all nutrients in biofertilizers are immediately available,

nor when they can become so. This initial contribution of soluble elements has been scarcely studied [23,43,44] since most references related to nutrients of residues focus on the decomposition of labile or recalcitrant matter.

The objective of this research is to assess physical and chemical properties and nutrient solubility from several organic residues. From each organic waste, elemental composition and aqueous extractable content were studied related to needed nutrients for people and plants (Na, K, Ca, Mg, Fe, Mn, Cu and Zn). Therefore, we deal with a first approximation of the waste potential for formulating technosols considering nutrient supply. Knowing short-term soluble nutrients from pruning residues allows farmers to add the residues to the soil under the nutritional request of their crops.

2. Materials and Methods

2.1 Selected Residues

Based on its availability (proximity to consider circular economy and zero waste strategy) and potentiality to be part of technosols, the following organic residues were selected:

- Almond tree pruning (AP)
- Commercial brown peat (CP)
- Olive tree (*Olea europaea* L.) pruning (OP)
- Pine (*Pinus halepensis*) needle fall (PN)
- Date palm (*Phoenix dactylifera* L.) leaf pruning (PP)
- Sewage sludge compost (SC)
- Vine (*Vitis vinifera*) pruning (VP)

Pruning and harvesting residues (AP, OP, PN, PP and VP) were collected from agricultural areas close to Elche (Alicante, Spain). SC was processed and obtained from Aspe Wastewater Treatment Plant (Alicante, Spain). PP was subjected to an initial shred

after pruning, and PN was collected directly from the ground surface in the closest *Pinus halepensis* forest area.

2.2. Residue Characterization and Methods

All residues were subjected to conditioning processes consisting of air drying at room temperature inside a greenhouse (reaching temperatures over 40 °C), shredded and sieved (2 mm). Residue characterization consisted of the analysis of bulk density (ρ_b), organic matter content (OM), moisture content (MC) and elemental composition. ρ_b was calculated volumetrically as a ratio between residue mass and volume by using the cylinder method. An LED digital drying and sterilization oven (J.P. SELECTA®, Conterm 2000253) was needed to get MC and OM (UNE-EN 13040) [45]. Biowaste samples were dried at 103 °C until the difference between two successive weightings was less than 0.1 g for MC and 0.01 g for OM. The determination of organic matter (OM), expressed as a percentage by weight of dry matter, also required a muffle (Nabertherm, controller P320) and was determined by loss on ignition at a temperature of 450 °C until the difference between two successive weightings is less than 0.01 g (UNE-EN 13039) [46].

Elemental composition was determined by atomic absorption spectrometer (AAS) (Thermo Scientific, iCE 3000 Series AA Spectrometer) after acid digestion (69% nitric acid + H₂O₂) of samples (0.2 g) in a microwave. AAS is calibrated before use by testing the absorbance with solutions of quantitative certificated standards. Instrumental parameters are listed in Table 1.

Table 1. AAS instrumental parameters.

Parameter	Na	K	Ca	Mg	Fe	Mn	Cu	Zn
Wavelength (nm)	589.0	766.5	422.7	285.2	248.3	279.5	324.8	213.9
Bandpass (nm)	0.5	0.5	0.5	0.5	0.2	0.2	0.5	0.5
Lamp current (mA)	max. 8	max. 8	max. 10	max. 4	max. 15	max. 12	max. 5	max. 10
Atomization mode	emission			absorption				
Flame type	air/acetylene							
Fuel flow rate (l min ⁻¹)	1.1	1.1	1.4	1.1	0.9	1.0	1.1	1.2
Detection limits (mg l ⁻¹)	0.005	0.010	0.08	0.005	0.06	0.03	0.04	0.01

The aqueous extraction of nutrients (1:10 w/v) of each residue was obtained by using 100 mL of deionized water added to 10 g of residue and shaking for 2 h. After filtering, the pH was measured by using a CRISON GLP 21 pH meter, electrical conductivity (EC) with a CRISON GLP 31 conductivity meter, and macro (Na, K, Ca, Mg) and micronutrients (Fe, Mn, Cu, Zn) composition with an AAS (Thermo Scientific, iCE 3000 Series AA Spectrometer).

Additionally, nutrient solubility index (I_N) was calculated as the percentage of nutrients extracted in aqueous solution with respect to elemental composition in each residue, both expressed in dry weight basis, according to Equation (1) [43]:

$$I_N = (W_N / C_N) \times 100 \quad (1)$$

N : macro or micronutrient; W_N : water extractable nutrient content; C_N : elemental composition nutrient content.

2.3. Statistical Analysis

Descriptive statistics were used to calculate the mean and standard deviation for each individual analysis of residues (five repetitions per each one). Analysis of variance (ANOVA) and Tukey's multiple comparisons test were conducted using SPSS Statistics (IBM SPSS Statistics for Windows, Version 26.0. Armonk, NY: IBM Corp).

3. Results and Discussion

The data found in the references about the production of the selected organic wastes in other Mediterranean regions provide us with interesting information on the amounts of waste produced. Our findings may be useful for them because European countries are asked to avoid burning pruning residues in 2023, and other countries may follow too. As well as for meeting circular economy.

Date palm (*Phoenix dactylifera* L.) is grown mostly in the Middle East and North Africa [47,48]. In southern Europe, it is also presented in the palm grove of Elche (Alicante, Spain), which is the largest on this continent (507.4 ha) and is recognized as a World Heritage by UNESCO [32]. Each date palm produces between 10–20 leaves and 20 kg of dry leaves per year [49,50], and despite the variety of ancestral uses of the different parts of a palm tree, the use of leaves as a soil amendment or substrate has not been studied in European soils in depth. However, in Middle Eastern and North African countries, there are references that tested its usefulness as a biofertilizer or substrate after composting [51–53] and Ahmed and Al-Dousari [49] successfully used whole palm leaves as mulching to recover degraded areas in Kuwait.

The FAO [54] considers that Spain produced 6,817,770 tons of grapes and 8,137,810 tons of olives in 2020. There is a scarce number of references that deal with the use of a substrate for the harvest benefit of vine pruning, and an example is Yilmaz et al. [40]. In this work carried out by Repullo et al. [20], they obtained 42.3 kg of fine pruning residues and 17.9 kg of thick residues per tree, with an average pruning of 10 olive trees (previous pruning was performed three years prior). In the Andalusian region (Spain), olive pruning residues account for between 1.95 and 4.5 million tons per year [21]. Studies have been carried out to verify shredded pruning olive tree residue's contribution to olive groves. Gomez-Muñoz et al. [21] concluded that soil benefits more if residues are provided without burning (greater carbon sequestration, increase in organic matter and reduction of erosion). Zipori et al. [16] state that the use of olive tree pruning is a sustainable practice to improve plant nutrition.

In 2020, more than 4 million tons of almonds with shells were produced worldwide [54], with Spain being the second largest producer. This means that almond pruning is available in many areas as a soil amendment. *Pinus halepensis* is widely distributed in Mediterranean climate areas, and needle fall production measured in Spain was between 2080 and 2218 kg ha⁻¹ year⁻¹ [55]. We have found various references that prove that needle fall contribution to soil nutrition has been carried out previously [55–57]. Sewage sludge is a by-product obtained from the treatment of urban wastewater. In Spain, around 1,200,000 dry matter tons are produced annually, mainly used for agricultural purposes (80%) due to their high nutrient content [58]. Sludges require stabilizing treatments to

reduce water content and pathogens and to ensure organic matter stability; composting is one of the most applied processes.

3.1. Physical and Chemical Characteristics of Wastes

It is important to ensure that nutrients released during decomposition are synchronized with the crop nutrient requirement curve [23]. Therefore, studies on the possibility of applying organic wastes to soil to take advantage of its nutrients must begin with an analysis of its physical and chemical properties and elemental composition. The results obtained for the selected waste are presented in Table 2.

For all residues, Table 2 shows a low ρ_b , between 0.23 and 0.40 g cm⁻³. Although OP and SC get the highest values, they are far from 1.6 g cm⁻³ of soil, as ρ_b can interfere with root growth [59]. In the work performed by Golabi et al. [59], organic amendments improved soil properties and succeeded in decreasing soil ρ_b to a greater extent than inorganic fertilizers. Similar results were achieved by Yilmaz et al. [40] and Almendro-Candel et al. [60]. This means that, in general, the use of these residues can contribute positively to the reduction of the bulk density of the soil. In such a way, all residues are suitable for reducing ρ_b soils.

Table 2. Bulk density (ρ_b), OM, MC, pH and EC of each residue, average (\bar{x}) and standard deviation (σ).

Residue	ρ_b (g cm ⁻³)		OM (%)		MC (%)		pH (units)		EC (μ S cm ⁻¹)	
	\bar{x}	σ	\bar{x}	σ	\bar{x}	σ	\bar{x}	σ	\bar{x}	σ
AP	0.36 a	0.006	93.2 b	0.6	8.0 b	0.03	4.66 a	0.007	665 b	0.8
CP	0.37 a	0.004	91.0 a	0.9	52.7 c	0.41	5.02 b	0.031	1447 a	3.1
OP	0.40 b	0.003	94.1 b	0.1	6.3 d	0.21	4.78 c	0.004	1444 a	3.0
PN	0.31 c	0.009	91.9 a	0.3	8.95 a	0.67	5.94 d	0.005	753 c	1.0
PP	0.26 d	0.010	90.9 a	0.3	8.6 ab	0.17	4.90 e	0.097	4358 d	4.0
SC	0.40 b	0.008	59.0 c	1.1	26.0 e	0.73	7.34 f	0.017	3380 e	1.0
VP	0.23 e	0.009	94.0 b	0.5	9.3 a	0.15	5.42 g	0.007	1286 f	0.6
F ¹	422 ***		1992 ***		8190 ***		2913 ***		6 × 10 ⁶ ***	

¹ F values followed by *** indicate significant differences at $p = 0.001$. By columns, mean values with letters in common are statistically equal to $p = 0.05$.

Table 2 shows variation in OM depending on the type of residue considered in our work. SC is the one with the lowest amount of OM, and the rest get high OM values in

the range of 90–94%. OM of VP (Table 2) is like that obtained by Yilmaz et al. [40]. These residues can contribute to an increase in OM in soil [20,25,28,53,61] and is important since they may modify physical soil properties [53,59,60,62], carbon sequestration [21,63], nutrient cycling and crop yield [28,59] and bioavailability of nutrients (Fe, Mn, Cu, Zn) [64,65]. Golabi et al. [59] proved that OM could reduce nutrient leaching. Therefore, all tested residues may improve soil OM according to the amount applied, even doubling its initial content [66] and the content of recalcitrant material [67]; it is, however, subjected to environmental conditions. Rovira and Vallejo [68] considered that in Mediterranean conditions (low precipitations and high temperatures), OM decomposes faster inside soil than on soil since moisture is better retained in lower layers. So, the MC of each residue is analyzed (Table 2); CP and SC get the highest content (52.7% and 26%, respectively), and VP (9.3%) is the lowest among the studied pruning waste. Another factor is that increases in temperatures in summer affect soil microbiota, which reduces mineralization [63].

One of the key factors that determines soil agricultural potential, supply and nutrient solubility is soil pH, since it affects microbial activity, cation exchange reactions related to soil aggregation and the mobility of heavy metals [15]. Most of the residues studied (Table 2) have an acid pH (between 4.66 and 5.94), except SC which has a pH of 7.34. This result agrees with Greco et al. [15], who state that the pH range of compost is between 7 and 9 (alkaline). SC can be an interesting option for managing acid soils, given that more than 40% of arable soils in the world are acidic [36]. Nevertheless, incorporating food waste compost into the soil can increase soil pH [59,69] or decrease soil pH with PN [57]. Based on the work of Parzych et al. [56], needle pH can vary according to species from 4.00 to 5.32. The result obtained for PN pH (Table 2) is above this range (5.94). Therefore, based on Parzych's et al. conclusions [56], these data confirm the acid reaction of pine needles, which can have consequences on the mobility of heavy metals. Results agree with those obtained by Ruiz-Navarro et al. [57]; soil pH near *Pinus halepensis* showed a slight decrease related to litter decomposition.

In addition, the allelopathic potential of PN should be kept in mind, as it can affect plant growth [70]. Moreover, the allelopathic interactions between crop residues and aqueous extracts can enhance or affect nutrient availability and yield crop [71]. The most

suitable soil pH to enhance nutrient absorption by plants is usually close to 6.5 [72]; PN has a pH closest to that value (Table 2). In any case, PP, OP and AP have lower pHs than PN. Most olive orchards are grown on calcareous soils, with a pH higher than 7.0 [16], so to increase microelement availability, its pruning wastes (OP) and AP residues application might reduce soil pH. PP has a pH of 4.90 (Table 2), while data on date palm compost shows a pH of 8.38 and 7.6 [52,53]. Previous work managed to reduce soil pH after applying date palm leaves compost [73]. The pH value achieved for VP (5.42) (Table 2) is like that (5.83) reported in other works [40], which led to a decrease in soil pH after the first year of application on alkaline soil. Therefore, AP, CP, OP, PN, PP and VP could be incorporated mainly in alkaline soils to control the pH. The proper choice of waste is key for crops since variations in soil pH can modify the availability of secondary macronutrients, micronutrients and trace elements that could be presented in the organic wastes and adsorbed in soil surfaces [12,16,28,72].

Among the residues considered, PP and SC (Table 2) have the highest EC. AP and PN showed the lowest EC. EC from SC is higher compared to data provided by Oueriemmi et al. [28] and like the one obtained by Jamroz et al. [43] and considerably lower than the results obtained by Pérez-Piqueres et al. [61]. This means there is high variability in SC depending on the origin of wastewater and the treatments applied to wastewater and sludge. Oueriemmi et al. [28] measured the increase in soil conductivity by application of SC, increasing soil EC according to the amount of applied SC from $750 \mu\text{S cm}^{-1}$ to more than $1577 \mu\text{S cm}^{-1}$. Despite this increase, they consider it far from a risk of salinization ($\geq 4000 \mu\text{S cm}^{-1}$). However, changes in soil pH, exchangeable sodium percentage and sodium adsorption ratio, among others, should be considered to assess crop vulnerability.

In this way, PP (EC: $4358 \mu\text{S cm}^{-1}$) should be applied with caution in soils since it could increase EC, and soils can be salinized as well as SC (EC: $3380 \mu\text{S cm}^{-1}$) although EC is less than $4000 \mu\text{S cm}^{-1}$. On the contrary, other references consider that the application of composted organic wastes does not significantly modify the conductivity of soil [59] or can decrease it, as the application of date palm compost ($3200 \mu\text{S cm}^{-1}$) reduced soil EC after 2 years [53]. A similar EC was shown by Abd El-Gaid and Nassef [52] for date palm leaves compost. The EC of PP ($4358 \mu\text{S cm}^{-1}$, Table 2) was higher

than the value obtained by the references mentioned above; it may be due to the treatment received during composting compared to the drying process chosen for this work. Furr et al. [74] did not find a relationship between the number of salts in irrigation water and the concentration of Na and Cl in the leaves of palm trees due to salinity tolerance. However, it should also be noted that EC can be increased by the contribution of organic matter applied to saline soil [53]. Considering the germination of most species and the possibilities of using some of these wastes as seed germination, this would not be affected by EC values below $1000 \mu\text{S cm}^{-1}$ [75], so residues such as AP and PN would be suitable for this purpose.

3.2. Elemental Composition and Soluble Nutrients

Hence, we are interested in addressing the contribution of soluble nutrients from organic residues prior to decomposition to determine its importance for the immediate supply of crops. The elemental composition of residues was analyzed, as well as the concentration of nutrients in aqueous extraction and their solubility index.

3.2.1. Elemental Composition

Tables 3 and 4 present the results from the analysis of macro and micronutrients (total content). The highest amount of nutrients follows the sequence $\text{SC} > \text{OP} > \text{PN} > \text{PP} > \text{VP} > \text{AP} > \text{CP}$. Although there are some references dealing with the organic residue's elemental composition, a previous work that compared the nutrient content of organic residues concluded that sewage sludge had the highest nutrient rate [23], which agrees with the data obtained. Navarro-Pedreño et al. [76] obtained slightly lower concentrations of nutrients, except for Mn and Zn. SC has an important mineral fraction compared with the rest of the residues, which means that it is possible to have an increased content of these nutrients analyzed.

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Table 3. Elemental macronutrient composition, average content (\bar{x}) and standard deviation (σ) for each residue.

Residue	Na (mg kg ⁻¹)		K (mg kg ⁻¹)		Ca (mg kg ⁻¹)		Mg (mg kg ⁻¹)	
	\bar{x}	σ	\bar{x}	σ	\bar{x}	σ	\bar{x}	σ
AP	263 b	47	1698 a	191	7559 b	509	924 c	63
CP	495 c	10	1138 d	17	6649 a	93	1173 b	25
OP	160 a	33	6889 c	123	10599 c	238	1220 b	29
PN	170 a	27	1648 a	81	14059 d	220	1838 a	60
PP	1079 d	32	6858 c	470	6861 a	277	2259 d	85
SC	1529 e	44	4585 b	20	64245 e	257	5815 e	35
VP	173 a	8	4620 b	352	7609 b	244	1746 a	80
F ¹	1151 ***		419 ***		21630 ***		3314 ***	

¹ F values followed by *** indicate significant differences at $p = 0.001$. By columns, mean values with letters in common are statistically equal to $p = 0.05$.

In the reverse series (highest to lowest), the elements ordered from presence in the residues are Ca > K > Fe > Mg > Na > Zn > Mn > Cu. The top 3 nutrients with maximum concentration values are Ca in SC > Fe in SC > Ca in PN, whilst the minimum concentration values are Zn in AP > Cu in AP > Cu in PP, ordered from highest to lowest (Table 3 and 4). These results are consistent with those of Oueriemmi et al. [28] and suggest that organic residues contain a large number of nutrients that can be profitable for plants.

Table 4. Elemental micronutrient composition, average content (\bar{x}) and standard deviation (σ) for each residue.

Residue	Fe (mg kg ⁻¹)		Mn (mg kg ⁻¹)		Cu (mg kg ⁻¹)		Zn (mg kg ⁻¹)	
	\bar{x}	σ	\bar{x}	σ	\bar{x}	σ	\bar{x}	σ
AP	45 b	7	5.7 b	0.9	4.0 a	0.3	4.6 a	1.7
CP	377 a	20	38.9 c	0.5	11.2 a	1.4	5.3 a	0.7
OP	44 b	3	15.0 d	1.6	4.9 a	0.3	12.4 b	0.6
PN	371 a	26	19.4 a	1.8	7.0 a	0.8	11.4 ab	1.0
PP	88 b	4	32.2 e	2.7	3.8 a	0.4	15.7 bc	0.9
SC	18989 c	127	94.4 f	0.6	79.7 b	14.6	249.5 d	8.4
VP	44 b	2	22.2 a	1.3	8.2 a	1.3	19.4 c	1.5
F ¹	81741 ***		1480 ***		99 ***		2907 ***	

¹ F values followed by *** indicate significant differences at $p = 0.001$. By columns, mean values with letters in common are statistically equal to $p = 0.05$.

Asam et al. [77] analyzed pine needle (*Pinus contorta*) where nutrient content was K > Ca > Mg > Mn > Fe > Zn > Cu, and in our case, PN follows the sequence Ca > Mg > K > Fe > Na > Mn > Zn > Cu. For PN nutrient composition, compared with data from

previous studies [55], K (950 mg kg^{-1}), Ca (7570 mg kg^{-1}), and Mg (1030 mg kg^{-1}) differ in part from Table 3 results. Related to micronutrients, a work carried out in Slovakia analyzed needles of various pine species other than *Pinus halepensis*, obtaining higher values for Mn, except for *Pinus nigra* and *Pinus wallichiana*, whose values are like those presented in Table 3 and 4. Similar values of Fe and Cu were observed in *Pinus wallichiana* and *Pinus musgo*. However, Zn concentrations presented in needles from Slovakia were much higher [56]. These variations may be associated with species, habitat and soil type.

Bendaly et al. [78] studied the critical interval of nutrient concentration in palm leaves versus yield (maximum value as toxicity limit) in Tunisia palm groves. By comparing the values obtained (Table 3 and 4), it should be noted that Mn is within the optimal yield range, and Ca and Mg are very close. Nevertheless, K is within the range estimated by Kolsi-Benzina and Zougari [79] in Tunisia, and Zn is like the one obtained by Ahmed and Al-Dousari [49] (Kuwait); Mg, Fe and Mn, also show values close to Marzouk's (Egypt) [80]. Therefore, variations in some nutrients such as Ca could result from differences in soil conditions, climate, and nutrient supplementation practices since the palm tree grove of Elche has an environmental, tourist, identity and heritage utility, while in the other, the main purpose is date production. The elemental composition of VP, except for Ca, Mg and Zn, nutrient concentration is higher in the work of Yilmaz et al. [40] than that obtained by us. Oueriemmi et al. [28] obtained similar nutrients concentration in SC for Mn and Zn, and higher for K, Mg and Cu.

3.2.2. Soluble Nutrients and Solubility Index

Tables 5 and 6 show the results from water extractable concentration for macro and micronutrients. The relevance of each organic residue according to the total amount of water extractable nutrient content is $PP > OP > VP > SC > CP > PN > AP$, and the elements with greater presence in the total aqueous extract are $K > Ca > Mg > Na > Fe > Zn > Mn > Cu$, ordered from highest to lowest. The top three soluble nutrients with maximum concentration values are K in $PP > K$ in $OP > Ca$ in PP , and the minimum are

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Cu in PN > Cu in AP > Cu in CP. What is important from those results is that the rapidly soluble nutrients may contribute to an increase in their concentrations in the soil solution and facilitate the plant absorption and accumulation in plant tissues with a single application on soil [28]. Several studies about nutrient content on organic residues have demonstrated its importance as a nutrient sink and availability for crop yield [11–14,55]. The use of these wastes to supply nutrients in a determined growth stage of a plant is one of the possibilities for adequate agricultural management, not only the use of them once during a period of cultivation.

Table 5. Water extract macronutrients average content (\bar{x}) and standard deviation (σ) of each residue.

Residue	Na (mg kg ⁻¹)		K (mg kg ⁻¹)		Ca (mg kg ⁻¹)		Mg (mg kg ⁻¹)	
	\bar{x}	σ	\bar{x}	σ	\bar{x}	σ	\bar{x}	σ
AP	199 b	33	1163 a	31	353 c	25	208 b	19
CP	316 d	35	616 b	31	963 d	37	386 a	11
OP	88 a	7	4688 c	69	725 a	19	397 a	14
PN	121 a	4	918 d	38	686 a	16	332 c	11
PP	791 c	31	4892 e	69	4330 e	73	1662 d	41
SC	807 c	61	1468 f	62	755 ab	39	163 e	18
VP	141 ab	22	2415 g	87	810 b	15	613 f	20
F ¹	368 ***		3670 ***		5491 ***		2379 ***	

¹ F values followed by *** indicate significant differences at $p = 0.001$. By columns, mean values with letters in common are statistically equal to $p = 0.05$.

Table 6. Water extract micronutrients average content (\bar{x}) and standard deviation (σ) of each residue.

Residue	Fe (mg kg ⁻¹)		Mn (mg kg ⁻¹)		Cu (mg kg ⁻¹)		Zn (mg kg ⁻¹)	
	\bar{x}	σ	\bar{x}	σ	\bar{x}	σ	\bar{x}	σ
AP	1.9 a	0.1	0.8 a	0.1	0.240 b	0.020	4.2 a	0.3
CP	1.9 a	0.2	5.7 b	0.3	0.091 b	0.009	4.3 a	0.3
OP	2.2 a	0.2	3.6 c	0.2	1.144 c	0.187	5.6 b	0.6
PN	8.4 b	0.5	2.1 d	0.2	0.437 a	0.046	4.7 a	0.4
PP	1.4 a	0.2	21.2 e	1.1	0.819 d	0.105	10.5 c	0.6
SC	24.7 c	1.6	0.4 a	0.1	0.522 a	0.051	4.0 a	0.2
VP	3.4 d	0.4	5.2 b	0.3	1.116 e	0.103	6.7 d	0.5
F ¹	669 ***		965 ***		91 ***		119 ***	

¹ F values followed by *** indicate significant differences at $p = 0.001$. By columns, mean values with letters in common are statistically equal to $p = 0.05$.

Comparing the data of total nutrient content regarding soluble nutrient concentration for each residue (Figure 1), it can be observed that there is no direct relation between a

higher nutrient concentration in elemental composition with the values of nutrients in aqueous extractions. SC findings are consistent with those of Jamroz et al. [43], who found a reduction in water-extractable macro and microelements due to composting process. Foereid [41] considers that although drying and composting treatments of organic waste generate a stable product, part of the nutrients can be lost, and the substrate obtained after drying can show low nutrient content. Occasionally, OM takes a long time to incorporate them by degradation into the soil profile due to the high content of recalcitrant material, as is the case for PN (lignified matter), which can be close to 60% of the total amount of organic matter and may explain PN results [67].

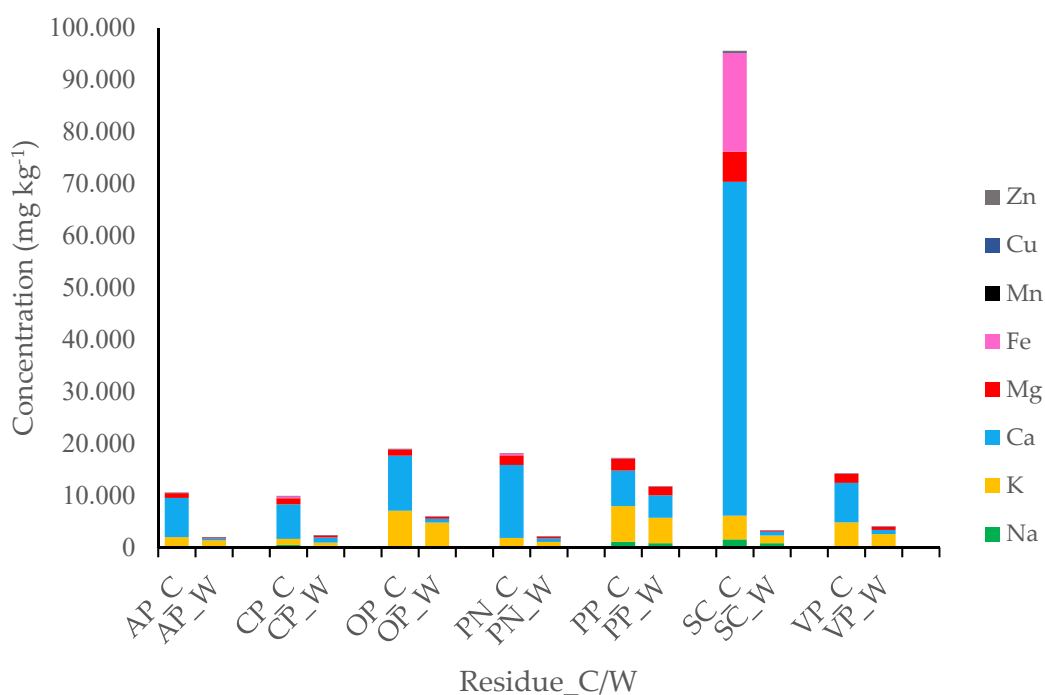


Figure 1. Total nutrient content (mg kg^{-1}) of each residue in elemental composition (C) versus aqueous extraction (W).

Extending the discussion, in most of the residues studied, the four nutrients with the highest elemental composition concentration correspond to macronutrients (Na, K, Ca

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and Mg), as expected, except for PN and SC, where Fe displaces Na (Table 5 and 6). Related to aqueous extraction, the highest concentrations are obtained by macronutrients too, with K being the majority, not Ca, as in the elemental composition. The presence of all nutrients in aqueous extraction indicates they are in part soluble in water, but to know the degree of solubility with respect to the total amount of nutrient composition, a nutrient solubility index (I_N) was calculated (Table 7).

Table 7. Solubility index (%) of each nutrient (I_N).

Residue	I_{Na}	I_K	I_{Ca}	I_{Mg}	I_{Fe}	I_{Mn}	I_{Cu}	I_{Zn}
AP	76	68	5	23	4	14	6	90
CP	64	54	14	33	1	15	1	82
OP	55	68	7	33	5	24	23	45
PN	71	56	5	18	2	11	6	42
PP	73	71	63	74	2	66	21	67
SC	53	32	1	3	0	0	1	2
VP	82	52	11	35	8	24	14	35

Petit-Aldana et al. [42] considered chemical composition as the main aspect that determines the rate of decomposition. In the case of water-extractable forms of nutrients prior to decomposition, other factors would be of importance in determining solubility. For instance, the content of recalcitrant materials could be a factor to consider. Notwithstanding, palm leaves are composed of 66.3% cellulose + hemicellulose and 22.53% lignin [81]; PP is the first residue with the highest amount of soluble nutrients in aqueous extraction after SC but the fourth respect to the total content of nutrients (Table 5 and 6). Therefore, the hydrophilic nature of palm leaf fibers could be a key factor [81]. In *Pinus halepensis* needles, despite their high recalcitrant content of lignin mentioned above, the decomposition on the soil leads to an increase in extractable K due to its rapid leaching capacity [11,16,57]. K, in general, is the nutrient with the second highest concentration in its elemental composition and the first in aqueous extraction (Table 5 and 6). Zipori et al. [16] found that K (apart from N and P) is the one that is taken up in the greatest quantity from the soil solution and is the most important for olive trees due to its high presence in olives. Olive pruning residues can provide 60 kg ha⁻¹ of K per year, although old olive tree leaves have less K content than younger ones. The K phytoavailable in agricultural soils is usually low, so fertilization is usually required for rapid crop development in the early stages of growth [36].

Table 8. Nutrients ordered from higher to lower concentration in elemental composition, aqueous extract and solubility index.

Residue	Elemental Composition	Soluble Nutrients	Nutrient Solubility Index (I _N)
AP	Ca > K > Mg > Na > Fe > Mn > Zn > Cu	K > Ca > Mg > Na > Zn > Fe > Mn > Cu	Zn > Na > K > Mg > Mn > Cu > Ca > Fe
CP	Ca > Mg > K > Na > Fe > Mn > Cu > Zn	Ca > K > Mg > Na > Mn > Zn > Fe > Cu	Zn > Na > K > Mg > Mn > Ca > Cu > Fe
OP	Ca > K > Mg > Na > Fe > Mn > Zn > Cu	K > Ca > Mg > Na > Zn > Mn > Fe > Cu	K > Na > Zn > Mg > Mn > Cu > Ca > Fe
PN	Ca > Mg > K > Fe > Na > Mn > Zn > Cu	K > Ca > Mg > Na > Fe > Zn > Mn > Cu	Na > K > Zn > Mg > Mn > Cu > Ca > Fe
PP	Ca > K > Mg > Na > Fe > Mn > Zn > Cu	K > Ca > Mg > Na > Mn > Zn > Fe > Cu	Mg > Na > K > Zn > Mn > Ca > Cu > Fe
SC	Ca > Fe > Mg > K > Na > Zn > Mn > Cu	K > Na > Ca > Mg > Fe > Zn > Cu > Mn	Na > K > Mg > Zn > Ca > Cu > Mn > Fe
VP	Ca > K > Mg > Na > Fe > Mn > Zn > Cu	K > Ca > Mg > Na > Zn > Mn > Fe > Cu	Na > K > Mg > Zn > Mn > Cu > Ca > Fe

In Table 8, the order of nutrients' elemental composition does not follow the same sequence as aqueous extractions and the nutrient solubility index. Ca, Mg, Fe and Zn focus our attention. Ca is the nutrient with the highest content in the elemental composition of all the residues studied. However, in aqueous extraction, Ca becomes the second in most of them. Interestingly, based on its solubility index, Ca is among the four elements with the lowest solubility index, and this may be related to its structural function as a cell wall constituent [11]. The same trend was found for Fe, being the nutrient with the lowest solubility index in all residues, opposite to results obtained by Jamroz et al. [43]. Noteworthy is the high solubility of Mg in PP (Table 7 and 8). The most striking result to emerge from the data is the behavior of Zn. Although Zn content lags in terms of elemental composition, it has a higher aqueous extraction, and the most interesting thing is found on the solubility index. Zn is the first of the four micronutrients, being the first in AP and CP. Previous works suggested that Zn solubility is minimum and depends on pH [29], and this may affect the importance of Zn fertilization from these organic wastes [82].

3.3. Correlation between Physical and Chemical Properties and Nutrient Content

As discussed above, nutrient solubility can be driven by elemental composition and its structural function. Although Jamroz et al. [43] indicate other factors such as pH, EC and OM may play a role too. Therefore, this paper provides significant correlation coefficients between elemental composition, water extractable nutrients content and

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physical and chemical properties of each residue (Appendix A. Table A1–A7). AP and VP (Table A1 and A7) show a mostly high correlation between the elemental composition of a nutrient and the soluble concentration of that nutrient. Therefore, the presence of soluble nutrients from AP and VP residues is associated with its elemental composition. In Table A1, nutrients' elemental composition versus its soluble forms, on most occasions, shows a significant and negative (–) linear correlation (<0.7). Additionally, in Table A1 for AP, a positive (+) linear correlation is observed between the elemental composition of a nutrient and the elemental composition of another nutrient, which is significantly high (>0.7). The same correlation applies to water extractable content between nutrients (Table A1). Usually, in Table A7 for VP, correlations are similar to AP (Table A1), but the correlation between the soluble form of one nutrient and that of another nutrient is negative. The nutrients that show a significant correlation between their content of elemental composition and their own aqueous extractable content are K, Ca and Fe (–) in AP; Na (+) and Zn (–) in CP; Mg (–), Fe (–) and Mn (+) in OP; Fe and Cu (+) in PN; Mg (+), Fe (–) and Zn (+) in PP; K and Zn (+) in SC; and Ca (+) in VP.

When addressing the importance of physical and chemical properties of the wastes related to elemental composition nutrient content and aqueous extract nutrient content, differences were observed on each of the residues. OM is the most important property for elemental composition because it has more significant correlations in AP (mainly negative), OP (positive and negative) and SC (positive and negative), and for water extraction nutrients in PN (positive and negative). EC is the most correlated property for elemental composition and water-extractable nutrients in PP, SC and VP. Bulk density (ρ_b) seems to be related to water-extractable nutrients in CP, OP and SC, as well as pH is highly correlated to PN and VP elemental composition. MC is associated with elemental composition nutrient content in OP (+, –) and AP (–) and with soluble nutrient content in CP (+). Comparing the degree of correlation between properties, we highlight OM/EC (–) for AP, PP and VP; pH/EC (–) for CP, PN and especially in VP and PP (that obtained a –1 maximum value); ρ_b /EC (–) for AP and PP.

3.4. Nutrients for Crop Nutrition and Human Health

As previously stated, K, Ca, Mg, Fe, Mn, Cu and Zn are essential nutrients for people and plants, and Na is beneficial for plants and essential for humans [29,37]. Our results indicate that it is possible to enhance the availability of all these nutrients, mainly Na, K, Ca, and Mg, in soil solution, as well as in micronutrients. Ca, Mg, Cu, Fe and Zn are one of the most lacking in the human diet [39]; therefore, if they are in optimal forms and conditions for plant uptake, this could be beneficial for human nutrition. The K needs of plants are higher than existing reserves in an assimilable form of primary elements in soil, so it is necessary to make contributions using fertilizers [17,34]. K is necessary for plant nutrition because it increases disease resistance and is involved in photosynthesis, carbohydrate metabolism and translocation of starches, seed quality and fruit formation. Humans take K for muscle and nerve activity and for proper fluid balance [5]. This element is critical for the adequate development of people.

Ca and Mg are secondary macronutrients, and the contribution of Ca from soil solution for the growth of crops is usually sufficient [16]; however, deficiency can be frequent in soils on highly weathered tropical soils [17]. This could have serious negative implications related to harvest because Ca stimulates microbial activity, reduces plant respiration, and promotes plant growth and fruit formation. Ca ingestion is vital to ensure muscle and nerve activity, immune system health, blood clotting, pressure regulation and healthy bones [5]. Mg lack in plants is observed all over the world, aids in enzyme functionality and plant use of Fe and P, mainly on strongly acidic soils [17,36] and PP could be an interesting option due to its high solubility index (Table 7) and its almost neutral pH (Table 2). Fe, Cu and Zn deficiencies usually occur in plants growing on soils on calcareous or alkaline soils (covering 25 to 30% of land surface), especially in arid and semi-arid environments, so lowering soil pH can improve its uptake [39]. Fe, Cu and Zn are involved in photosynthesis and promote plant growth. Fe acts as an O₂ carrier, Cu promotes plant reproduction and fruit flavor, and Zn takes part in seed formation. The human body needs Fe to deliver oxygen to the tissues and for brain and muscle functioning; Cu for Fe metabolism; and Cu, as a component of enzymes, DNA, RNA and

proteins, promotes immune system health, as well as contributes to the perception of taste [5].

PP is the residue with the highest amount of K, Ca, Mg and Mn in aqueous extraction (Table 5 and 6) and the one that obtains the highest solubility index for these nutrients and high solubility rates for the rest of the nutrients (Table 7). OP can provide an extra provision of Cu due to its significant concentration in soluble form and high solubility (Table 6 and 7). SC and PN achieved the greatest amounts of Fe in the aqueous extract (Table 6). However, the Fe solubility index is 0 and 2, respectively (Table 7). Consequently, it is convenient to prioritize the use of VP, which provides the highest I_{Fe} (Table 7). Soluble Zn can be increased mainly with PP application (Table 6); although it shows a high I_{Zn} , AP obtains the highest (Table 7). The importance of an efficient nutrient supply to crops is undeniable, as well as its connections to soil, ecosystems and human health [83–85].

4. Conclusions

The use of organic wastes as amendments/substrates or forming technosols can improve crop nutrients availability and yield, ensure the presence of minerals for human nutrition, as well as ecosystem services provision. In addition, this practice would help solve the soil problems mentioned by the FAO, comply with United Nations Sustainable Development Goals and promote a circular economy in the agricultural sector.

SC, OP and PN are the three residues with the highest presence of nutrients in their elemental composition. On the other hand, if we need to apply residues to reinforce crop nutrition in a specific phase or need, residues with a greater amount of required soluble nutrients are a more advisable option. PP, OP and VP are the three residues with the most amount of soluble nutrients. Moreover, PP is the residue whose nutrients show the highest solubility indices. Incorporating crop residues into the soil is a valid option as an extra supply of rapidly soluble nutrients as well as a nutrient contribution by these by-products with a first rainwater or irrigation; however, this has been poorly studied

The presence of nutrients in elemental composition indicates that they may be available in an aqueous soil solution. However, the elemental composition does not follow the same order of the quantity of each element that could be extracted by water, as it happens for SC and PN. In fact, nutrients such as Ca show a high presence in aqueous extraction but compared to the total amount of nutrients in waste, its solubility index is low. The solubility index can be important in synchronizing the supply of nutrients with the growth phases of crops and its nutrients requirements. In such a way, organic wastes can be selected and added along the period of cultivation to supply the nutrients needed along the growth of plants, not at once. Moreover, it is convenient to continue expanding studies to determine the accurate formula for residue application, as it was developed in the past for the use of inorganic fertilizers.

Appendix A

Supplemental and visual data related to the correlation matrix of each residue are added (Table A1–A7). The objective of this data collection is to measure the degree of association between elemental composition nutrient content, water-extractable nutrient content and physical and chemical properties. The correlation coefficient can take a range of values from +1 to -1, so:

- -1 indicates a perfect negative linear correlation between variables
- 0 indicates that there is no linear correlation between variables
- 1 indicates a perfect positive linear correlation between variables

A positive association (highlighted in green) indicates as the value of one variable increases so does the value of the other. A value less than 0 (highlighted in red) indicates a negative association; that is, as the value of one variable increases, the value of the other decreases. The more intense the color, the greater relation. We have considered the correlation highly significant when the result is >0.7 or <0.7 .

SOLUBLE ELEMENTS RELEASED FROM ORGANIC WASTES TO INCREASE AVAILABLE NUTRIENTS FOR SOIL AND CROPS

Table A1. Correlation coefficients between elemental composition nutrient content, water extractable nutrient content and physical and chemical properties of AP.

	<i>C_Na</i>	<i>C_K</i>	<i>C_Ca</i>	<i>C_Mg</i>	<i>C_Fe</i>	<i>C_Mn</i>	<i>C_Cu</i>	<i>C_Zn</i>	<i>W_Na</i>	<i>W_K</i>	<i>W_Ca</i>	<i>W_Mg</i>	<i>W_Fe</i>	<i>W_Mn</i>	<i>W_Cu</i>	<i>W_Zn</i>	<i>pb</i>	<i>pH</i>	<i>EC</i>	<i>OM</i>	<i>MC</i>	
<i>C_Na</i>	1																					
<i>C_K</i>	0.81250432	1																				
<i>C_Ca</i>	0.14327245	0.69335048	1																			
<i>C_Mg</i>	0.86626341	0.9950799	0.61854512	1																		
<i>C_Fe</i>	0.67413918	0.97831421	0.82756994	0.95297963	1																	
<i>C_Mn</i>	0.95883748	0.94459288	0.41840093	0.97246642	0.85612062	1																
<i>C_Cu</i>	0.98669643	0.70692206	-0.01952985	0.77351933	0.54509325	0.89991791	1															
<i>C_Zn</i>	0.96137206	0.62065928	-0.13467434	0.69528889	0.44479613	0.84364022	0.9933311	1														
<i>W_Na</i>	0.45613064	-0.14817116	-0.81538089	-0.04946006	-0.34979792	0.18465959	0.59473872	0.6834617	1													
<i>W_K</i>	-0.83802062	-0.99897819	-0.66007463	-0.99854082	-0.96795354	-0.95846261	-0.7381656	-0.65546141	0.10332386	1												
<i>W_Ca</i>	0.13906918	-0.46429609	-0.96014142	-0.37426233	-0.63767508	-0.14785138	0.29821278	0.40627469	0.94469896	0.42379356	1											
<i>W_Mg</i>	-0.03572803	-0.61161216	-0.99417026	-0.53021846	-0.76221844	-0.3180315	0.12721697	0.24072851	0.87304801	0.57523102	0.98468175	1										
<i>W_Fe</i>	-0.90370987	-0.98385774	-0.55320505	-0.99674689	-0.92545627	-0.9880851	-0.82208223	-0.75095348	-0.03119771	0.99094014	0.29830675	0.4601598	1									
<i>W_Mn</i>	-0.01995167	-0.59904995	-0.99234481	-0.51677149	-0.75190751	-0.3030293	0.14285489	0.25601641	0.88063512	0.56224986	0.98731089	0.99987546	0.44609067	1								
<i>W_Cu</i>	-0.25990463	-0.77409514	-0.99290929	-0.70756473	-0.88843357	-0.52340339	-0.09946044	0.01592788	0.74077987	0.74469275	0.92010617	0.97430366	0.64831024	0.97062761	1							
<i>W_Zn</i>	-0.11693002	-0.67396233	-0.99964706	-0.59745264	-0.81236473	-0.39412441	0.04608383	0.16095073	0.8304728	0.63988533	0.96722812	0.99668377	0.53087918	0.99527542	0.98940084	1						
<i>pb</i>	0.01479043	0.2929071	0.47910061	0.25351677	0.36589125	0.15094978	-0.06385303	-0.11853266	-0.42220475	-0.27529675	-0.47523975	-0.48218457	-0.21963436	-0.48216447	-0.46922399	-0.48037954	1					
<i>pH</i>	0.31525387	-0.18286099	-0.70020936	-0.10312115	-0.34371761	0.08847334	0.43356336	0.51044276	0.81406752	0.14671011	0.78968736	0.74140898	0.03750667	0.74671443	0.64532085	0.71111909	-0.60138839	1				
<i>EC</i>	0.65422693	0.37532036	-0.1716118	0.43284768	0.24305493	0.55123464	0.68918675	0.70282852	0.53705177	-0.40202111	0.35650917	0.24457326	-0.47650414	0.25501358	0.08885109	0.18977456	-0.73908124	0.816496581	1			
<i>OM</i>	-0.86735765	-0.52157274	0.18673139	-0.59440138	-0.35264263	-0.7424619	-0.90694741	-0.9203901	-0.67530013	0.5554322	-0.43182248	-0.28305664	0.64933293	-0.29687912	-0.07800747	-0.2106671	0.39999357	-0.104163245	-0.92462309	1		
<i>MC</i>	-0.7532166	-0.79575657	-0.41996847	-0.80995845	-0.74062465	-0.81168906	-0.69187389	-0.63727142	-0.06293435	0.80320783	-0.20751033	0.34202251	0.81563467	0.330279	0.50022762	0.40121853	-0.62113508	-2.14284E-17	0	0.19768339	1	

Table A2. Correlation coefficients between elemental composition nutrient content, water extractable nutrient content and physical and chemical properties of CP.

	<i>C_Na</i>	<i>C_K</i>	<i>C_Ca</i>	<i>C_Mg</i>	<i>C_Fe</i>	<i>C_Mn</i>	<i>C_Cu</i>	<i>C_Zn</i>	<i>W_Na</i>	<i>W_K</i>	<i>W_Ca</i>	<i>W_Mg</i>	<i>W_Fe</i>	<i>W_Mn</i>	<i>W_Cu</i>	<i>W_Zn</i>	<i>ρb</i>	<i>pH</i>	<i>EC</i>	<i>OM</i>	<i>MC</i>	
<i>C_Na</i>	1																					
<i>C_K</i>	-0.33486222	1																				
<i>C_Ca</i>	0.77587396	-0.85427578	1																			
<i>C_Mg</i>	0.56011776	-0.96814859	0.95721653	1																		
<i>C_Fe</i>	-0.53299483	0.97574945	-0.94734274	-0.99947543	1																	
<i>C_Mn</i>	-0.93701176	-0.01536149	-0.50663576	-0.23547459	0.20387558	1																
<i>C_Cu</i>	0.85545201	-0.77444172	0.9904485	0.90817406	-0.89414105	-0.62067403	1															
<i>C_Zn</i>	-0.86485446	0.76264642	-0.98773809	-0.90030238	0.88573355	0.6350239	-0.99983004	1														
<i>W_Na</i>	0.92278503	-0.4867443	0.83505751	0.67316297	-0.65146757	-0.79897609	0.8871992	-0.8928872	1													
<i>W_K</i>	0.10573156	0.16700137	-0.05374335	-0.11882145	0.12547362	-0.17351681	-0.02112534	0.01673342	-0.26916641	1												
<i>W_Ca</i>	0.8432277	-0.05902705	0.50457603	0.27590822	-0.2488502	-0.87261377	0.59842829	-0.61011128	0.57130169	0.60851839	1											
<i>W_Mg</i>	0.75848002	0.26745806	0.23926437	-0.0363327	0.06399689	-0.90379544	0.36213445	-0.37803935	0.47988638	0.53324435	0.93680076	1										
<i>W_Fe</i>	0.2062442	-0.1124505	0.18880959	0.15357154	-0.14881185	-0.17657886	0.1999477	-0.20114763	-0.12939443	0.96090512	0.63458165	0.46736374	1									
<i>W_Mn</i>	-0.15776425	0.9523447	-0.72473603	-0.87921787	0.89183612	-0.18546965	-0.62943024	0.61577607	-0.41051455	0.43361072	0.21509941	0.49555697	0.17037665	1								
<i>W_Cu</i>	0.80024819	0.26224752	0.26583161	-0.01794063	0.04960469	-0.94626875	0.39308797	-0.40953457	0.56267231	0.40673374	0.9081723	0.98971225	0.34173186	0.46327876	1							
<i>W_Zn</i>	0.90223081	-0.33365481	0.72124339	0.53311872	-0.50923171	-0.83397198	0.78929078	-0.79724721	0.98333586	-0.32924252	0.54541026	0.51782165	-0.23262265	0.28288063	0.61405912	1						
<i>ρb</i>	0.9670886	-0.46391319	0.84406805	0.6648105	-0.64121623	-0.85412414	0.90421329	-0.91094682	0.8510745	0.27081242	0.87987317	0.7223271	0.40813633	0.24232504	0.73306452	0.78872695	1					
<i>pH</i>	-0.50254497	-0.4377095	0.01567304	0.25123071	-0.27625923	0.69588062	-0.09703707	0.1119671	-0.5365599	0.36970376	-0.29742093	-0.53820238	0.49070839	0.38872381	-0.64428765	-0.68031337	0.06862071	1				
<i>EC</i>	0.22051955	0.39408135	-0.1419775	-0.28778787	0.30257779	-0.38059611	-0.06824985	0.05829297	0.3918819	-0.68509804	-0.10139169	0.15312712	-0.79792883	0.22723641	0.28189874	0.54328843	0.03391492	-0.915249233	1			
<i>OM</i>	-0.95198524	0.34441018	-0.75585938	-0.55578307	0.53043804	0.88270606	-0.8285653	0.83708779	-0.98606136	0.20125202	-0.64916964	-0.60205769	0.10045338	0.25317028	-0.68331532	-0.99092765	0.07340175	0.55846018	-0.45241825	1		
<i>MC</i>	0.86159592	0.1575474	0.36988009	0.09044732	-0.05869308	-0.97279137	0.49195381	-0.50756436	0.76731459	0.01494514	0.75035081	0.85243209	-0.02313082	0.26972241	0.91790599	0.84027092	0.04814856	-0.725764496	0.57885444	-0.9425126	1	

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Table A3. Correlation coefficients between elemental composition nutrient content, water extractable nutrient content and physical and chemical properties of OP.

	<i>C_Na</i>	<i>C_K</i>	<i>C_Ca</i>	<i>C_Mg</i>	<i>C_Fe</i>	<i>C_Mn</i>	<i>C_Cu</i>	<i>C_Zn</i>	<i>W_Na</i>	<i>W_K</i>	<i>W_Ca</i>	<i>W_Mg</i>	<i>W_Fe</i>	<i>W_Mn</i>	<i>W_Cu</i>	<i>W_Zn</i>	<i>ρb</i>	<i>pH</i>	<i>EC</i>	<i>OM</i>	<i>MC</i>	
<i>C_Na</i>	1																					
<i>C_K</i>	0.98808731	1																				
<i>C_Ca</i>	-0.86629216	-0.7790963	1																			
<i>C_Mg</i>	-0.92630022	-0.97325077	0.61422771	1																		
<i>C_Fe</i>	-0.99805098	-0.99576509	0.83343079	0.9480077	1																	
<i>C_Mn</i>	-0.70105462	-0.80244638	0.25109404	0.9180762	0.74418877	1																
<i>C_Cu</i>	0.97302673	0.92593314	-0.95816496	-0.81439319	0.95673427	-0.51763644	1															
<i>C_Zn</i>	-0.07502955	0.07932478	0.56312714	-0.30622432	0.01265558	-0.65849773	-0.30304785	1														
<i>W_Na</i>	0.00403088	0.15787592	0.49604168	-0.380517	0.06642616	-0.71592765	-0.22676831	0.99687077	1													
<i>W_K</i>	-0.77109777	-0.85989901	0.34993197	0.95417417	0.80932834	0.9946292	-0.60341308	-0.57706692	-0.63981978	1												
<i>W_Ca</i>	0.15850652	0.00466952	-0.63053543	0.22519827	0.09658287	0.59297069	0.382007	-0.99646755	-0.98671099	0.5064433	1											
<i>W_Mg</i>	0.83381895	0.90884144	-0.44656707	-0.98036702	0.86664302	-0.97821511	0.68397721	0.4879209	0.55539453	-0.99444778	-0.41289334	1										
<i>W_Fe</i>	0.78956984	0.68572507	-0.99054481	-0.50015982	0.74973632	-0.11592551	0.90983941	-0.67117205	-0.61047305	-0.21810751	0.73105473	0.3195943	1									
<i>W_Mn</i>	0.00179828	-0.15211721	-0.50109469	0.3751199	0.06060876	0.71184573	0.23244174	-0.99731462	-0.99998301	0.63532907	0.98764137	-0.55053766	0.61507957	1								
<i>W_Cu</i>	0.00693656	-0.04361931	-0.16933155	0.11700026	0.01364518	0.22857558	0.08208795	-0.32679365	-0.32717671	0.20310461	0.32414592	-0.17497147	0.20615266	0.3272184	1							
<i>W_Zn</i>	0.93614848	0.97910644	-0.63533823	-0.99963446	0.95626536	-0.90702334	0.82978497	0.28037502	0.35537553	-0.94573474	-0.19877423	0.97467762	0.52338853	-0.34992086	-0.1086939	1						
<i>ρb</i>	0.31053185	0.45252111	0.2039367	-0.64435493	-0.3689937	-0.8928236	0.08373515	0.92078147	0.94799209	-0.84225041	-0.88556007	0.78155704	-0.33580615	-0.94618819	-0.22723742	0.62357258	1					
<i>pH</i>	0.75644683	0.79477009	-0.50197018	-0.81649638	0.77422854	-0.74937708	0.66528405	0.24948158	0.31015698	-0.77890702	-0.1833112	0.80035231	0.4088785	-0.30574899	-0.64090854	0.81621352	0.45786056	1				
<i>EC</i>	-0.68452074	-0.6120549	0.91724251	0.4996465	0.65531889	0.27523664	-0.79156801	0.51405308	0.41592253	0.33728808	-0.61903353	-0.39638409	-0.96565903	-0.42305762	-0.79839853	-0.51311001	-0.00254189	0	1			
<i>OM</i>	-0.78993611	-0.82994518	0.52418487	0.85263042	0.80849202	0.78254076	-0.69472619	-0.26052239	-0.32388297	0.81337755	0.19142364	-0.8357719	-0.42697341	0.31927991	0.59331218	-0.85233504	-0.50220696	0.927389288	0.05961965	1		
<i>MC</i>	0.82382754	0.76049484	-0.88763859	-0.63200828	0.80056828	-0.32934671	0.88198507	-0.40896114	-0.3448018	-0.41364875	0.47431791	0.49480348	0.86415635	0.3496067	-0.30308403	0.64888853	-0.05362748	0.232495277	-0.5	-0.54732691	1	

Table A4. Correlation coefficients between elemental composition nutrient content, water extractable nutrient content and physical and chemical properties of PN.

	<i>C_Na</i>	<i>C_K</i>	<i>C_Ca</i>	<i>C_Mg</i>	<i>C_Fe</i>	<i>C_Mn</i>	<i>C_Cu</i>	<i>C_Zn</i>	<i>W_Na</i>	<i>W_K</i>	<i>W_Ca</i>	<i>W_Mg</i>	<i>W_Fe</i>	<i>W_Mn</i>	<i>W_Cu</i>	<i>W_Zn</i>	<i>pb</i>	<i>pH</i>	<i>EC</i>	<i>OM</i>	<i>MC</i>	
<i>C_Na</i>	1																					
<i>C_K</i>	0.9480079	1																				
<i>C_Ca</i>	0.05430222	0.36925616	1																			
<i>C_Mg</i>	0.1529209	0.45947393	0.99508428	1																		
<i>C_Fe</i>	-0.90050613	-0.71529945	0.38530223	0.29202266	1																	
<i>C_Mn</i>	-0.24182755	-0.53805541	-0.98201936	-0.99588726	-0.20416963	1																
<i>C_Cu</i>	-0.82887417	-0.60774086	0.51359994	0.42610305	0.98967288	-0.342386	1															
<i>C_Zn</i>	-0.21781778	-0.51709848	-0.98637742	-0.99781918	-0.22825623	0.99969569	-0.3654592	1														
<i>W_Na</i>	-0.50560796	-0.44559903	0.07829395	0.02734762	0.50130494	0.01949711	0.47828579	0.00675841	1													
<i>W_K</i>	-0.71821284	-0.51116392	0.49344225	0.41713102	0.87859997	-0.34372465	0.89359084	-0.36399161	0.8023713	1												
<i>W_Ca</i>	0.78404163	0.56755909	-0.50873796	-0.42573935	-0.94610662	0.34614079	-0.95873593	0.36809568	-0.69772756	-0.98430124	1											
<i>W_Mg</i>	0.52987486	0.25652163	-0.74243398	-0.68223619	-0.81298476	0.62128898	-0.8712583	0.63838997	-0.64964877	-0.9489978	0.94122724	1										
<i>W_Fe</i>	0.78406957	0.59097652	-0.43533852	-0.35309396	-0.91416144	0.27481073	-0.91763093	0.29634933	-0.7854773	-0.99499546	0.9910758	0.92354887	1									
<i>W_Mn</i>	-0.58306353	-0.49415889	0.15211933	0.0927302	0.60503955	-0.03759845	0.58620828	-0.05264006	0.9918386	0.87064312	-0.78318684	-0.72829994	-0.85795046	1								
<i>W_Cu</i>	-0.73737676	-0.50942922	0.55485458	0.47600926	0.92306218	-0.39977759	0.94447239	-0.42085951	0.70847783	0.98957724	-0.9973562	-0.96237115	-0.98909479	0.79147949	1							
<i>W_Zn</i>	0.24537691	0.40133247	0.54272653	0.5614666	0.00963161	-0.5737771	0.09326168	-0.57089318	-0.76283828	-0.25633319	0.12983271	0.0048396	0.25935208	-0.68771079	-0.12341369	1						
<i>pb</i>	-0.20856149	-0.00399872	0.59653207	0.56969743	0.45256942	-0.54024212	0.51347252	-0.5487026	-0.48548951	0.13221683	-0.28254294	-0.31254071	-0.15240883	-0.37205841	0.27281025	0.89281847	1					
<i>pH</i>	-0.57318028	-0.80416018	-0.84934522	-0.89744276	0.15982902	0.93371879	0.01667685	0.9246032	0.20299324	-0.02529359	0.00304207	0.32918171	-0.05720345	0.18335574	-0.06555627	-0.57506632	-0.11042356	1				
<i>EC</i>	0.76550903	0.9066005	0.60911259	0.67876155	-0.44220612	-0.73663717	-0.31655419	-0.72147985	-0.06864659	-0.11191428	0.20084682	-0.13900145	0.20900667	-0.10310397	-0.1298485	0.24444088	-0.04447853	0.904534034	1			
<i>OM</i>	0.74579494	0.50083245	-0.60642016	-0.52620772	-0.9533076	0.4482931	-0.9806053	0.46987281	-0.57847593	-0.9504292	0.98642467	0.94988565	0.95612265	-0.67680127	-0.98528308	-0.03463194	-0.50738515	0.035926856	0.1559078	1		
<i>MC</i>	0.78562801	0.58560779	-0.45678186	-0.37415702	-0.9249848	0.29534454	-0.93102568	0.31704398	-0.13839005	-0.66817192	0.78885222	0.67503371	0.71148345	-0.26197504	-0.76138186	-0.36795985	-0.78946327	0.190940654	0.42692452	0.868022	1	

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Table A5. Correlation coefficients between elemental composition nutrient content, water extractable nutrient content and physical and chemical properties of PP.

	C_Na	C_K	C_Ca	C_Mg	C_Fe	C_Mn	C_Cu	C_Zn	W_Na	W_K	W_Ca	W_Mg	W_Fe	W_Mn	W_Cu	W_Zn	pb	pH	EC	OM	MC	
C_Na	1																					
C_K	-0.74024683	1																				
C_Ca	0.41568717	-0.91920513	1																			
C_Mg	0.23685616	-0.82853575	0.98208544	1																		
C_Fe	0.23608559	-0.82809142	0.98193569	0.99999969	1																	
C_Mn	0.83045082	-0.98929112	0.85188714	0.73793714	0.73740169	1																
C_Cu	0.72385496	-0.07195221	-0.32661956	-0.49886988	-0.49955706	0.21675915	1															
C_Zn	-0.52576612	0.96110464	-0.99220797	-0.95095523	-0.95070961	-0.91050157	0.20631502	1														
W_Na	-0.4824873	0.50053787	-0.39452347	-0.32147093	-0.32113914	-0.51948276	-0.2021068	0.43507804	1													
W_K	-0.34593837	0.3207589	-0.2313013	-0.17540644	-0.17515792	-0.340876	-0.18402548	0.26371652	0.98031807	1												
W_Ca	-0.72722345	0.18189574	0.17986349	0.34280092	0.34346071	-0.30858813	-0.8921682	-0.06859843	0.60823029	0.60750552	1											
W_Mg	0.31593438	-0.80405712	0.9026583	0.898772	0.89868759	0.73482058	-0.35644193	-0.88750239	-0.69468237	-0.58790623	0.03436232	1										
W_Fe	-0.72241473	0.96898209	-0.88769045	-0.79856637	-0.79813082	-0.95971839	-0.07732637	0.92918708	0.69613173	0.54258113	0.29067653	-0.88102681	1									
W_Mn	0.07080543	0.25947284	-0.39247788	-0.43391971	-0.43406128	-0.1996249	0.37132075	0.35736974	0.81496396	0.84430378	0.08760703	-0.74668825	0.46656967	1								
W_Cu	-0.91453689	0.92299654	-0.71295901	-0.57211168	-0.57147559	-0.9633226	-0.40953054	0.79208589	0.66577316	0.51250727	0.54627275	-0.6726023	0.9395844	0.25725382	1							
W_Zn	-0.93230315	0.85744537	-0.61387675	-0.46258953	-0.46191779	-0.9128649	-0.50316013	0.70185209	0.27992245	0.10150355	0.43163461	-0.39394068	0.76939495	-0.18234073	0.89842599	1						
pb	0.54166051	-0.58774494	0.47782972	0.39819724	0.39783195	0.6045902	0.20041536	-0.52109901	0.35340967	0.52634861	0.09928121	0.0692395	-0.37475252	0.61006787	-0.4602209	-0.78234989	1					
pH	-0.03630182	0.0149782	0.0009955	0.00858312	0.0086144	-0.02028996	-0.03847248	0.00404092	0.86259574	0.94340742	0.47142909	-0.42151505	0.26161139	0.87156406	0.19901775	-0.23280213	0.39984219	1				
EC	-0.76424591	0.22475293	0.01423892	0.12463364	0.1251021	-0.31817422	-0.87579774	0.05798058	-0.77680517	-0.93095704	0.70128968	0.40398583	0.0110948	-0.91493529	0.31409514	0.70889537	-0.86984547	-1	1			
OM	0.03125738	-0.04460073	0.0420228	0.03841162	0.03839352	0.04374297	0.00061142	-0.04358527	0.82680903	0.91849639	0.42976346	-0.38802356	0.20356919	0.86958434	0.13199336	-0.29928135	0.3559101	0.993340245	-0.99867922	1		
MC	-0.18675186	0.39597141	-0.42627179	-0.4166541	-0.41658207	-0.36864191	0.12929133	0.42426024	-0.59658911	-0.74272965	-0.46179102	0.00068889	0.15905095	-0.63415755	0.15508627	0.50690409	-0.55973369	0.917742229	0.8660254	-0.92572912	1	

Table A6. Correlation coefficients between elemental composition nutrient content, water extractable nutrient content and physical and chemical properties of SC.

	<i>C_Na</i>	<i>C_K</i>	<i>C_Ca</i>	<i>C_Mg</i>	<i>C_Fe</i>	<i>C_Mn</i>	<i>C_Cu</i>	<i>C_Zn</i>	<i>W_Na</i>	<i>W_K</i>	<i>W_Ca</i>	<i>W_Mg</i>	<i>W_Fe</i>	<i>W_Mn</i>	<i>W_Cu</i>	<i>W_Zn</i>	<i>ρb</i>	<i>pH</i>	<i>EC</i>	<i>OM</i>	<i>MC</i>	
<i>C_Na</i>	1																					
<i>C_K</i>	0.30704504	1																				
<i>C_Ca</i>	-0.99909827	-0.26637853	1																			
<i>C_Mg</i>	0.35312468	0.99880551	-0.31309787	1																		
<i>C_Fe</i>	0.92132099	0.65290871	-0.90398937	0.68909498	1																	
<i>C_Mn</i>	-0.6832675	-0.90468995	0.65166158	-0.92440648	-0.91339976	1																
<i>C_Cu</i>	-0.73105067	-0.87382799	0.70143242	-0.89651722	-0.93882123	0.99771381	1															
<i>C_Zn</i>	-0.95674301	-0.01688849	0.96822956	-0.06566053	-0.76835355	0.44128273	0.50091868	1														
<i>W_Na</i>	0.09061463	0.89289765	-0.05245881	0.88144483	0.43684568	-0.7250476	-0.68596698	0.17696902	1													
<i>W_K</i>	0.56986696	0.85682798	-0.53844932	0.87249983	0.8036469	-0.91307777	-0.90595024	-0.33600125	0.53916392	1												
<i>W_Ca</i>	-0.28581836	0.82416429	0.32621202	0.79551732	0.10922256	-0.50434565	-0.44484542	0.55220177	0.84994516	0.51884754	1											
<i>W_Mg</i>	-0.67491529	-0.60179199	0.65595722	-0.62766903	-0.78308923	0.764731	0.77702534	0.52392748	-0.1896566	-0.92728618	-0.19708724	1										
<i>W_Fe</i>	-0.42478443	-0.39107409	0.41171174	-0.40829804	-0.49796254	0.49143761	0.49846295	0.32506712	0.06363191	-0.7855212	-0.13073799	0.92694923	1									
<i>W_Mn</i>	0.04946238	0.8728039	-0.0106411	0.86158592	0.39599699	-0.69239293	-0.6515571	0.21567669	0.64837969	0.84713562	0.84421859	-0.66988383	-0.63943826	1								
<i>W_Cu</i>	0.32734066	-0.25345792	-0.34175662	-0.23029879	0.1570943	0.04668206	0.01341554	-0.41971104	-0.66183192	0.26961001	-0.46029901	-0.59695044	-0.78670171	0.05512903	1							
<i>W_Zn</i>	-0.56663718	0.60993211	0.60110971	0.57059193	-0.2017934	-0.2143062	-0.14781653	0.78180496	0.68891631	0.27562372	0.9509887	0.0282233	-0.00286032	0.72321863	-0.47375954	1						
<i>ρb</i>	0.18719894	0.38724632	-0.1711885	0.39248626	0.30731639	-0.38221493	-0.3744017	-0.07652014	-0.04204994	0.72482382	0.26756824	-0.83108069	-0.96755383	0.71738707	0.73082569	0.19848317	1					
<i>pH</i>	-0.37744244	-0.61757967	0.35567089	-0.62465108	-0.55260136	0.6417254	0.63468824	0.20922065	-0.82313846	-0.28640267	-0.40631361	0.00855699	-0.35223952	-0.16581116	0.73383918	-0.20449196	0.46785805	1				
<i>EC</i>	0.93201858	0.33082598	-0.94699286	0.3607171	0.75893615	-0.56267318	-0.59507519	-0.99994122	-0.12430061	0.77744506	-0.1319462	-0.95426281	-0.9999904	0.57492393	0.80608551	-0.46179964	0.99970394	0.240192231	1			
<i>OM</i>	0.59429735	0.88244469	-0.56214509	0.89875096	0.83354562	-0.9435599	-0.93670408	-0.35398569	0.59003166	0.99655156	0.53102251	-0.90462995	-0.73462205	0.83231032	0.2035939	0.27585529	0.65928545	0.339885834	0.73473942	1		
<i>MC</i>	-0.23421947	0.0867505	0.24226755	0.0755625	-0.15084133	0.03694567	0.05630135	0.27443867	-0.25936502	0.37139568	0.21528476	-0.49568514	-0.77261193	0.55115468	0.69327777	0.28998782	0.8208787	0.594223121	0.8660254	0.28295569	1	

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Table A7. Correlation coefficients between elemental composition nutrient content, water extractable nutrient content and physical and chemical properties of VP.

	<i>C_Na</i>	<i>C_K</i>	<i>C_Ca</i>	<i>C_Mg</i>	<i>C_Fe</i>	<i>C_Mn</i>	<i>C_Cu</i>	<i>C_Zn</i>	<i>W_Na</i>	<i>W_K</i>	<i>W_Ca</i>	<i>W_Mg</i>	<i>W_Fe</i>	<i>W_Mn</i>	<i>W_Cu</i>	<i>W_Zn</i>	<i>pb</i>	<i>pH</i>	<i>EC</i>	<i>OM</i>	<i>MC</i>	
<i>C_Na</i>	1																					
<i>C_K</i>	0.04645054	1																				
<i>C_Ca</i>	0.25055823	0.97869506	1																			
<i>C_Mg</i>	0.01702653	0.99956668	0.97222726	1																		
<i>C_Fe</i>	0.68154099	0.76264727	0.87920258	0.74327736	1																	
<i>C_Mn</i>	0.89229199	0.49241676	0.66062738	0.46658375	0.93850157	1																
<i>C_Cu</i>	0.18293877	0.9905607	0.99760096	0.98609657	0.84411041	0.60707307	1															
<i>C_Zn</i>	0.88670994	0.50301323	0.66974957	0.47735462	0.94264976	0.99992537	0.61673599	1														
<i>W_Na</i>	0.46813485	0.201798	0.29150972	0.18823262	0.45006248	0.49788667	0.26265663	0.49724074	1													
<i>W_K</i>	0.94468598	0.27479566	-0.46041291	-0.24722614	-0.81276334	-0.94697346	-0.4000318	-0.9442146	-0.68517802	1												
<i>W_Ca</i>	0.80052748	0.62413419	0.76945779	0.60112299	0.97569525	0.9797363	0.72414089	0.98165213	0.37866895	-0.86464344	1											
<i>W_Mg</i>	0.87688111	0.08542744	0.26286999	0.05969034	0.62987976	0.80196999	0.20430001	0.79756609	0.83260778	-0.9500773	0.67182704	1										
<i>W_Fe</i>	0.52799277	0.58702595	-0.46019809	-0.60316131	-0.08754868	0.19555301	-0.50516185	0.18594681	-0.37234079	-0.22032705	0.13234219	0.15389033	1									
<i>W_Mn</i>	0.03922625	0.99539887	-0.97271972	-0.9951786	-0.75450027	-0.48391021	-0.98502011	-0.49450152	-0.28031384	0.2892172	-0.60457488	-0.12463881	0.64447062	1								
<i>W_Cu</i>	0.09654865	0.43182809	-0.39895318	-0.43503512	-0.25474995	-0.11228043	-0.41194618	-0.11755745	0.74016876	-0.19832527	-0.28480729	0.49318191	-0.20802152	0.34519384	1							
<i>W_Zn</i>	0.14064613	0.6559263	0.66435351	0.65243045	0.57081214	0.41795107	0.66469058	0.42423811	0.82899324	-0.45687904	0.40653445	0.50981472	-0.76323795	-0.72349156	0.39747465	1						
<i>pb</i>	0.40059598	0.53123708	-0.59743438	-0.51989387	-0.64934195	-0.59018162	-0.57797318	-0.59351513	0.37661002	0.3204634	-0.71172183	-0.01093732	-0.34409558	0.45361579	0.86435026	0.17684453	1					
<i>pH</i>	0.36063774	0.7480855	0.79932016	0.73813111	0.7821383	0.65311811	0.78586972	0.65905576	-0.19911319	-0.37548149	0.78701774	0.0724138	0.08231886	-0.68713212	-0.80179173	0.09516276	0.13766461	1				
<i>EC</i>	0.94331242	0.71726779	-0.80008769	-0.70576316	-0.9388352	-0.99341334	-0.77446066	-0.99231278	-0.10043913	0.98735117	-0.99072804	-0.91832098	-0.18951902	0.65676725	0.87909068	-0.21622293	0.95375317	-1	1			
<i>OM</i>	-0.4430745	0.5856372	0.47671495	0.59921036	0.14280418	-0.12045939	0.51572057	-0.11139733	-0.66884519	0.43179886	0.07969336	-0.67718286	-0.21711018	-0.52319183	-0.89799277	-0.16050968	-0.24152539	0.609046041	-0.99460059	1		
<i>MC</i>	0.32415499	0.41058326	-0.33156513	-0.42047974	-0.09175732	0.09570325	-0.35979366	0.08927135	0.80559654	-0.40423369	-0.09045727	0.66942632	-0.06509893	0.33039427	0.97280245	0.39927339	0.66191753	-0.233126202	0.8660254	-0.83912893	1	

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SOLUBLE ELEMENTS RELEASED FROM ORGANIC WASTES
TO INCREASE AVAILABLE NUTRIENTS FOR SOIL AND CROPS

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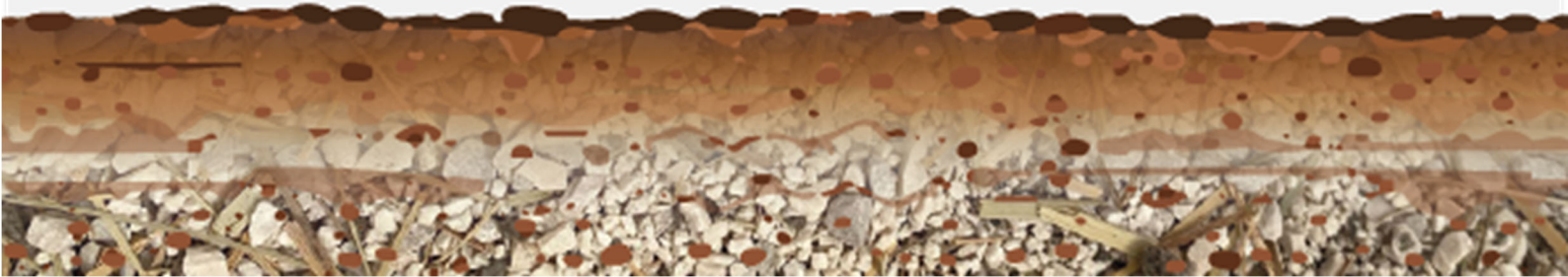
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CAPÍTULO 7: NITROGEN MANAGEMENT IN FARMING SYSTEMS UNDER THE USE OF AGRICULTURAL WASTES AND CIRCULAR ECONOMY.

Este capítulo corresponde con el trabajo:

Rodríguez-Espinosa, T., Papamichael, I., Voukkali, I., Pérez Gimeno, A., Almendro Candel, M.B., Navarro-Pedreño, J., Zorpas, A.A., Gómez Lucas, I., 2023. Nitrogen management in farming systems under the use of agricultural wastes and circular economy. *Science of The Total Environment*, 876, 162666. DOI:

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ABSTRACT

Population growth leads to an increase in the demand for energy, water, and food as cities grow and urbanize. However, the Earth's limited resources are unable to meet these rising demands. Modern farming practices increase productivity, but waste resources and consume too much energy. Agricultural activities occupy 50% of all habitable land. After a rise of 80% in 2021, fertilizer prices have increased by nearly 30% in 2022, representing a significant cost for farmers. Sustainable and organic farming has the potential to reduce the use of inorganic fertilizers and increase the utilization of organic residues as a nitrogen (N) source for plant nutrition. Agricultural management typically prioritizes nutrient cycling and supply for crop growth, whereas the mineralization of added biomass regulates crop nutrient supply and CO₂ emissions. To reduce overconsumption of natural resources and environmental damage, the current economic model of "take-make-use-dispose" must be replaced by "prevention-reuse-remake-recycle". The circular

economy model is promising for preserving natural resources and providing sustainable, restorative, and regenerative farming. Technosols and organic wastes can improve food security, ecosystem services, the availability of arable land, and human health. This study intends to investigate the nitrogen nutrition provided by organic wastes to agricultural systems, reviewing the current state of knowledge and demonstrating how common organic wastes can be utilized to promote sustainable farming management. Nine waste residues were selected to promote sustainability in farming based on circular economy and zero waste criteria. Using standard methods, their water content, organic matter, total organic carbon, Kjeldahl nitrogen, and ammonium levels were determined, along with their potential to improve soil fertility via N supply and technosol formulation. 10% to 15% of organic waste was mineralized and analyzed during a six-month cultivation cycle. Through the results, the combination of organic and inorganic fertilization to increase crop yield is recommended, as is the search for realistic and practical methods of dealing with massive amounts of organic residues within the context of a circular economy.

1. Introduction

Due to the increasing global population, the demand for energy, water and food is growing as the cities become more developed and urbanized. However, the Earth's resources are scarce and have a limited capacity to meet these rising needs (Aznar-Sánchez et al., 2020). The current economic model of “take-make-use-dispose” must be replaced by “prevention-reuse-remake-recycle” (Papamichael et al., 2022). The implementation of modern farming practices rapidly improves productivity, however with a high cost in terms of resources overconsumption and unsustainable energy use. This is evident as half of the habitable land is now used for agriculture (Kristinn et al., 2021).

To develop more sustainable future, environmental threats such as pollution, climate change, and biodiversity must be addressed. Specifically, it is estimated that by 2050, the

need for food production will increase by 5.1 billion tonnes (FAO, 2017; Willett et al., 2019). Given that agricultural ecosystems are the primary food providers, this will put tremendous stress on them. Every year, approximately 90 billion tons of primary resources are extracted and used worldwide, while 10 % of them are being recycled. Furthermore, farming accounts for about 70 % of global freshwater withdrawals and for approximately 31 % of GHGs emissions, making farming a significant contributor to climate change (Aznar-Sánchez et al., 2020; Ferrari Machado et al., 2021). Besides that, according to Circle Economy data in 2019, agriculture, along with the food sector, had the second largest material footprint with 21.3 billion tons and a carbon footprint of 10 billion tons of CO₂ equivalent (eq.), ranking third after transportation and housing (Circle Economy, 2019; Velasco-Muñoz et al., 2022). Agricultural intensification has also been driven by increased use of chemical fertilizers, which has eroded the quality of farming land. Mainly due to accumulation and losses of nitrogen, phosphorus and metals (Golia et al., 2009), that pollute water bodies, reduce soil functions and soil biodiversity (De Vries et al., 2022). Chemical fertilizers use increased from about 12 million tons in 1961 to more than 110 million tons by 2018. By now, the use of nitrogen and phosphorus, exceeds planetary boundaries by a factor of two (Steffen et al., 2015; Springmann et al., 2018; CEAT, 2021) illustrating the huge challenge of improving sustainability in the farming sector, taking into account that most imminent nitrate and ammonia pollution.

1.1. The use of fertilizers in farming

Fertilizers are a major expense for farmers. Traditionally, fertilizers have been responsible for approximately 35 % of maize and wheat production costs, and nearly 15–20 % of rice production costs. Worldwide fertilizer rates are influenced by the balance of both supply and demand, which is supported by production costs. Prices are also affected by agricultural seasonality and the timing of fertilizer purchases throughout the year (Baffes and Koh, 2021; Mangisoni, 2021). Fertilizers price variation through the year is closely related to the cropping cycle, with high prices just before harvest and much lower prices just after harvest especially in remote areas, due to increased transportation costs during the rainy season (Cedrez et al., 2020). Since the beginning of 2022, fertilizers

prices have increased by almost 30 %, following the 80 % increase of 2021. Prices are rising as a result many factors, including but not limited to: (i) increased resources costs, (ii) supply interruption caused by sanctions from Russian taking into consideration that the country is the leading exporter of fertilizers, and (iii) the trade restrictions taking place in China which postponed exports of fertilizers to ensure domestic availability (Nyondo et al., 2021; USDA, 2022). According to the World Bank (2020), the global fertilizer market in 2021 amounted to more than 193 billion US dollars, signifying a 12 % increase over 2020. The fertilizer market is expected to exceed 240 billion US dollars by 2030 (Fig. 1).

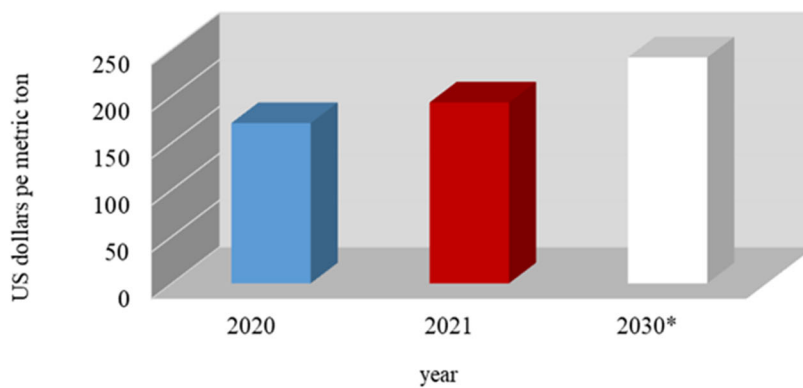


Fig. 1. Global inorganic fertilizer market size in 2020 and 2021, with a forecast for 2030 (Statista, 2022).

Specifically, according to Research Dive Analysis Report (2022) the global fertilizer market is expected to garner a revenue of \$252 billion between 2022 and 2030, rising from \$195 billion in 2021, at a health compound annual rate of growth (CAGR) of 3.6 %. Regarding the type of fertilizer, in 2021, the global inorganic fertilizer market had leading market share and is estimated to produce revenue of \$230 billion by 2030, increasing from \$172 billion in 2021. The dry fertilizer sub-segment is foreseen to dominate the market and generate a revenue of \$202 billion by 2030, growing from \$152 billion in 2021 with a CAGR of 3.3 %. Based on application the agriculture sub-segment is anticipated to have a leading market share and produce a revenue of \$110 billion by 2030, rising from \$83 billion in 2021. Finally, the analysis shows that the market for fertilizer

in Asia- Pacific is the most dominant and fastest growing. The Asia–Pacific fertilizer market accounted \$99 billion in 2021 and is estimated to grow with CAGR of 3.8 %.

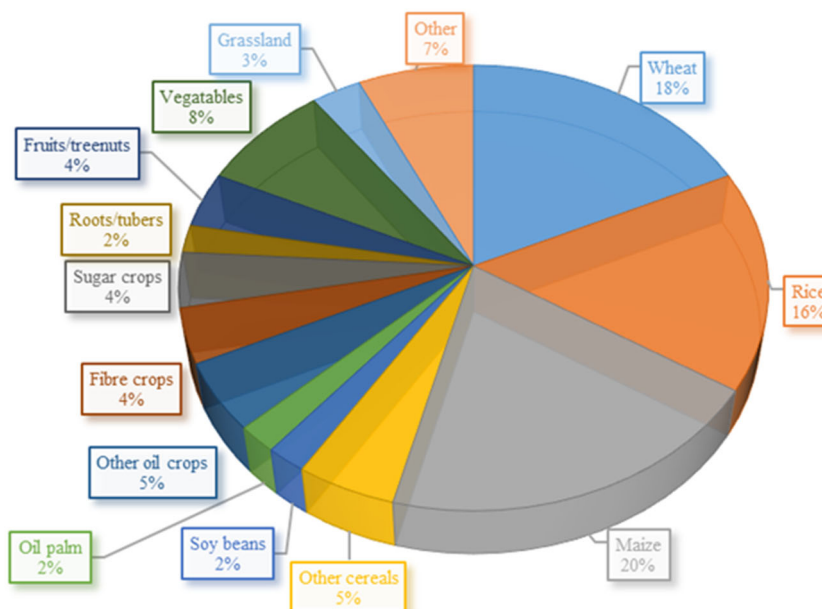


Fig. 2. Global N fertilizer (%) use by different types of crops (IFA, 2022)

According to FAO (2019) maize, wheat, and rice account for more than half of all harvested land on Earth. Specifically, maize is the most produced crop globally with an average yield of 1.1 billion tons/yr, followed by wheat and rice, amounting to 765 and 755, million tons, respectively. A billion tons of their production is used for human consumption products, 750 million tons end up as animal feed while the remaining amount is processed for industrial use or wasted. Specifically for wheat alone, 65 % of its production is used for human consumption, 17 % from animal feed and 12 % for biofuels production or other uses. Furthermore, rice is the crop with the biggest contribution to food staple (Shiferaw et al., 2011; FAO, 2019; Ritchie et al., 2022). IFA (2022) indicating that cereal crops accounted for 59 % of global fertilizer N consumption in 2018. Maize receives the most N fertilizers, accounting for 20 % of total global use, followed by wheat 18 % and rice 16 %. Due to the fact that soybeans remove N from the atmosphere, its contribution to global N consumption is minimal, less than 2 %. Furthermore, oil crops

make a minor contribution to global N fertilizer consumption approximately up to 7 %. The remaining amount is shared between fibre crops such as cotton, sugar, roots and tubers (10 %), fruits and vegetables (12 %), grassland and other crops (10 %) (Fig. 2).

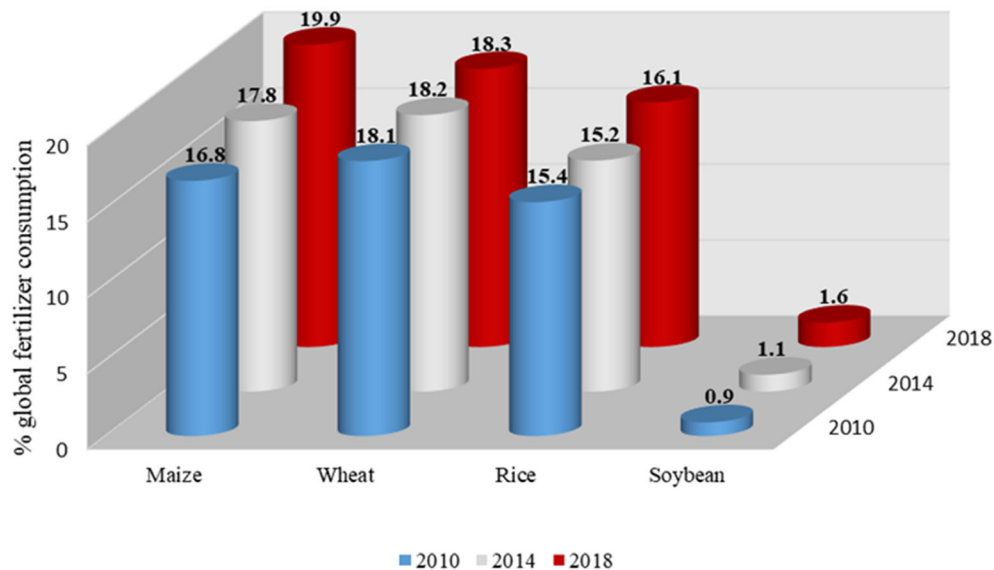


Fig. 3. Changes in the relative shares (%) of global N fertilizer consumption for the top four fertilizer consuming crops during 2010 to 2018 (IFA 2022)

Fig. 3 shows the worldwide trend for the four main fertilizer consuming crops (maize, wheat, soybean, and rice) for 2010, 2014 and 2018. In 2014 57.3 Mt. N applied to cereals accounting 55.9 % of world fertilizer N consumption. Wheat was the main crop receiving N fertilizers, accounting 18.2 % of global use, followed by maize with 17.8 % and rice with 15.2 %. Overall, crop shares of total fertilizer consumption in 2018 remained similar to those reported in 2014, with cereals accounting for 59 % of global N consumption. However, in 2018 the main crop receiving the highest amount of N fertilizers was maize accounting for 20 % of total global use. The change in the main crops share of global N fertilizer consumption reveals the changes in the world's crop area over the last decade. In 2018, global maize area increased by about 30 million ha (18 %) over 2010, while soybean area increased by nearly 22 million ha (21 %). Conversely, rice area increased by only 5 million ha (3 %), while total wheat area remained relatively unchanged (IFA,

2022). This is mostly due to the fact that maize and soybean growing as globally used, traded feed and energy commodities. Rice, on the other hand, is cultivated and consumed primarily for human consumption, with only about 10 % traded and used for energy production.

1.2. Reducing nitrogen losses from fertilizer use

Reducing nitrogen (N) losses from inorganic fertilizers in soils is one of the major goals in agriculture (Navarro-Pedreño et al., 1996a) while diminishing the use of inorganic fertilizers and promoting the addition of organic residues as a source of N for plant nutrition would be a desirable objective for sustainable agriculture. The Farm to Fork Strategy of the European Union (EU) urges Member States to reduce nutrient losses by at least 50 % and the use of fertilizers by 20 %, as well as to achieve 25 % of agricultural land use for organic farming by 2030 (EC, 2020). To bring about the change, Farm to Fork Strategy proposes the use of organic waste as renewable fertilizers. This practice can become widespread sooner rather than later as common agricultural policy strategic plans (CAP) can significantly contribute to the mitigation of adverse environmental burdens due to the use of inorganic fertilizers like soil toxicity (EU Regulation 2021/ 2115).

Although crop yield has increased worldwide from 1,100,750 tons per hectare in 2019 to 1,114,524 tons per hectare in 2021 (FAOSTAT, 2021, 2023), it is estimated that by 2050, crop yields will decrease by 6 to 13 % (Brunelle et al., 2015). Moreover, efficient use of N in EU agriculture is low (60 %), so agroecological practices that reduce N releases are vital (De Vries et al., 2022; Brunelle et al., 2015; Mosier et al., 2001). Excess nutrients applied to soil can lead to undesirable impacts, including economic loss due to an increased resources consumption, a crop yield reduction, unbalancing the nitrogen cycle that is associated with ecosystem eutrophication and acidification, soil degradation, N leaching, and Greenhouse gasses (GHGs) emissions (N₂O) contributing to climate change (Galloway et al., 2008; Golia et al., 2009; Herrero et al., 2010; Zhang et al., 2013; Sainju et al., 2017; Sainju et al., 2019; Anas et al., 2020; De Vries et al., 2022; Naz et al., 2022). Nitrogen plays a crucial role in agricultural crops and constitutes a key nutrient to

sustain crop yields due to its involvement in biomass production (Sainju et al., 2019; Anas et al., 2020). Therefore, N fertilizers are increasingly utilized in farming to enhance crop quality and yield. In fact, some authors consider inorganic fertilizer application rate higher than necessary (Zipori et al., 2020). However, each season crop up-takes only 40–50 % of N available by organic or inorganic sources (Mosier et al., 2001). Furthermore, nutrients in organic residue elemental composition have different solubility index (Oliver and Gregory, 2015; Cavalli et al., 2018; Jamroz et al., 2020), which hinders predicting the amount and time they will be available (Foereid, 2019). Therefore, it is key to ensure that nutrient release during organic residue decomposition is synchronized with crop nutrient requirements (Parr and Colacicco, 1987; De Vries et al., 2022).

1.3. Organic farming

In the EU alone, in 2014 only 38 % of N fertilizer input was provided by manure waste, and 45 % by mineral fertilizers (EU Eurostat, 2020). N contribution from sewage sludge, compost and industrial waste is insignificant and there is no data from other organic residue provisions (EU Eurostat, 2017). The cycling and supply of nutrients to support crop growth is essential and often a main focus of farm management practices (Gliessman, 2007). Mineralization of added biomass regulates the nutrient release and supply to crops as well as carbon dioxide (CO₂) emissions into the atmosphere (Guntiñas et al., 2012). Sustainable and organic farming requires the return of nutrients, organic matter and other resources removed from the soil through harvesting by the recycling, regeneration and addition of organic materials and nutrients (IFOAM, 2014).

In 2019, there were 72.3 million hectares of organic agricultural land worldwide, and 1.5 % of agricultural land is organic. Global organic food sales heading towards the 110 billion euros in 2019. The top market was the United States (44.7 billion euros), the European Union (41.4 billion euros) and China (8.5 billion euros). Per capita global consumption is 14.0 euros, getting the highest data in Denmark (344 euros) (Willer et al., 2021). In 2018, there were 13 million hectares of organic farming for EU-27. Although it only represents 8 % of the total EU agricultural surface, between 2012 and 2018,

sustainable farming has increased significantly by 3.5 million hectares (EU Eurostat, 2020). Curiously, in 2020, the use of mineral nitrogenous fertilizers for European crops remains on a high level too (6.9 % more than in 2010), as 10 million tonnes were needed to cover the demand of the market. However, the geopolitical context has increased nitrogenous fertilizer prices, associated with high costs of energy production (EU Eurostat, 2022). Brunelle et al. (2015) estimated a fertilizer price increase of 0.8 % to 3.6 % per year from 2005 to 2050. Although a reduction in crop farming fertilizer consumption is expected, currently, 6.5 % of raw materials costs are related with fertilizers and soil improvers (EU Eurostat, 2020). This trend could be enhanced by replacing synthetic fertilizers with organic ones. Organic fertilizers are carbon-based mixtures that raise the growth and productivity of crops (Organic Facts, 2017). Organic nutrients are steadily and slowly released, avoiding the possibility of a boom-and-bust cycle. Moreover, organic matter is increased, strengthens the structure, and inhibits topsoil erosion while being comparatively less expensive (Martey, 2018). Additionally, the air circulation as well as soil drainage could also be improved (Pramanik et al., 2007; Sisay and Sisay, 2019; Kandpal, 2021). Organic farming, which primarily depends on organic compounds rather than inorganic fertilizers, is becoming more prominent among both the research community and consumers (Chen et al., 2014). Organic fertilizers with high efficiency could significantly raise crop production without depleting soil structure, making their use beneficial to both food supply and environmental preservation (Cen et al., 2020). Organic fertilizers value should be measured on the basis of its yield contribution (Parr and Colacicco, 1987) and of its rate of efficient nutrient input.

1.4. Circular economy and nitrogen management

Therefore, in order to minimize natural resources overconsumption and restore environmental impacts, there is an imperative need to reshape the existing economic model of “take-make-use-dispose” towards a new one that will focus on “prevention-reuse-remake-recycle” (CEAT, 2021). In this context, the circular economy model is a promising approach for keeping natural resources, providing sustainable, restorative, and regenerative agriculture in the existing context of resource insufficiency, climate change,

environmental pollution, and rising food demand (Kuisma and Kahiluoto, 2017; Stegmann et al., 2020; Velasco-Muñoz et al., 2021). Referring to the farming sector, circular agriculture is a principle that promotes the long-term use of existing agricultural inputs and products, serving as a driving force in the future agrifood system (Vasa et al., 2017).

Circularizing agriculture is based on three key aspects to be taken into consideration. Firstly, the efficient use of inputs and prevents wastage, secondly, the promotion of environmental, economic and social sustainability and thirdly the regeneration of systems that enable the closure of nutrient loops and minimize outputs (Zabaniotou et al., 2015; Burgo-Bencomo et al., 2019; Morseletto, 2020; Velasco-Muñoz et al., 2022). Circular economy in the farming sector could be seen as an economic growth driver, as a business strategy plan, or a multi-layered sustainability action (Noya et al., 2017; McCarthy et al., 2019; Nattassha et al., 2020).

In order to enhance the circular economy in the agriculture/farming sector, all stages of the food chain, including growing to consuming and disposing, should be designed to take into consideration sustainable development by default (Kristinn et al., 2021). The combination of mixed crop livestock, as well as the promotion of organic farming and water recycling, is a critical element of a circular agriculture model, aiming at the reduction of CO₂ emissions and the efficient use of natural resources (Huybrechts et al., 2018; Velasco-Muñoz et al., 2022). Furthermore, emphasis should be given to the promotion of a comprehensive set of policies and strategies that will focus on the investigation of technologies and research for circular farming, to strengthen institutions and incentives for the adoption of circular economy, and to enhance international cooperation (Kristinn et al., 2021). Circular farming is divided in two different cycles, the biological and the technical (Figs. 4a, b). The biological cycle recovers value from waste in order to convert it into new valuable products that aid crop production, food processing, and energy production. The technical cycle applies to farming technologies by promoting the preserve, return, renew and reuse technologies that increase farming efficiency while reducing waste and cost (CEAT, 2021).

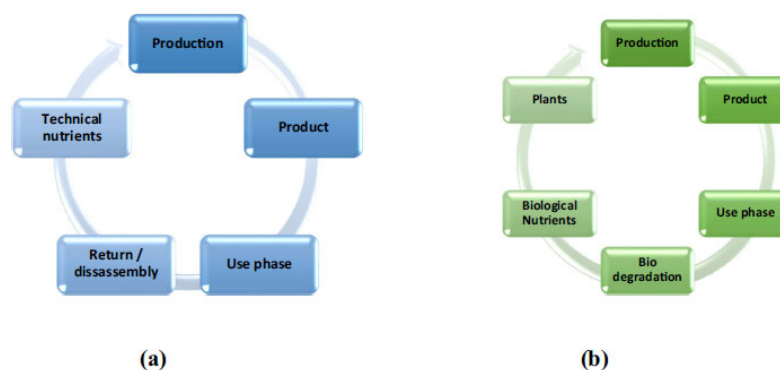


Fig. 4. Technical and Biological Cycles in the Circular AgroFarming Economy: (a) Circular technical cycle for products for services and (b) Circular Biological cycle for products for consumption (Wautelet, 2018)

The concept of circular farming economy is not a new innovative concept, taking into consideration that it was extensively used from pre- industrial societies. However, it has been side-lined by modern intensive farming practices that prioritize profit over environmental protection. As mentioned above, the circular economy model is already successfully implemented in farming practices such as: (i) the conversion of biological waste including agricultural stalks and leaves, as well as livestock manure, into fertilizers rich in Nitrogen, Phosphorus and Potassium (NPK); (ii) the wastewater reuse, arising from animal production and irrigation runoff, which can be reused for pastures and plant production after their treatment; (iii) the use of the produced biomass from plant and animal in order to produce biofuels; and (iv) waste minimization through the promotion of 3R strategies (reduce, reuse, recycle) (Patricio et al., 2018; Lüdeke-Freund et al., 2019; McCarthy et al., 2019; Nattassha et al., 2020).

Application of organic wastes to soil and the use of technosols can enhance food security, ecosystem services provision, cultivated land availability and human health (Anwar et al., 2015; Rodríguez-Espinosa et al., 2021a; Rodríguez-Espinosa et al., 2021b). The Food and Agriculture Organization (FAO) of the United Nations (UN), defends organic soil nutrition as a replacement of inorganic fertilization (FAO, 2017). Due to its high nutrient content (Parr and Colacicco, 1987; Navarro-Pedreño et al., 1996b; Rokia et al., 2014; Coull et al., 2021; Oueriemmi et al., 2021; Rodríguez-Espinosa et al., 2023b) using organic waste without mineral supplement can ensure crop yield (Hossain et al.,

2017; Bendaly Labaied et al., 2020; Pisciotta et al., 2021) and reduce available fractions of metals (Golia et al., 2017). However, organic waste can entail hidden risk, related to heavy metals and emerging contaminants content (FAO, 2022; Rodríguez- Espinosa et al., 2023a).

Such initiatives are in line with the Sustainable Development Goals (SDGs) of the UN and mitigation of Climate Change as the reduction of inorganic fertilizers and the use of organic wastes contribute positively to the circular economy and pollution control.

The positive impacts of organic agriculture on health, incomes, and the environment are facilitated by its own well-defined standards and market based certification systems, which ensure premium prices for organic producers. This has helped achieve high consumer awareness of its benefits and increased consumer demand both in developed and in developing countries. Most importantly, organic agriculture fosters gender equality as it creates meaningful work, It offers economic opportunities; promotes health; encourages biodiversity; and ensures equitable work This makes organic agriculture a crucial development strategy in the SDGs era, as its benefits are not only sustainable, but most importantly, enhance the well-being of humanity and that of the planet (Kristinn et al., 2021). With an emphasis on SDGS, organic farming contributes directly or/and indirectly to all the 17 goals. Regarding SDG 1, Organic farming is an important anti-poverty approach, particularly in rural areas, as it provides employment, lowers input costs for small-scale farmers, and raises revenues by providing higher prices for produce. Also improves farm biodiversity and resiliency in the face of increasingly several extreme weather conditions. Concerning SDG 2, due to the fact that organic farming provide more diverse crop production, the threat of significant losses caused by seasonal variations and poor harvests, is reduced, enhancing food security. About SDG 3, the chemical-free farming practices of organic farming could improve the well-being of both farmers and consumers. By increasing women's employment opportunities and empowering them through additional income, organic farming contribute to SDG 5. With regard to SDG 6 the minimization of chemical fertilizer application and the proper soil management reduce runoff, as fertilizers that are not recovered by crops causes eutrophication. Furthermore, groundwater pollution and salinization are also limited. Organic farming is progressively practiced in urban areas and endorses sustainable cities by food recycling

and organic wastes through composting that could be used in urban agriculture sector, contributing both in SDG 11 and 12. Concerning SDG 13, and given that agriculture is becoming increasingly vulnerable to changes in environmental conditions as a result of climate change, organic farming could provide solutions by creating resilient productive bases while also offsetting the consequences of climate change (UN, 2015).

Although there are differences between crops, plants uptake nitrogen in soil mineral forms (except leguminous) and the availability of nitrogen from wastes is subjected to the presence of inorganic forms (ammonium and nitrate preferable) presented in the wastes or provide after a mineralization process of the organic matter which is associated to the C/N ratio (Jat et al., 2018). Mineralization process is subjected to several factors, among others: environmental conditions and soil microbial biomass (Spohn et al., 2016). At the same time, depending on the type of waste, lignin and polyphenol content, temperature and soil moisture play a key role, and the type of soil is another limiting factor that affects the mineralization rates (Mafongoya et al., 1998; Deenik, 2006; Carranca et al., 2018; Taguas et al., 2021). Moreover, the type of ecosystem management and land cover significantly affected the mineralization of soil N (Gundersen et al., 2009). For instance, using a leguminous cover cropping for crops that are fertilized with pruning residue can ensure N availability (Pisciotta et al., 2021).

Under these conditions, it is necessary to understand local environment and organic waste characteristics to reach good conditions that could favor the release of inorganic nitrogen for crops. This process usually takes some weeks and affects the easily decomposed organic matter coming from the addition of wastes. However, we should note that lower N content crop residue would be incorporated into the soil, and higher N content and low C/N ratio crop residues can be placed on the soil surface to lower down the risk of N losses and CO₂ emissions as Jat et al. (2018) indicated for Vertisols. Soil taxonomy orders influence chemical changes of elements due to its physicochemical properties (Golia et al., 2018; Li et al., 2020).

The relation between nitrogen mineralization and immobilization is the key to nitrogen cycle in the soil (Cabrera et al., 2005). The organic residues applied to the soil undergo decomposition by microbial biomass and there will be net N mineralization with release of inorganic N. However, we should consider that if the amount of N from the organic

waste is equal to the amount required by soil biomass there will be no net mineralization. On the other hand, if the amount of N present in the residue is smaller than that required by the microbial biomass, additional inorganic N will need to be immobilized from soil to complete the decomposition process of organic matter (Corbeels et al., 1999a, 1999b).

For N mineralization, linear and nonlinear models have been used in order to obtain data related to measure the increment of mineralization or cumulative data. Initially, most of the experiments done to determine the N mineralization have been typically performed under temperature and water content conditions optimal or close to optimal for the mineralization processes (Gordillo and Cabrera, 1997; Agomoh et al., 2018) and later considering other environmental factors like pH, soil type, soil management and others (Deenik, 2006; Sierra and Desfontaines, 2018; Braos et al., 2020).

Although there are a lot of factors that can affect the mineralization process of the nitrogen from the use of organic wastes in soils, the application of farming and organic wastes is part of the strategic zero waste action and the circular economy. Moreover, the comparison between residues under the same conditions to have in mind the possibility of providing inorganic nitrogen for crops, should be analysed to help farmers make informed decisions and sustain adequate yields. The main objective of the current study is to understand the nitrogen nutrition provided from organic wastes to cropping systems, reviewing the state of the art and giving an example of the possibilities of nitrogen fertilization available from common organic wastes to promote sustainable farming management.

2. Materials and methods

2.1. State of the art

To analyze the state of the art related to nitrogen fertilization by using organic wastes, the PRISMA method (Preferred Reporting Items for Systematic Reviews and Meta-Analysis; www.prisma-statement.org) was used (Fig. 5). The proposed literature was carried out in accordance with the PRISMA process, which includes 27 routes and

encompasses the well defined stages of a systematic review, such as eligibility criteria and related information sources, strategy exploration, selection process, results and data synthesis (Ortiz-Martínez et al., 2019; Voukkali and Zorpas, 2022). The PRISMA 2020 checklist includes seven sections and topics (Title, Abstract, Introduction, Methods, Results, Discussion, and Other Information) and 27 sub criteria to be met.

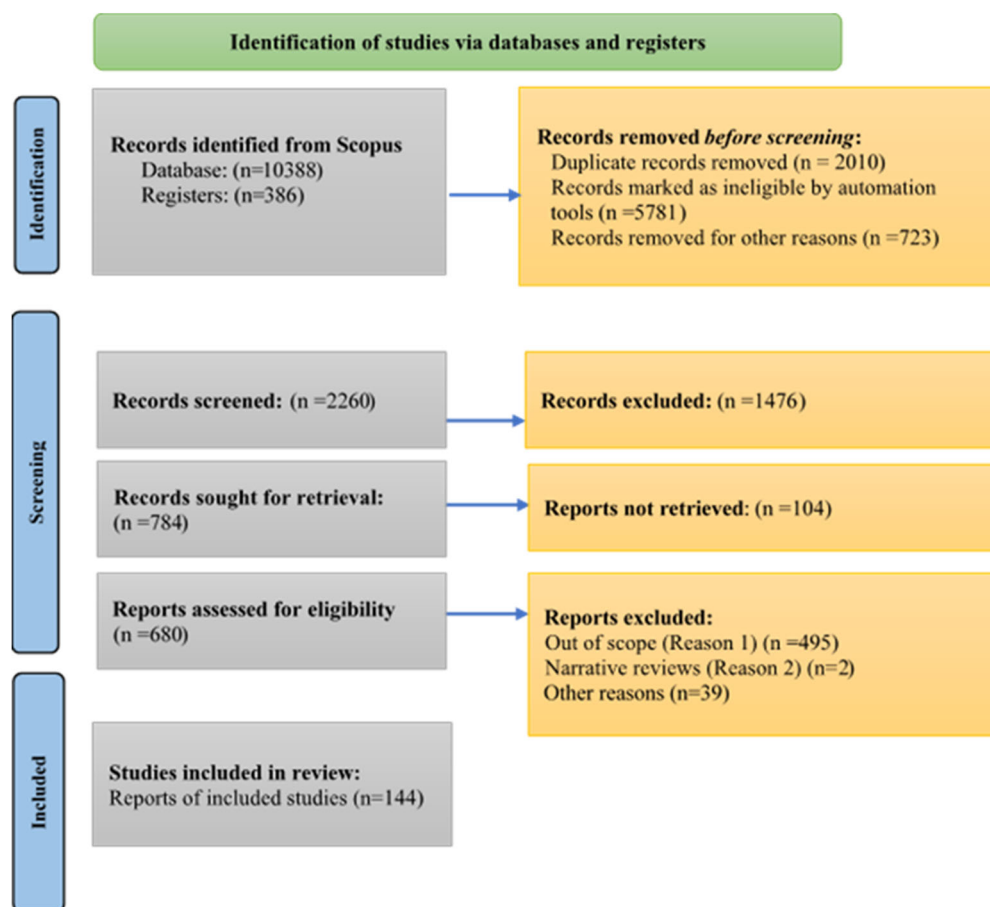


Fig. 5. PRISMA 2020 flowchart for systematic reviews that involves searches of databases and registers exclusively.

Specifically the characteristics (inclusion criteria) that the article must have in order for it to be eligible for enclosure in the literature review cover: (i) research/papers/studies related with farming and circular economy, organic and inorganic fertilizers; (ii) articles published from 1990 since today, enabling for a space - time comparison of the numerous

studies, and also providing the opportunity for the latest data that reflects the current existing situation; (iii) research mentioning comprehensive outcomes and/or information/data (review papers) for an integrated approach of the topic under study; (iv) methodical demonstration and synthesis of findings; (v) records identified using the keywords chosen by the authors. On the other hand, the characteristic (exclusion criteria) that disqualify the articles from inclusion in the literature review include: (i) narrative reviews, since those studies lack a sufficient scientific foundation; (ii) studies that are not useful to the proposed research, articles that merge information that is not exclusively related to the specific research; and (iii) available papers in languages other than English (iv) everything not included in the inclusion criteria.

For the literature review, the database of Scopus was preferred. As Scopus database option search were “title, abstract, keywords” the following keywords were used: *circular economy* AND *model* OR *farming* AND *circular economy* OR *Inorganic fertilizer in farming*, OR *organic fertilizer in farming*, OR *waste from farming*, OR *organic waste and characterization* OR *nitrogen fertilizers*, OR, *N liberation*, OR *Mineralization process*. All authors participated in the literature review, in order to implement measures to reduce random errors and bias during the research process.

The process started with screening of the titles and the abstract for potential inclusion, taking into account the mentioned criteria. In case of inconsistencies as to whether a specific study/report/manuscript should be included or excluded, these were resolved through extensive discussion among the authors. The 162 references obtained by the Scopus were cross checked with Mendeley software in order to identify any duplicated studies. Full papers were downloaded for further evaluation, when the review team was unsure if a particular paper met or not the inclusion criteria. The Authors collected and evaluated data from 10,388 papers linked to the studied topic.

2.2. Selected residues

Following the strategy to promote sustainability in agriculture, several organic residues were selected on the criteria of circular economy and zero waste strategy. Their potential use to improve soil fertility, centred in N supply, and also the possibility of forming part of formulated technosols. These wastes were the following:

- Almond tree pruning (AP)
- Commercial brown peat (CP)
- Hay straw (HS)
- Olive tree (*Olea europaea* L.) pruning (OP)
- Pomegranate (*Punica granatum* L.) peel (PG)
- Pine (*Pinus halepensis*) needle fall (PN)
- Date palm (*Phoenix dactylifera* L.) leaf pruning (PP)
- Sewage sludge compost (SC)
- Vine (*Vitis vinifera*) pruning (VP)

The origin of these farming (pruning and harvesting) residues (AP, HS, OP, PG, PN, PP and VP) was from Mediterranean agricultural areas close to Elche (Alicante, Spain) and produced in their farming systems. The quantities of such waste produced in Spain and in other countries were studied by Rodríguez-Espinosa et al. (2023b). The sewage sludge compost (SC) was obtained from Aspe Wastewater Treatment Plant (Alicante, Spain). Domestic wastewater undergoes preliminary treatment, primary treatment, secondary treatment and disinfection. Sludge is thickened, digested in an aerobic environment and dewatered, removing water from the solids using centrifuges. Finally, the remaining solids are composted (EPSAR, 2019). From gardening and forest areas, PP

were obtained from Palm Tree orchards of Elche and PN were collected directly from the ground surface in a nearby *Pinus halepensis* forest area.

2.3. Residue characterization

Water content (WC), organic matter (OM), total organic carbon (OC), Kjeldahl nitrogen (N) and ammonium were determined according to the standard procedures. All residues were subjected to a previous conditioning process consisting of air drying at room temperature inside a greenhouse (reaching temperatures over 40 °C) for a month, shredded and sieved previously to the elemental analysis (2 mm).

After that, WC in the samples (five repetitions per each one) was determined by drying at 105 °C (AENOR, UNE-EN 13040, 2008), using a LED digital drying and sterilization oven (J.P. SELECTA®, Conterm 2000253). OC was determined by oxidation (Iglesias and Pérez, 1992; Puyuelo et al., 2011) and OM was determined by loss on ignition at a temperature of 450 °C in a muffle furnace (Nabertherm, controller P320), expressed as percentage by weight of dry matter (AENOR, UNE-EN 13039, 2001).

Mafongoya et al. (1998) recommended Kjeldahl method for analysis of total N (except oxidized N) of organic materials. Samples (five repetitions per each one) were digested in a bloc-digest 20 sample sites (P-Selecta 4000631) equipped with a temperature and time regulator (P-Selecta 4000051) and distilled by a Foss Kjelttec 2100 distilling unit (EN 13342: 2000; Jones, 2001; FAO, 2021; Doyeni et al., 2022). The ratio C/N was determined by using the values obtained for OC and N.

2.4. Sceneries of mineralization of the organic residues

There are several methodologies and models employed to know the mineralization of nitrogen in soils. Recently, Agomoh et al. (2018) proposed a model to calculate net N mineralization from the cumulative amounts of leached N for amended soil, measured as

soil inorganic N concentration at time t and corrected for mineralization in the unamended soil and for initial soil inorganic N concentration, and the cumulative net N mineralized ($\% N_{min}$), or the percentage of manure organic N (N_{org}) mineralized between the start of the experiment and time t , was calculated as depicted in Eq. (1):

$$\%N_{min} = \left[\frac{N_{min(t)}}{N_{org}} \right] \times 100 \quad (1)$$

Other methods were proposed by Thuriès et al. (2001), Geisseler et al. (2019), Armando Tamele et al. (2020) and Rakesh et al. (2021), among others. However, in this work related to the N supply by organic wastes during a cultivation period, it is used the approach given by Jat et al. (2018) who indicated that the net C mineralized from the added organic source varied between 11.1 and 14.0 % among the crop residues used in their work.

Although there are a lot of methods and the results are affected by the experimental design and the environmental factors, including soil type as a key factor, we assumed, based on the previous works, an expected mineralization of organic wastes under two sceneries for a cycle of cultivation (approximately six months): 10 % and 15 % of organic matter mineralized. This assumption was based on literature consultation and helps with the comparison of the ability of those organic wastes to supply nitrogen for plant nutrition. Similar percentages for the N mineralization presented in organic matter (sceneries 1 and 2: 10 % and 15 %) are expected. However, this should be considered as an approach to facilitate the comparison because local conditions and characteristics of the different wastes can vary.

Additionally, the influence of the ratio C/N in the organic wastes was investigated as it has an important role for mineralization. The potential ratio C/N that favor the mineralization is around 20–30 as optimal to achieve aerobic and anaerobic microbial metabolism and, below that, N release for plan nutrition starts while a rapid mineralization will pass when this ratio is around 10 (Thuriès et al., 2001; Puyuelo et al., 2011; Repullo et al., 2012; Gomez-Muñoz et al., 2016). A limit for the comparison of the availability of

N for plants from organic wastes when the ratio C/N is below 30 is assumed. Over this ratio, the mineralization of the waste would need an additional source of N to mineralize effectively. This source of N in cropping systems comes from the soil organic matter and the nitrogen fertilization.

Several nitrogen fertilizers are used for crops. Three of them were considered to compare the amount needed to add for some crops with the supposed amount of the organic fertilization needed in order to achieve the required nitrogen to supply to selected crops. These commercial fertilizers were: ammonium sulfate (21 % of N) which is a soluble fertilizer used as a source of S (24 % of S) and N (Powlson and Dawson, 2021); ammonium nitrate (60 % of N) used as fertilizer as well as and urea fertilizer (46 % of N), both important sources of N for crops (Furtado da Silva et al., 2020).

3. Results and discussion

3.1. Organic waste characterization

The characterization related to carbon and nitrogen in the organic residues analysed is presented in Table 1. Results are shown in fresh weight -f. w.- (after drying at room temperature) and dry weight -d.w.- (after drying at 105 °C). The processed materials (CP and SC) get the highest rates of WC (527 and 260 g kg⁻¹, respectively) even after a month of drying them at room temperature. As soil moisture is a crucial factor for decomposition of organic matter, particularly in dry climates (Rovira and Vallejo, 1997), the water content of the wastes is important for the mineralization. The pruning and harvesting residues have WC (f.w.) content between 63 and 98 g kg⁻¹ (OP and HS). Hence, with low water content, its addition to the soil can even prevent nutrient leaching (Golabi et al., 2017). Organic residues are a good source of organic matter due to the high presence in their composition, between 875 and 950 g kg⁻¹ d.w., and SC has a low rate of OM (590 g kg⁻¹ d.w.). The last waste comes from the wastewater treatment and the presence of organic matter is lower than the one of farming wastes. All of them can improve soil properties, carbon sequestration and nutrient availability for crops (Papafilippaki et al., 2015; Gomez- Muñoz et al., 2016; Golabi et al., 2017; Almendro-Candel et al., 2018;

Oueriemmi et al., 2021; Taguas et al., 2021). OC varied between 266 (SC) to 427 g kg⁻¹d.w. (HS), and this has influenced in the ratio C/N. All pruning and harvesting residues showed low total N content (4.3–9.3 g kg⁻¹ d. w.). However, SC achieves 22.6 g kg⁻¹ d.w., but its N content does not exceed the percentage of 2.5 % needed to promote nutrient mineralization as Anguria et al. (2017) indicated. PP is the pruning residue that has the highest total N content (9.3 g kg⁻¹ d.w.) being the most beneficial rate for decomposition.

Table 1. Water content (WC) Organic matter (OM), organic carbon (OC), total nitrogen content and C/N ratio of the studied residues.

Residue	WC (g kg ⁻¹ f.w)	OM (g kg ⁻¹ d.w.)	OC (g kg ⁻¹ d.w.)	N (g kg ⁻¹ d.w.)	C/N
AP	80	932	392	4.4	89
CP	527	910	409	8.0	51
HS	98	950	427	4.3	99
OP	63	941	395	7.2	55
PG	82	875	376	5.4	70
PN	90	919	414	5.4	77
PP	86	909	409	9.3	44
SC	260	590	266	22.6	12
VP	93	940	395	4.6	86

The C/N ratio indicated that SC would have a trend to easily mineralize whereas HS has the highest value. This can be reflected in the slow or null N release and its availability for crops. Notwithstanding, it is important to remember that farming managing systems is the key for the adequate use of all of these organic wastes.

3.2. Major crops and N demand

The selected crops and their nitrogen demand are presented in Table 2. This provides previous research findings into foreseeable N demand (kg ha⁻¹) of the listed crops. It can be seen that sugarcane and cereals require a large proportion of N to ensure crop yield (200–300 and 100–300 kg ha⁻¹, respectively) followed by vegetables and fruit trees. Curiously, Wang et al. (2022) considered that N application of more than 300 (kg ha⁻¹) can be excessive and trigger a reduction on soil N availability and microbial activity.

Moreover, Navarro-Pedreño et al. (1996a) demonstrated that this excess of nitrogen added to farming systems in Mediterranean environments, can be a source of nitrogen pollution and increase the cost of the farming systems without increment of the yield.

Table 2. Selected crops and nitrogen demand expected based on the literature review.

Crop type	N demand (kg ha ⁻¹)	Reference
Cereals	100–300	Lloyd et al., 1997
Fruits/tree nuts	110	IFA, 2022
Mature fruit trees	108	Carranca et al., 2018
Roots/tubers	65	IFA, 2022
Sugarcane	200–300	Furtado da Silva et al., 2020
Tomato and bean	60–100	Ganeshamurthy et al., 2022
Vegetables	190	IFA, 2022

3.3. N mineralization from residues and amount of residue needed for meeting N demand

This work provides the N mineralization (N_{\min}) from organic residues within the framework of two expected sceneries: 10 % and 15 % of organic matter mineralized, as stated in Section 2. Data from Table 3 were calculated relying on 10 % of mineralization and Table 4 on 15 %. The amounts were expressed in kilograms of residues needed per hectare to supply N_{\min} requirements of crops (Table 2) considering their moisture (after drying at room temperature, f.w.). The minor value of N demand of each type of crop presented in Table 2 for each crop was used in order to prevent excessive N input, as stated before (Wang et al., 2022).

From both tables (Tables 3 and 4), a large quantity of residues per hectare is needed for most of the crops and wastes. As expected, the number of residues in Table 4 is higher than those obtained in Table 3. SC and PP are the residues that can be applied to a lesser extent to meet N demand of crops. It is worth mentioning that these amounts of residues are calculated for N supply (assuming the rate of mineralization and that all nitrogen should be supplied by organic wastes), one of the most present nutrients in organic residues.

Being aware of the logistical and environmental challenge handling huge amounts of organic residues, a more realistic and practical approach is advisable. To ensure quality and crop yield authors suggest combining organic with synthetic fertilization (Parr and Colacicco, 1987; Chatzistathis et al., 2021; Wang et al., 2022). Wang et al. (2022) concluded that organic and inorganic based fertilization plans can increase soil N availability by accelerating soil organic N mineralization and a N input of 150 kg ha⁻¹ can be favorable for most of the crops. In addition, farms that only use inorganic fertilizers and in short supply of organic waste undergo soil organic carbon and N reduction and soil degradation (Hasnat et al., 2022). In this sense, a combined fertilization considering the positive effects of organic residues joined to a controlled inorganic fertilization would achieve good yields and avoid the negative impact of the only use of inorganic fertilizers.

Moreover, both fertilization materials have advantages and disadvantages. Inorganic fertilizers are fuel-based sources and can lead to environmental pollution, soil degradation and reduction of soil microorganisms' activity, including an important carbon footprint for their production and transport. Despite this, the main benefit of using inorganic fertilizers is the immediate provision of nutrients of high mineralization rate that enhance crop yield. Whereas organic residues application enhances ecosystem sustainability, circular economy strategy, soil properties and fertility, and microorganism's biomass. However, organic residues have contamination drawbacks, but the main inconvenience is short-term nutrient availability (Chatzistathis et al., 2021; Rodríguez-Espinosa et al., 2023a). One of the major challenges of using combined organic and inorganic fertilization is the synchronization of nutrients demand of each crop along its life cycle with input application. This is even more difficult when only organic fertilization is used. However, an adequate study of the soils and the environmental conditions can help to understand the mineralization rate and promote the use of a sustainable soil management in farming systems.

Considering the requirements of nitrogen nutrition as stated in Table 2, Table 5 provides the amount of each inorganic fertilizer (mentioned before) needed for crops. In this case, the amount that would be applied is lower than the amount of organic fertilizers needed.

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Table 3. Scenery 1: 10% of N mineralization (N_{\min}) and amount of each residue needed for meeting the N demand of crops.

	N_{\min} (g kg ⁻¹ d.w ^a)	Cereals (tons ha ⁻¹ f.w ^b)	Fruits/tree nuts (tons ha ⁻¹ f.w)	Mature fruit trees (tons ha ⁻¹ f.w)	Roots/tubers (tons ha ⁻¹ f.w)	Sugarcane (tons ha ⁻¹ f.w)	Tomato, bean (tons ha ⁻¹ f.w)	Vegetables (tons ha ⁻¹ f.w)
AP	0.44	247.04	271.74	266.80	160.57	494.07	148.22	469.37
CP	0.80	264.27	290.70	285.41	171.78	528.54	158.56	502.11
HS	0.43	257.83	283.61	278.45	167.59	515.65	154.70	489.87
OP	0.72	148.23	163.05	160.09	96.35	296.45	88.94	281.63
PG	0.54	201.73	221.90	217.87	131.12	403.45	121.04	383.28
PN	0.54	203.50	223.85	219.78	132.28	407.00	122.10	386.65
PP	0.93	117.64	129.41	127.06	76.47	235.29	70.59	223.52
SC	2.26	59.79	65.77	64.58	38.87	119.59	35.88	113.61
VP	00.46	239.68	263.65	258.856	155.79	479.36	143.81	455.40

^a d.w: dry weight.

^b f.w: fresh weight.

Table 4. Scenery 2: 15% of N mineralization (N_{\min}) and amount of each residue needed for meeting the N demand of crops.

	N_{\min} (g kg ⁻¹ d.w ^a)	Cereals (tons ha ⁻¹ f.w ^b)	Fruits/tree nuts (tons ha ⁻¹ f.w)	Mature fruit trees (tons ha ⁻¹ f.w)	Roots/tubers (tons ha ⁻¹ f.w)	Sugarcane (tons ha ⁻¹ f.w)	Tomato, bean (tons ha ⁻¹ f.w)	Vegetables (tons ha ⁻¹ f.w)
AP	0.29	370.55	407.61	400.20	240.86	741.11	222.33	704.05
CP	0.53	396.41	436.05	428.12	257.66	792.81	237.84	753.17
HS	0.29	386.74	425.41	417.68	251.38	773.48	232.04	734.80
OP	0.48	222.34	244.58	240.13	144.52	444.68	133.40	422.45
PG	0.36	302.59	332.85	326.80	196.68	605.18	181.55	574.92
PN	0.36	305.25	335.78	329.67	198.41	610.50	183.15	579.98
PP	0.62	176.47	194.11	190.58	114.70	352.93	105.88	335.29
SC	1.51	89.69	98.66	96.87	58.30	179.38	53.82	170.41
VP	0.31	359.52	395.48	388.28	233.69	719.05	215.71	683.09

^a d.w: dry weight.

^b f.w: fresh weight.

Table 5. Amount of each commercial fertilizer (expressed as kg ha⁻¹) needed for supplying the N demand of the selected crops.

	Cereals	Fruits/tree nuts	Mature fruit trees	Roots/tubers	Sugarcane	Tomato and bean	Vegetables
Ammonium sulphate	476	524	514	310	952	286	905
Ammonium nitrate	167	183	180	108	333	100	317
Urea fertilizer	217	239	235	141	435	130	413

Considering 150 kg ha^{-1} of N input as the optimum demand, it was found a contrast between the amounts of urea fertilizer needed with the kilograms of organic residue that should be applied. The amount of pruning and harvesting residue (farming wastes) must be applied, approximately, between 400 and 1000 times more than urea fertilizer. SC and CP have to be applied 200 and 600 times more, respectively.

3.4. Ratio C/N

As stated before, the C/N ratio is a crucial factor in the success of N mineralization from organic residue and can be considered as a quality indicator of organic inputs (Parr and Colacicco, 1987; Mafongoya et al., 1998). Hence proper quantity and quality of organic residue is needed for ensuring N supply (Wingeyer, 2007). In Table 1, the C/N ratio of those organic residues studied is shown. SC is the one with the lowest C/N ratio (12) since it has proportionally the highest total N content ($22.6 \text{ g kg}^{-1} \text{ d.w}$), so it is the most favorable residue for enhancing mineralization. The pruning and harvesting residues obtain a C/N ratio between 44 and 99 (PP and HS, respectively), that is above the optimum C/N ratio. CP gets a C/N ratio of 51, similar to the one obtained by PP or OP. Our findings (Table 1) are consistent with those obtained by previous studies (Table 6).

Non-manure animal wastes, animal manures, compost, sewage sludge and municipal solid wastes are low C/N ratio wastes (1–17 or 29) and have high total nitrogen content, reaching 156 g kg^{-1} in non-manure animal wastes (Table 6). These are considered high quality organic inputs because they can release nutrients rapidly. However, they can become an environmental pollution source due to heavy metal and N content and leaching (Mafongoya et al., 1998; Wingeyer, 2007; Anwar et al., 2015; Chojnacka et al., 2022; Rodríguez-Espinosa et al., 2023a). On the other hand, pruning residues achieve a higher C/N ratio (43.9–139) and low total N content (Table 6).

Consequences of applying pruning residue to soil, with high C/N ratio (Tables 1 and 6), are N immobilization and a depletion of N available in soil (Gomez-Muñoz et al., 2016; Carranca et al., 2018). Residue C/N initial ratio can increase during the decomposition process as concluded by Cavalli et al. (2018) which maize straw C/N ratio

changed from 51 to 68. However, Yilmaz et al. (2017) did not obtain a N depletion after vine pruning addition. Authors agree pruning residue decomposition process is slow and can have a long-term nutrient contribution for crops (Repullo et al., 2012; Gomez-Muñoz et al., 2016; Carranca et al., 2018; Cavalli et al., 2018; Pisciotta et al., 2021).

Table 6. Organic carbon (OC), total nitrogen content (N) and C/N ratio of waste (g kg⁻¹).

Waste	OC (g kg ⁻¹)	N (g kg ⁻¹)	C/N	References
Animal manures	–	11.4–117.6	13–29	Parr and Colacicco, 1987
	379	22	17	Thuriès et al., 2001
	376	61	6	
Compost	122.3	13.3	9.2	Pascual et al., 1997
Fruit waste	–	7–19	35	Parr and Colacicco, 1987
Maize straw	–	–	51–68	Cavalli et al., 2018
Municipal solid waste	225.8	16.4	13.8	Pascual et al., 1997
Non-manure animal wastes	–	10–140	3–5	Parr and Colacicco, 1987
	545	146	4	Thuriès et al., 2001
	471	152	3	
	175	156	1	
Pruning residue (olive)	462	10.6	43.9	Gomez-Muñoz et al., 2016
Sewage sludge	393.5	53.1	7.4	Pascual et al., 1997
	396	47.3	–	Nicolás et al., 2012
Tress (leaves)	–	5–15.1	40–80	Parr and Colacicco, 1987
Tress (leaf and litter)	–	–	10–32	Mafongoya et al., 1998
Vegetable residues	–	16–37	11–27	Parr and Colacicco, 1987
Vine pruning residue	543	3.9	139	Yilmaz et al., 2017
	503	11	–	Nicolás et al., 2012
Wheat straw	–	2.1–9.4	80–130	Parr and Colacicco, 1987

Recommendations based on N content and C/N ratio of pruning residues are that its application needs to complement with other sources of nitrogen that can be inorganic fertilizers or organic fertilizers with a low C/N ratio. The last combination could be the most useful as a sustainable strategy based on a circular economy.

3.5. Cost saving and organic fertilizer

Fig. 6 shows the price variance for the main inorganic fertilizers for 2015–2021 and a forecast to 2035. Urea cost 229 U.S. dollars per metric ton in 2020, 275 in 2024, and 330 in 2035. In 2020, phosphate rock cost 76 \$/metric ton. By 2035, it is expected to cost 130 \$/ton. Triple superphosphate (TSP) was 265 \$/metric ton in 2020 and expected to reach 400 \$/metric ton by 2035. In 2020, diammonium phosphate (DAP) cost 312 U\$/metric ton, with a 2035 prediction of 450 U\$. In 2020, potassium chloride cost 218 dollars per metric ton. By 2035, it will cost 300 dollars.

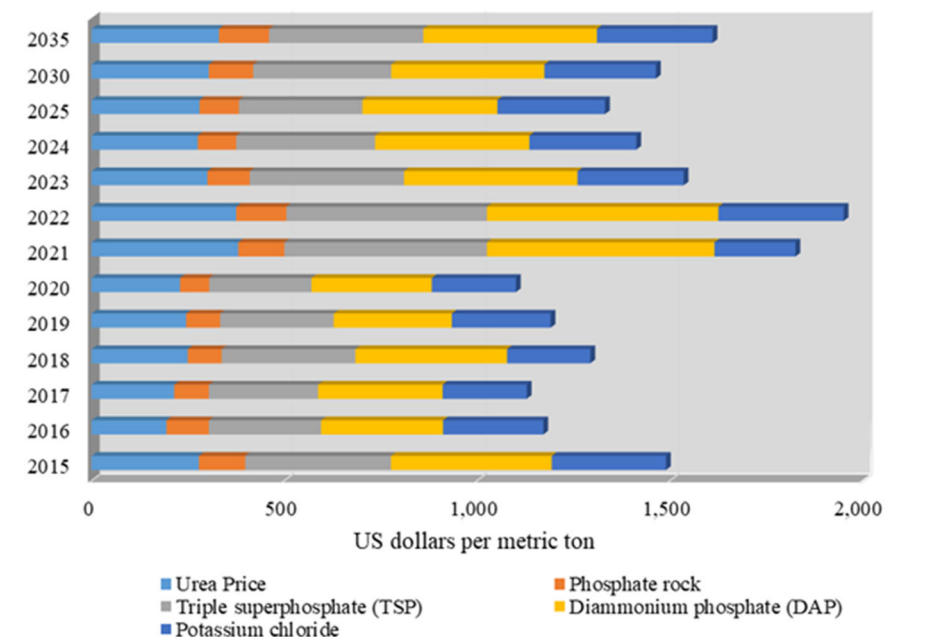


Fig. 6. Price inorganic fertilizers from 2015 to 2021 to 2035 (in U.S. dollars per metric ton) (Statista, 2022)

As mentioned, crop productivity-boosting inorganic fertilizers are now a major environmental issue (Serpil, 2012; Kumar et al., 2019). Fertilizer use is becoming

counterproductive as long-term inorganic fertilizer use may harm crops and plants since chemical-based water-soluble fertilizer leaches, starving the soil (Manivannan et al., 2009; Schulz and Glaser, 2012; Lim et al., 2015; Kandpal, 2021). While farming relies more on organic fertilizers due to rising fertilizer prices, organic fertilizer's economic benefits are still unclear.

Over time, organic fertilizers may be worth the extra cost as they can improve soil after crops absorb nutrients while longer feeding improves soil texture and composition. Inorganic fertilizers are cheaper but add fewer nutrients over time (Gopinath and Mina, 2011; Loncaric et al., 2013; Cen et al., 2020). Martey (2018) illustrated that organic fertilizer users produce and earn more than inorganic fertilizer producers as productivity boosts crop income. Organic matter from green and animal manure increases crop yield over time since organic fertilizer reduces soil degradation and evapotranspiration. Lal (2006) found that root zone soil organic matter greatly increases crop yield. Profitability analysis shows organic fertilizer increases productivity, harvest income, and average annual net returns. Loncaric et al. (2013) found that soil fertility strongly impacts organic fertilization. Added to the fact that organic fertilization could solve agricultural issues like manure, crop yield, soil fertility, manure is 46 % cheaper than inorganic fertilizers which directly affect farmers' costs and savings. Massive, automated plants produce millions of tons of inorganic fertilizers while on the contrary, organic fertilizers are made locally. Thus, organic fertilizer production creates jobs, especially in rural areas with few options. Still, some cost implications still need to be tackled like the fact that machinery and equipment costs make organic-inorganic fertilization 13–39 % more expensive than mineral fertilization.

3.6. Circular Economy transition of the farming sector

Considering the need to transition to a new economic model that extends product life cycles, several researchers have examined the potential of integrating the circular economy into the agriculture sector (Sartore et al., 2018; Maestre-Valero et al., 2019; Aznar-Sánchez et al., 2020; Maquet, 2020; Suresh and Samuel, 2020; Timonen et al.,

2021; Velasco- Muñoz et al., 2022). To improve circular economy in the farm sector, three fundamental principles must be followed: (i) efficient resource use and process optimization that minimizes resource use and prevents waste; (ii) long-term economic and environmental sustainability; (iii) and regenerative systems that close nutrient cycles and reduce leaking (Morseletto, 2020; Velasco-Muñoz et al., 2022). Eliminating waste and pollution improves system efficiency (Ellen MacArthur Foundation, 2015). The second principle of “keeping products and materials in use” suggests maximizing product and by-product quality throughout the supply chain. Finally, replacing scarce inputs with renewable resources in “regenerating natural systems” improves ecosystems (Ellen MacArthur Foundation, 2019a).

With the same philosophy, the “organic farming action plan”, proposed by the EC under the EU Green Deal for the expansion of organic production, is an ambitious strategy with the aim to transform organic farming to a more sustainable farming practice that respects the three pillars of sustainable development and therefore enable meeting the SDGs (El Chami, 2020). The plan's main target is to have at least 25 % of EU agricultural land under organic farming and a significant increase in organic aquaculture by 2030. To meet this goal and support the organics sector the strategy includes financial support for organics through rural development commitments. The EU intends to invest at least 30 % of its budget to research and innovation acts in agribusiness that is specific to or relevant to the organic sector. Elevated crop yields, genetic diversity are examples of such challenges. Furthermore, technical support and the exchange of evidence - based practices and advancements will provided (EU Green Deal, 2019).

Resource scarcity, environmental damage, and uncontrolled waste production are changing the circular economy model while processes and consumption patterns must be altered for a smooth integration of the model into the farming sector (Ghisellini et al., 2016; Ghisellini and Ulgiati, 2020; IPCC, 2021; van Langen et al., 2021; Rótolo et al., 2022a, 2022b). Only 2 % of usable resources are returned to farming for reuse, and 98 % become environmental pollutants and waste, deeming the use of a circular economy model of utmost importance (Ellen MacArthur Foundation, 2019a, 2019b). Circular economy principles in agriculture could boost GDP by 0.1 % by 2030 and create over 100,000 jobs, according to the EU alone (European Commission, 2018). Farmers may

profit 3000€/hectare from circularity while simultaneously reducing pollution and adverse effects of linear production processes (i.e. soil toxicity, GHGs emissions, human health implications etc.) (Ellen MacArthur Foundation, 2021; Velasco-Muñoz et al., 2022).

Reusing and recycling farming waste can boost local economies and reduce environmental damage. Since these wastes are unavoidable, farms would benefit economically and environmentally. Additionally, animal digestion produces biomass, biofuel, and manure-based organic fertilizer while reducing greenhouse gases and improves soil fertility. Barros et al. (2020) found that recycling and reusing agricultural waste could improve industrial symbiosis. Farm or cooperative components that circulate can boost profits and reduce environmental impact. Simultaneously, farming waste makes biofertilizer biochar which has the ability to boost fertility, climate resilience, and profitability (Yrjälä et al., 2022). Khan and Ali (2022) found that Circular bio-based Europe (CBE), which combines circular economy and bio economy, is becoming more and more popular concerning aspects of food security and sustainable development. Sustainable biomass, increased product life cycle, waste reuse, biofuels and bioenergy, composting, and recycling are CBE's goals (Armanda et al., 2019; Stegmann et al., 2020). At the same time, composting had the greatest market potential while bio-fertilizers are cost-effective and should be used more. Lastly, concerning anaerobic digestion has additional benefits to environmental impact mitigation but uses less farming waste as a feed.

Sekabira et al. (2021) noted the CBE model in an African Farming System study. In their study, the authors mention that after urban consumption, organic waste could collect, recycle, and return to rural areas for reuse on farms. Urban organic waste can be recycled and used on farms since reusing organic waste closes nutrient loops, recharges soil nutrients, and adds organic matter for sustainable productivity (van der Wiel et al., 2019). However, the benefits from CBE approach will only be apparent when there is effective coordination between producers and consumers. Therefore, it would definitely be useful to emphasize on families that are strongly dependent on agriculture as a market for compost and livestock supplies as well as customers as a marketplace for CBE foods.

Precision farm monitoring technologies, which have become more common in the past 30 years, can precisely change input rates regionally, according to Basso et al. (2021). Research has shown that integrating a package of digital agriculture techniques to settle spatial and temporal variation in environmental factors like soil, weather, and topography using hindcasting, nowcasting, and forecasting datasets can significantly improve nutrient-use efficiency and climate mitigating risk (Basso et al., 2019; Martinez-Feria and Basso, 2020).

In applying the circular economy strategy, many researchers study the obstacles to a smooth transition from linear to circular (Ritzén and Sandström, 2017; Aznar-Sánchez et al., 2020; Dieckmann et al., 2020; Grafström and Aasma, 2021; Velasco-Muñoz et al., 2021). Cavicchi et al. (2022) research which focuses on obstacles faced by Australian farming enterprises indicated that initial innovation costs, lack of energy knowledge, insufficient time, inability to assess energy-efficiency initiatives' success, tax complexity, and inflexibility of practices must be addressed to promote circular economy strategy. According to Dieckmann et al. (2020), there are six barriers related with the implementation of CE including financial, structural, regulatory operational, attitudinal and technological issues. In the same sense, Galvão et al. (2018), highlight that the main obstacles for the transition to CE related with policy and legislation, technological innovation, financial and economic aspects, customer behaviour and habits.

Business success requires circular product and bioeconomy production financial incentives. Regarding Circular products, the business should focus to design products that could be repaired, reused, resold, recycled, producing less waste as possible and enabling a systemic shift towards a CE (Rótolo et al., 2022a, 2022b) SMEs may lack financial or technical resources for cleaner production technology. Incentives are intended to address market failures that obstruct or delay the transition to circular products and services. Those incentives should have the potential to add value, minimized risk investments, and boost the competitiveness of value chains, resulting in gross environmental benefits when contrasted to linear economies. Furthermore, targeted financial support could play an important role in promoting innovation and encouraging CE practices. Lowering tax rates on reuse, repair, and remanufacturing actions, such as value added taxes, could encourage circular designs and business models while also promoting the circulation of valuable

products. Other financial intensives could also motivate the use of recycled materials and the adaptation of restorative production of food (EC, 2021).

Proper regulation should foster business-government-investor cooperation (Fanelli, 2021; Jalo et al., 2021; Arora et al., 2022). According to Borrello et al. (2016), regulatory restrictions, a lack of reverse logistics, geographic dispersion of industries, customer awareness, demand for technology innovation, and uncertain investment opportunities and incentives are the main barriers to adopting the circular economy model. Rótolo et al. (2022a, 2022b) found that citizens, entrepreneurs, educators, administrators, and politicians must collaborate to overcome circular economy adoption barriers while incentives, financial support, education, awareness, research, innovation, and circular strategies are deemed necessary for a holistic approach towards agri-circular transition (Sgroi, 2022).

Xia and Ruan (2020) examined farm stakeholders (government, farmers, enterprises) and their key considerations for circularity. Regarding government weaknesses they concluded that policies, legislation, and administrative mechanisms are inadequate as there are no scientific priority policies or financial incentives. Tax policy is given less weight by the government and lastly the existing infrastructure is insufficient. Farmers have a limited environmental awareness level, as well as inadequate knowledge and skills. Finally, for enterprises the production costs remain high, there is a clear lack of technological innovation, and there is a significant imbalance between market demand and supply.

4. Conclusion

To reduce natural resource overconsumption and restore environmental impacts, the existing economic model must be reshaped to allow for a smooth transition from linear to circular supply chains. In this context, the circular economy model is a promising approach for conserving natural resources and providing sustainable, restorative, and regenerative agriculture in the face of resource scarcity, climate change, pollution, and rising food demand. Reusing and recycling farm waste can help local economies while

also reducing environmental impact. Recycling and reusing agricultural waste may improve industrial symbiosis, while farm or cooperative components that circulate may increase profits while decreasing environmental impact. According to EU legislation, strategies, and incentives, combining the circular economy and bioeconomy can maintain and strive for food security and sustainable development. The implementation of a circular economy in farming practices could significantly contribute to the UN SDGs for the creation of an innovative and sustainable society (SDG 11), characterized by responsible consumption and production (SDG 12). At the same time, aside from recycling, other market opportunities include sustainable biomass, increased product life cycle, waste reuse, biofuels and bioenergy, composting, and recycling, while the use of bio-fertilizers in combination with inorganic fertilizers is suggested as a more environmentally friendly and cost-effective option. According to the study's findings, SC and PP are the organic and pruning residues with the highest total N content and the lowest C/N ratio among the wastes examined. As a result, both residues may provide the best conditions for N mineralization. Considering 150 kg ha^{-1} of N input as the optimum demand, the amount of pruning and harvesting residue (farming wastes) must be applied, approximately, between 400 and 1000 times more than urea fertilizer. Organic and inorganic fertilizers have advantages and disadvantages; therefore, a balanced combination can be critical for sustainable farming, taking advantage of both positive and negative effects. However, other minerals besides nitrogen nutrients should be considered in order to have a holistic approach to organic waste utilization in the farming sector.

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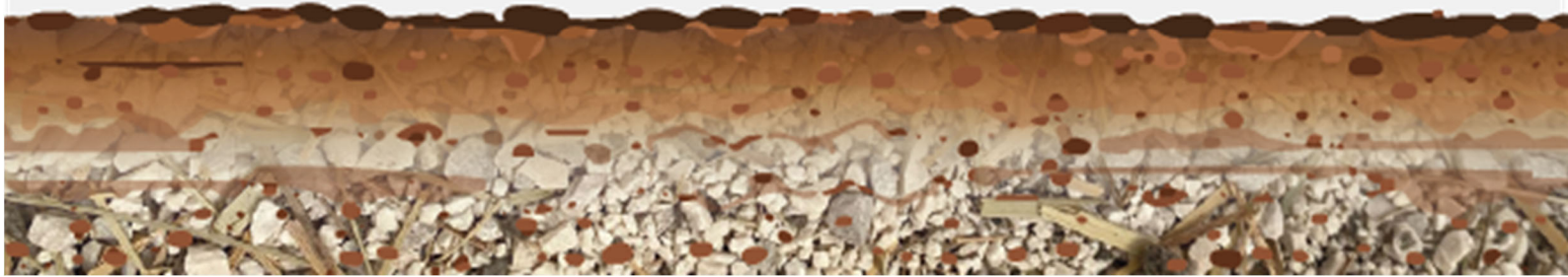
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CAPÍTULO 8: ENVIRONMENTAL RISK FROM ORGANIC RESIDUES.

Este capítulo corresponde con el trabajo:

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ABSTRACT

Soil nutrient imbalance is a global threat to food security and ecosystem sustainability but adding organic residues or constructing anthropogenic soils and technosols can optimize it. However, FAO considers organic residues not “risk-free”, mainly due to their heavy metal content. Despite the fact that applying pruning residues to soil is a worldwide fertilization practice, its potential heavy metal risk has been poorly studied. This work characterizes Cu, Zn, Cd, Cr, Ni and Pb elemental composition concentration and their solubility content in almond tree pruning, commercial peat substrate, hay straw, olive tree pruning, pomegranate peel, pine needle, date palm leaf pruning, sewage sludge compost and vine pruning. Furthermore, we compare the legal frameworks governing heavy metal content in agricultural substrates to heavy metal concentration in each residue. Results show that commercial peat substrate is the only one among those studied that surpasses the threshold value for Cr in agricultural substrates. All pruning residues met the heavy metal threshold value; hence, their application to soil involves minimal soil toxicity. Moreover, the solubility index of heavy metals and the maximum quantity of each residue are crucial to discerning a heavy metal-free organic fertilization plan.

1. Introduction

Consequences for crops, human health and ecosystems due to improper use of inorganic fertilizers have been widely debated. However, an efficient supply of nutrients to the soil is increasingly necessary since soil nutrient imbalance is a global threat to food security and ecosystem sustainability [1]. To optimize soil nutrient cycles and solve functional problems, the Food and Agriculture Organization (FAO) of the United Nations (UN) [2] and other authors [3–5] propose adding organic residues or constructing technosols [6–8], in line with sustainable agriculture, circular economy strategy and Sustainable Development Goals (SDGs) [9–11]. At the same time, the European Green Deal (EGD) aims towards carbon neutrality until 2050, with midterm goals of at least 55% decrease in greenhouse gas emissions by 2030. EGD enables European countries and, by extension, citizens to benefit from sustainable practices toward green transition [12]. In this regard, the European Commission proposed innovative objectives linked directly and indirectly with EGD (i.e., European climate Law, Farm to Fork strategy) in order to establish cutting edge research and innovation in order to preserve the natural environment and ensure, among others, sustainable soil management [13,14]. In addition, applying organic residues synchronized with crop nutritional requirements can be key to its yield due to the rapid supply of soluble nutrients [15–18].

FAO defines organic fertilizer as “one derived from living organisms, such as manure, green manure, compost and crop residues, and municipal wastes” [19]. Although organic fertilizers' benefits are unquestionable (improve physical properties, microbial activity, nutrient supply, biodiversity and ecosystem services provision and CO₂ storage, among others) [5,9,17,18,20–22], according to FAO [23], they are not “risk-free” either, and is mainly associated with the material that it is made of, such as excreted matter or industrial process waste. Consequently, aspects to keep in mind are heavy metal concentration, polluting substances (microplastics, chemical substances, pharmaceutical products and other emerging contaminants), salt concentration and the presence of pathogenic microorganisms [24–26]. Although a priori crop residues are the ones with

the lowest risk of toxicity or pathogenicity, this work focuses on dangers that are not so obviously related to crop residues' nutrient content and transfer. Both the lack and excess of nutrients in soils pose problems for public health (i.e., malnutrition, human diseases), for the development of crops (i.e., food insecurity) and for ecosystem sustainability [23,27,28].

Plants need nutrients for their development. Depending on the amount of nutrients required by plants, they are categorized as macronutrients (N, P, K, Ca, Mg and S) or micronutrients (Fe, Mn, B, Mo, Cu, Zn and Cl) and are considered essential in completing the stages of the plant life cycle. Na, Si, Co and V are essential for some plants. In addition, plants uptake from the soil solution; other elements are not essential (Cd, Cr, Ni, Pb, Hg, As, Li, Rb, Al, Se, etc.) if they are in available forms [23,29]. However, when concentrations of these elements in the soil are unbalanced due to excess or deficiency, they can lead to plant toxicity or malnutrition, respectively. Deficiency-yield-toxicity margins of the elements depend mainly on the type of element, plant species, soil physical-chemical properties and climatic conditions [28,30]. In general, plants have better tolerance for macronutrient excess than micronutrients, where the limits between yield and loss are closer [29].

Among micronutrients, although Cu and Zn are heavy metals (HMs), both are essential micronutrients for human and animal nourishment. Moreover, other HMs, such as Cd, Cr and Pb, are essential too [30] but only at very low concentrations to avoid ecosystem contamination and food chain accumulation [28], as Cd and Pb are the most toxic elements to the human body [27]. Knowing the HM concentration that plants uptake from soil solution and store in edible parts is vital for human health, as well as knowing the HM concentration in non-edible tissues that can be applied to soil, as when HM concentration is high, a loop of contamination can be initiated. Moreover, HMs affect soil microorganisms, which hinders organic waste decomposition [28].

HM presence in agricultural soil, due to anthropogenic causes, may be related to inorganic fertilizers or waste application [30]. In the European Union, even though the amount of agricultural land affected is not very high, it is estimated that 137,000 km² (6.24%) of agricultural land has an HM concentration above the guideline values [31]. Following the FAO's recommendation [2,23], we provide an analysis of some nutrients

and HM legal threshold concentrations, depending on the crop residue applied to the soil. Currently, we do not have a legal framework on a European level for the formulation and use of anthropogenic man-made soils and technosols that sets technical and safety criteria for crops, the environment and human health [32].

Characterization and monitoring of residue mixtures are important, as well as the soil to which they are applied, since there may be an enhancement or a reduction in adverse effects, as in the case of metal mobilization and leaching [8]. Therefore, this work analyzes Cu, Zn, Cd, Cr, Ni and Pb elemental composition concentration in organic residues and their solubility content that may pose a risk after soil application, as HM can cause great concern [33]. In addition, the legal framework related to HM content in agricultural substrates is compared to the heavy metal concentration in each residue. Furthermore, this research calculates from what number of applications organic residues can entail a potential HM risk.

2. Materials and Methods

2.1. Selected Residues

Based on its availability (proximity to consider circular economy and zero waste strategy) and potentiality to be part of technosols (considering man-made and transformed soils), the following organic residues were selected:

- Almond tree pruning (AP).
- Commercial brown peat (CP).
- Hay straw (HS).
- Olive tree (*Olea europaea* L.) pruning (OP).
- Pomegranate (*Punica granatum* L.) peel (PG).
- Pine (*Pinus halepensis*) needle fall (PN).

- Date palm (*Phoenix dactylifera* L.) leaf pruning (PP).
- Sewage sludge compost (SC).
- Vine (*Vitis vinifera*) pruning (VP).

Pruning and harvesting residues (AP, HS, OP, PG, PN, PP and VP) were collected from agricultural areas close to Elche (Alicante, Spain). SC was processed and obtained from Aspe Wastewater Treatment Plant (Alicante, Spain). PP was subjected to an initial shredding after pruning and PN was collected directly from the ground surface in a nearby *Pinus halepensis* forest area.

2.2. Residue Characterization and Methods

All residues were subjected to conditioning processes consisting of air drying at room temperature inside a greenhouse (reaching temperatures over 40 °C), shredded and sieved (2 mm).

HM elemental composition (Cu, Zn, Cd, Cr, Ni and Pb) was determined by atomic absorption spectrometer (AAS) (Thermo Scientific, iCE 3000 Series AA Spectrometer, Waltham, MA, USA) after acid digestion (69% nitric acid + H₂O₂) of samples (0.2 g) in a microwave [34]. AAS is calibrated before use by testing the absorbance with solutions of quantitative certificated standards. AAS detection limits are Cu, 0.04; Zn, 0.01; Cd, 0.005; Cr, 0.02; Ni, 0.01 and Pb, 0.02 mg L⁻¹. Cr is evaluated as total Cr content.

HM aqueous extraction (1:10 w/v) of each residue was obtained by using 100 mL deionized water added to 10 g of residue and shaking for 2 h. After filtering, HM soluble content was measured by using AAS (Thermo Scientific, iCE 3000 Series AA Spectrometer).

Additionally, HM solubility index (I_{HM}) was calculated as the percentage of HM extracted in aqueous solution with respect to elemental composition in each residue, both expressed in dry weight basis, according to Equation (1) [35]:

$$I_{HM} = (W_{HM}/C_{HM}) \times 100 \quad (1)$$

where

*W*_{HM}: heavy metal;

*W*_{HM}: water extractable heavy metal average content;

*C*_{HM}: heavy metal average concentration in elemental composition.

2.3. Statistical Analysis

Descriptive statistics were used to calculate mean and standard deviation for each individual analysis of residues (five repetitions per each one). Analysis of variance (ANOVA) and Tukey's multiple comparisons test were performed to compare the mean value of HM content by using SPSS Statistics (v.26).

3. Results and Discussion

3.1. Elemental Composition

Table 1 provides the total content of Cu, Zn, Cd, Cr, Ni and Pb results in organic residue elemental composition (dry matter).

As expected, SC is the residue with the highest concentration of those studied HM (Table 1). The most striking result to emerge from our data (Table 1) is that Cd and Cr

presence has been detected in CP, which is provided as a gardening substrate. Nevertheless, no organic pruning or harvesting residues studied (AP, HS, OP, PG, PN, PP and VP) achieve Cd, Cr, Ni or Pb concentrations above the equipment detection limit. Consequently, they can be used as an essential micronutrient source (Cu, Zn) if their legal threshold concentration is not exceeded and thus does not pose a threat to soil toxicity.

Cu concentration in SC (79.7 mg kg^{-1}) is higher among the other residues (Table 1). CP includes 11.2 mg kg^{-1} of Cu elemental composition, which is similar data to pruning residue although a bit higher, as Cu concentration in pruning residue is between 3.6 and 8.2 mg kg^{-1} .

Regarding Zn elemental composition, SC achieves the highest concentration (Table 1). Curiously, PG has the second-highest Zn content compared with the other pruning residues. Woody or more lignified residues have a lower Zn concentration, between 4.6 and 31.3 mg kg^{-1} . These findings suggest that all studied residues (except for AP) can provide more Zn than the commercial peat studied (CP). SC and CP have similar Cd concentrations (0.686 and 0.625 mg kg^{-1} , respectively). However, there are high levels of Cr in SC (26.4 mg kg^{-1}) than in CP (2.8 mg kg^{-1}). SC is the only waste that provides Ni and Pb.

Although SC is at the top of the HM concentration in Table 1, data are much lower than those detected by consulted references. Milik et al. [36] and Alonso et al. [37] obtained Cd (1.16 mg kg^{-1}), Ni (53.85 mg kg^{-1}), Pb (23.92 mg kg^{-1}), Cd (2.69 mg kg^{-1}), Cr (53.9 mg kg^{-1}), Ni (28.4 mg kg^{-1}) and Pb (108 mg kg^{-1}), respectively. However, the data obtained (Table 1) for Cr (26.4 mg kg^{-1}) are higher than the one achieved by Milik et al., Cr (15.32 mg kg^{-1}) [36]. It is worth mentioning that there are raised levels of HM in SC from several European countries, compared to Table 1 values [36]. For instance, SC values obtained for Cu vary from 1467.13 to 237.5 mg kg^{-1} ; Zn from 7026.66 to 620.5 mg kg^{-1} ; Cd from 36.81 to 1.5 mg kg^{-1} ; Cr from 210.35 to 38.4 mg kg^{-1} ; Ni from 214.29 to 19.3 mg kg^{-1} and Pb from 221.5 to 48.2 mg kg^{-1} . The presence of HM in wastewater fluctuates as it is closely linked to the amount and type of industrial activity developed

in each city. Therefore, for this type of waste, where HM elemental composition is highly variable, characterization of each batch is needed.

The presence of HM in peat bogs has been studied before. Sypalov et al. [38] considered that HM concentration varies depending on the depth at which each peat sample was taken, while the concentration ranges from Cu, 0.98–3.92 mg kg⁻¹; Zn, 3.89–23.8 mg kg⁻¹; Cd, 35.3–125 µg kg⁻¹; Cr, 0.18–1.89 mg kg⁻¹; Ni, 0.46–1.9 mg kg⁻¹ and Pb, 0.59–10.2 mg kg⁻¹. Similar research reached even higher values of HM in peat, as 333, 8.8 and 245 mg kg⁻¹ for Zn, Cd and Pb, respectively [39], thus explaining the presence of HP in CP (Table 1).

References related to HM elemental composition content in pruning residue are scarce. Musa Ozcan et al. [40] analyzed the presence of HM in pomegranate peel. HM concentration in PN can vary on the strength of spice type: Cu, 0.705–1.48; Zn, 6.45–22.2; Cd, 0.021–0.091; Ni, 0.144–0.351 and Pb, 0.172–0.147 mg kg⁻¹ [41] and of needle age too: Cu, 3.7–11.2; Zn, 18.6–59.2; Cd, 0.1–2.5 and Ni, 3.5–17.1 mg kg⁻¹ [42]. Al-Busaidi et al. [43] obtained HM in PP elemental composition: Cu, 0.001; Zn, 6.5–12.92; Cd, 0.001; Ni, 9.93–10.19 and Pb, 0.001 mg L⁻¹.

3.2. Soluble Elements and Solubility Index

HM water extractable content is shown in Table 2 (dry matter).

Table 1. HM elemental composition, average content (Ave.) and standard deviation (Std.) of each residue.

Residue	Cu (mg kg ⁻¹)		Zn (mg kg ⁻¹)		Cd (mg kg ⁻¹)		Cr (mg kg ⁻¹)		Ni (mg kg ⁻¹)		Pb (mg kg ⁻¹)	
	Ave.	Std.	Ave.	Std.	Ave.	Std.	Ave.	Std.	Ave.	Std.	Ave.	Std.
AP	4.0 a	0.3	4.6 a	1.7	nd	-	nd	-	nd	-	nd	-
CP	11.2	1.4	5.3 ab	0.7	0.629	0.005	2.8	0.4	nd	-	nd	-
HS	3.6 a	0.1	31.3	3.7	nd	-	nd	-	nd	-	nd	-
OP	4.9 a	0.3	12.4 c	0.6	nd	-	nd	-	nd	-	nd	-
PG	5.3 a	0.2	110.8	2.0	nd	-	nd	-	nd	-	nd	-
PN	7.0 a	0.8	11.4 bc	1.0	nd	-	nd	-	nd	-	nd	-
PP	3.8 a	0.4	15.7 cd	0.9	nd	-	nd	-	nd	-	nd	-
SC	79.7	14.6	249.5	8.4	0.686	0.108	26.4	0.7	6.2	0.5	10.8	1.9
VP	8.2 a	1.3	19.4 d	1.5	nd	-	nd	-	nd	-	nd	-
F ¹	100.4 ***		2474 ***									

¹ F values followed by *** indicate significant differences at p= 0.001. By columns, mean values with letters in common (a, b, c, d) are statistically equal to p=0.05. nd: under detection limit.-: not calculated.

Table 2. HM water extractable average content (Ave.) and standard deviation (Std.) of each residue.

Residue	Cu (mg kg ⁻¹)		Zn (mg kg ⁻¹)		Cd (mg kg ⁻¹)		Cr (mg kg ⁻¹)		Ni (mg kg ⁻¹)		Pb (mg kg ⁻¹)	
	Ave.σ	Std.	Ave.	Std.	Ave.	Std.	Ave.	Std.	Ave.	Std.	Ave.	Std.
AP	0.240 ab	0.020	4.2 ab	0.3	nd	-	nd	-	nd	-	nd	-
CP	0.091 a	0.009	4.3 ab	0.3	nd	-	nd	-	nd	-	nd	-
HS	1.024 de	0.267	7.8 d	1.9	nd	-	nd	-	nd	-	nd	-
OP	1.144 e	0.187	5.6 bc	0.6	nd	-	nd	-	nd	-	nd	-
PG	1.797	0.329	13.9	1.0	nd	-	nd	-	nd	-	nd	-
PN	0.437 b	0.046	4.7 ab	0.4	nd	-	nd	-	nd	-	nd	-
PP	0.819 cd	0.105	10.5	0.6	nd	-	nd	-	nd	-	nd	-
SC	0.522 bc	0.051	4.0 a	0.2	nd	-	nd	-	nd	-	0.38	0.25
VP	1.116 de	0.103	6.7 cd	0.5	nd	-	nd	-	nd	-	nd	-
F ¹	45.0 ***		89.6 ***									

¹ F values followed by *** indicate significant differences at p= 0.001. By columns, mean values with letters in common (a, b, c, d, e) are statistically equal to p=0.05. nd: under detection limit. -: not calculated.

Curiously, in SC and CP, the Cd, Cr Ni and Pb water extractable content are below equipment detection limits, compared to elemental composition values (Table 1), except for Pb in SC (0.38 mg kg^{-1}). These findings suggest that, in general, Cu and Zn are the most soluble elements among the studied metals. Scaling soluble Cu results from highest concentration to lowest, the order revealed is $\text{PG} > \text{OP} > \text{VP} > \text{HS} > \text{PP} > \text{SC} > \text{PN} > \text{AP} > \text{CP}$. In such a way, all studied residues provide more Cu in a short time than CP, and PG can release the most quantity (1.797 mg kg^{-1}). Related to Zn water extractable content (Table 2), the list of studied residues scaled from the highest to lowest are $\text{PG} > \text{PP} > \text{HS} > \text{VP} > \text{OP} > \text{PN} > \text{CP} > \text{AP} > \text{SC}$. PG has the highest concentration of soluble Cu and Zn. Nevertheless, CP and SC are at the bottom, SC, due to the loss of soluble elements during the composting process [35,44].

It is important to be aware of the presence of rapidly soluble HM because, with the first rain or irrigation, they would be released into the soil solution, so the HM solubility index (I_{HM}) is calculated (Table 3).

Table 3. Solubility index (%) of each metal (I_{HM}).

Residue	I_{Cu}	I_{Zn}	I_{Ca}	I_{Cr}	I_{Ni}	I_{Pb}
AP	6	90	-	-	-	-
CP	1	82	-	-	-	-
HS	29	25	-	-	-	-
OP	23	45	-	-	-	-
PG	34	13	-	-	-	-
PN	6	42	-	-	-	-
PP	21	67	-	-	-	-
SC	1	2	-	-	-	4
VP	14	35	-	-	-	-

-: not calculated.

It can be seen from the data in Table 3 that Zn and Cu are the metals with the highest solubility index, with certain peculiarities associated with residue origin and composition. Zn achieves the highest rates of solubility in most of the residues. AP involves 90% of Zn solubility, and the list from top to bottom is $\text{AP} > \text{CP} > \text{PP} > \text{OP} > \text{PN} > \text{VP} > \text{HS} > \text{PG} > \text{SC}$. Although AP and CP have a low concentration of Zn in their elemental composition

(Table 1), most of Zn is in a soluble form (between 90 and 82%, respectively) (Table 3). However, PP is the second residue related to the concentration of soluble Zn (Table 2) and PP has the third place for solubility index (67%).

Residues with higher I_{Cu} are $PG > HS > OP > PP > VP > PN > AP > CP > SC$. Notwithstanding, SC is the residue with the lowest I_{Cu} and I_{Zn} , and is the only one that has I_{Pb} (4%). Accordingly, although SC is the residue with the highest concentration of Cu and Zn in its elemental composition (Table 1), its low I_{Cu} and I_{Zn} show that SC can have an optimum performance as a long-term nutrient source. None of the pruning residue, nor CP, have I_{Cd} , I_{Cr} , I_{Ni} and I_{Pb} . So, in addition to its high I_{Cu} and I_{Zn} , pruning residues can rapidly release Cu and Zn to nourish crops.

Although the bibliography on the subject is scarce and focuses mainly on SC, Milik et al. [36] considered Ni and Cd in SC as the most easily movable elements. However, other references obtain high rates of exchangeable Ni and Zn among the elements studied in this article [37]. Even so, Alonso et al. [37] concluded that the rapidly soluble HM percentage in SC is low, at only 7%.

3.3. Potential Toxicity

The presence of soluble HM can be a short-term harmful potential indicator. However, HM total concentration is needed to ensure crops, environment and human safety since they can become bioavailable over time. Although there is no Cd, Cr, Ni or Pb concentration in the elemental composition of pruning residues (above equipment detection limit) (Table 1), this paper checks whether its Cu and Zn content fulfill legal requirements, as well as whether Cu, Zn, Cd, Cr, Ni and Pb concentrations in SC and CP, can entail a certain risk.

Regulations taken as reference include Council Directive 86/278/EEC [45] related to environmental protection, and in particular soil protection, when sewage sludge is used in agriculture. It was transposed into Spanish law by the Real Decreto 1310/1990 [46]. For the rest of the analyzed residues, we investigated the Spanish Real Decreto 865/2010

[47] regarding crop substrates. Regulation EU 2019/1009 [48] lays down rules on fertilizing and amending products, establishing HM content that cannot be exceeded depending on type and use (Table 4).

Comparing data of elemental composition HM total content (Table 1) with respect to the threshold value (Table 4), SC complies with Council Directive 86/278/EEC [45] and with Real Decreto 1310/1990 [46]. In the same way, pruning residues AP, HS, OP, PG, PN, PP and VP met permissible limits according to Real Decreto 865/2010 [47] and EU 2019/1009 [48]. On the contrary, Cr elemental composition concentration (Table 1) in CP (2.8 mg kg^{-1}) exceeds EU 2019/1009 [48] threshold. Furthermore, Cd elemental composition in CP (0.629 mg kg^{-1}) is close to the maximum extent (0.7 mg kg^{-1}) permitted by applicable law Real Decreto 865/2010 [47]. Cd is a metal with high toxicity, mobility and bioavailability, so the interest is focused on soil and plant health. These characteristics are self-evident in the most restrictive threshold value in current law compared with the other HM (Table 4).

Table 4. Threshold value (mg kg^{-1} dry matter) for metals in substrates, amendments and fertilizers used in agriculture.

Substance	C.D. 86/278/EEC [45] and		R.D 865/2010 [47]	EU 2019/1009 [48]
	R.D. 1310/1990 [46]			
	Soil pH < 7	Soil pH > 7		
Cu	1000	1750	70	200 (GM)/300 (OF, L, SI)/600 (OMF) *
Zn	2500	4000	200	500 (GM)/800 (OF, L, SI)/1500 (OMF) *
Cd	20	40	0.7	1.5 (GM, OF)/2 (L, SI)/3-60 ¹ (OMF) *
Cr	1000	1500	70	2
Ni	300	400	25	50 (GM, OF, SI, OMF)/90 (L) *
Pb	750	1200	45	120

* GM: growing medium. OF: organic fertilizer. L: liming material. SI: organic and inorganic soil improver. OMF: organo-mineral fertilizer. ¹ Related to phosphorus content.

None of the water-extractable HM content (Table 2) supposes a non-compliance of the threshold value for metals in substrates, amendments and fertilizers used in agriculture (Table 4).

Table 5. Threshold value (mg kg⁻¹ dry matter) for metals in agricultural soil.

Substance	C.D. 86/278/EEC [45] and R.D. 1310/1990 [46]		UNEP [49]		
	Soil pH < 7	Soil pH > 7	Threshold Value ¹	Lower Guide Value ¹	Higher Guide Value ¹
Cu	50	140/210 *	100	150	200
Zn	150	300/450 *	200	250	400
Cd	1	3	1	10	20
Cr	100	150	100	200	300
Ni	30	75/112 *	50	100	150
Pb	50	300	60	200	750

* 140, 300 and 75 mg kg⁻¹ are limits defined by C.D 86/278/EEC; 210, 450 and 112 mg kg⁻¹ by R.D 1310/1990.

¹ “Threshold value is equally applicable for all sites and it indicates the need for further assessment of the area. If guideline value is exceeded, the area has a contamination level which presents ecological or health risks. Different guideline values are set for industrial and transport areas (higher guideline value) and for all other land uses, like agriculture areas (lower guideline value)”.

Another key aspect to consider is prior HM concentration in agricultural soils where pruning residues will be applied. Table 5 presents the HM concentration threshold in agricultural soils that cannot be exceeded to set organic residues. SC application is controlled by Council Directive 86/278/EEC [45] and Real Decreto 1310/1990 [46]. In addition, Table 5 provides international HM concentration limits considered by the UN Environment Programme (UNEP) for agricultural land [31,49], chosen by the wide range of legal approaches in each European country.

If HM concentrations in the soil do not exceed the threshold in Table 5, it will depend on the quantity and frequency of each residue application. As a preliminary approach, SC is the only residue with HM concentration in its elemental composition (Table 1) that surpasses the Table 5 threshold value. Cu and Zn elemental composition concentrations in SC (79.7 and 249.5 mg kg⁻¹, respectively) rise above threshold data for acidic soils [45]. Acidification of soils increases the solubility of HM and their absorption by plants [36]. Furthermore, Zn elemental composition in SC (249.5 mg kg⁻¹) is higher than the threshold value stipulated by UNEP (200 mg kg⁻¹) [49]. To conclude, due to the HM concentration variability of SC (stated before) and Cu and Zn elemental composition concentration surpassing the Table 5 threshold, SC is the residue that can involve potential soil toxicity.

It is worth mentioning the difference between permissible limits established according to each regulation (Tables 4 and 5).

3.4. HM Contribution to Soil

This paper calculates HM contribution by applying 30,000 kg ha⁻¹ of each residue to soil (Table 6) from elemental composition and extractable content obtained in Tables 1 and 2. Table 6 illustrates that though high HM concentration can be available in the soil after SC application, very low quantity is rapidly available in their soluble forms. Pruning residue contributes to most of the release of soluble metals (Cu and Zn).

Table 6. HM concentration added to soil by applying 30,000 kg ha⁻¹ of each residue (related to its elemental composition and aqueous extract content).

Residue	Elemental Composition (kg ha ⁻¹)						Aqueous Extract (kg ha ⁻¹)					
	Cu	Zn	Cd	Cr	Ni	Pb	Cu	Zn	Cd	Cr	Ni	Pb
AP	0.120	0.138	-	-	-	-	0.007	0.126	-	-	-	-
CP	0.336	0.159	0.019	0.085	-	-	0.003	0.129	-	-	-	-
HS	0.108	0.939	-	-	-	-	0.031	0.234	-	-	-	-
OP	0.147	0.372	-	-	-	-	0.034	0.168	-	-	-	-
PG	0.159	3.324	-	-	-	-	0.054	0.417	-	-	-	-
PN	0.210	0.342	-	-	-	-	0.013	0.141	-	-	-	-
PP	0.114	0.471	-	-	-	-	0.025	0.315	-	-	-	-
SC	2.391	7.485	0.021	0.793	0.186	0.323	0.016	0.120	-	-	-	0.011
VP	0.246	0.582	-	-	-	-	0.033	0.201	-	-	-	-

-: not calculated.

However, this paper estimates how many applications of 30,000 kg ha⁻¹ per year and residue in agricultural soil can be performed without surpassing the HM guideline value (Figures 1 and 2). Real Decreto 1310/1990 [46] is used as a reference, although this law has to do with SC application. Real Decreto 1310/1990 [46] HM threshold values are Cu: 12; Zn: 30; Cd: 0.15; Cr: 3; Ni: 3; Pb: 15 kg ha⁻¹ year.

As expected, HM elemental composition concentration is the limiting factor (Figure 1). SC is the residue that can exceed Zn and Cr thresholds with four applications, Cu threshold with five applications, Cd threshold with seven applications and Ni with 16 applications per year. CP showed non-compliance with the Cd threshold after eight applications per year. All pruning residues do not surpass Real Decreto 1310/1990 [46] HM permissible levels after monthly application over a one-year period. In fact, except for PG, where Zn can be exceeded after nine applications per year, the rest of the pruning residues needed between 32 and 217 applications per year to surpass HM critical levels. Related to soluble HM concentration (Figure 2), the HM threshold value (only for three elements) is exceeded by applying between 72 applications of PG and 4396 applications of CP.

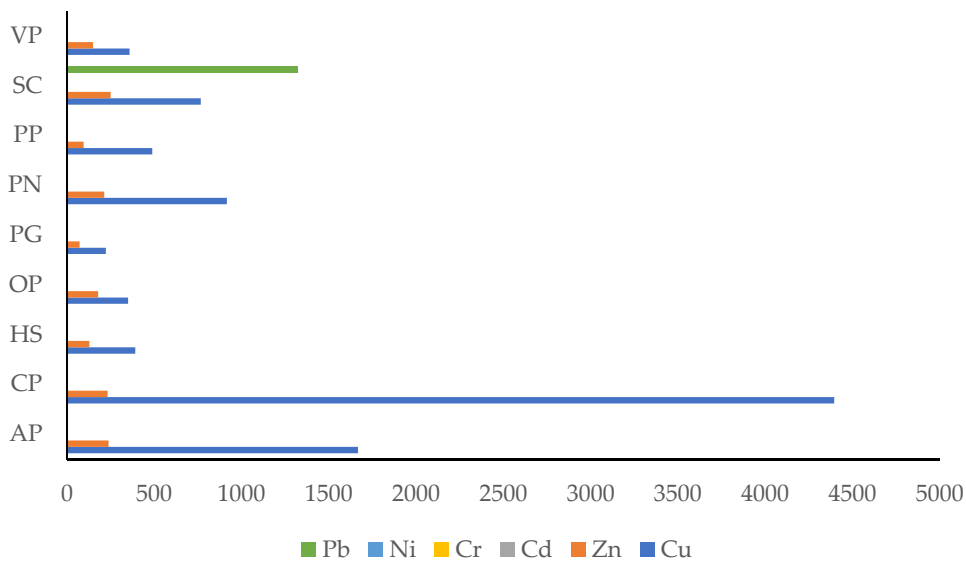


Figure 1. How many applications of 30,000 kg ha⁻¹ per year and residue are needed to exceed HM threshold stipulated by Real Decreto 1310/1990 [47], relying on elemental composition content.

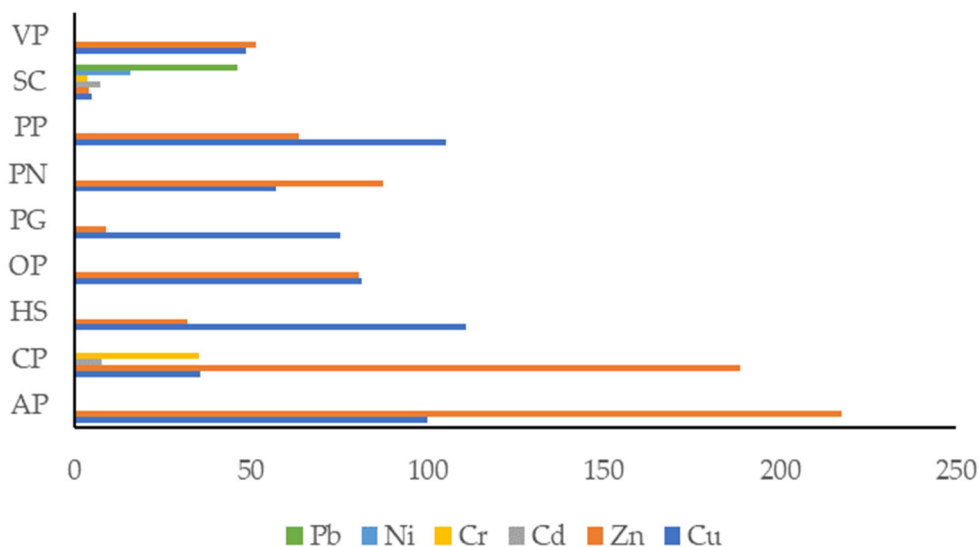


Figure 2. How many applications of 30,000 kg ha⁻¹ per year and residue are needed to exceed HM threshold stipulated by Real Decreto 1310/1990 [47], relying on aqueous extract content.

Several authors consider there to be a small risk of exceeding trace element toxicity limits by applying residues to soil [24,50,51], thus confirming these results. However, organic fertilizer from animal sources can entail a higher toxicity risk to soil and human health than organic fertilizer from plant residues [52–54]. The presence of HM in the elemental composition of pruning residues a priori does not involve a potential risk for soil or crops but depends on HM concentration, mobility, bioavailability and HM crop tolerance. Soil toxicity prevention is linked with food and water security (SDGs 2 and 6), pollution of marine (SDG 14) and terrestrial (SDG 15) environments due to land-based nutrients, as well as urban development (SDG 11) [55,56].

4. Conclusions

The application of pruning residues contributes to improving soil properties, ecosystem functioning, ecosystem services provision, food security and nutrition despite the fact

that FAO urges the analysis of HM content in organic residues, which has been poorly studied, especially in relation to pruning residues.

Regarding the HM concentrations obtained, SC is the one with the highest content in the elemental composition. However, SC has very low HM solubility rates, so their availability must be tested in the long term. Although HM concentration in SC elemental composition met permissible limits for agricultural substrates, Cu and Zn content are above the HM concentration threshold in agricultural soils that cannot be exceeded to set organic residues. In addition, SC is the residue with more use constraints since an application of $30,000 \text{ kg ha}^{-1}$ can be made less than four times per year. CP has Cu, Zn, Cd and Cr in its elemental composition, which can be a matter of concern due to its use as a gardening substrate. Its I_{Cu} , I_{Cd} , I_{Cr} , I_{Ni} and I_{Pb} are very low or practically nonexistent; on the contrary, its I_{Zn} is 82%. Moreover, CP is the only residue among those studied that exceeds the threshold value for Cr in agricultural substrates.

None of the organic pruning or harvesting residues (AP, HS, OP, PG, PN, PP and VP) achieved Cd, Cr, Ni or Pb concentrations above the equipment detection limit. All pruning residues met HM threshold values; hence, their application to the soil does not involve any potential soil toxicity. Pruning residues can be an effective soil amendment and an invaluable source for short and long-term soil nutrition because of their high Cu and Zn solubility (between 6 and 34% and 13 and 90%, respectively) and because $30,000 \text{ kg ha}^{-1}$ can be applied to soil 31 to 216 times (except PG). These findings suggest that Cu and Zn are the most soluble elements among the studied metals. Due to the variability in residue origin, environmental conditions and adaptive mechanisms of each species, it would be useful to have a legal framework at the European level or the formulation and use of technosols that sets technical and safety criteria for crops.

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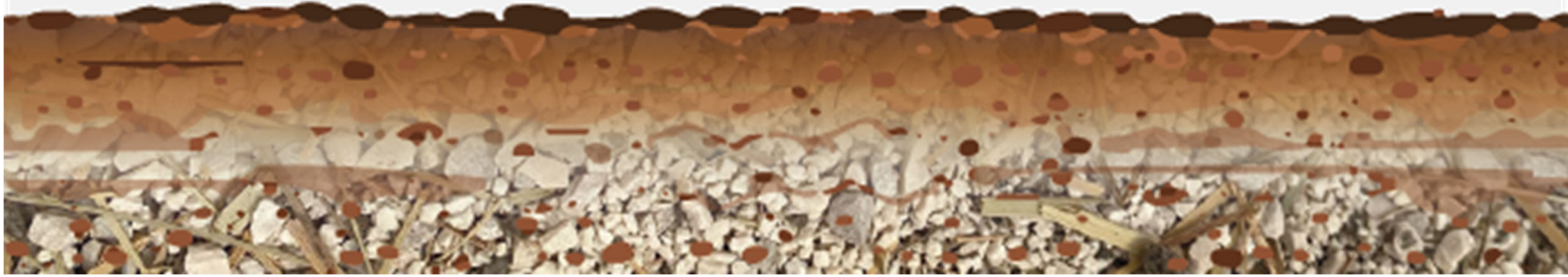
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CAPÍTULO 9: *LOW-QUALITY IRRIGATION WATER TREATED USING WASTE BIOFILTERS*

Este capítulo corresponde con el trabajo:

Rodríguez-Espinosa, T., Pérez Gimeno, A., Almendro Candel, M.B., Gomez Lucas, I., Navarro-Pedreño, J. 2023. Low-quality irrigation water treated using waste biofilters. *Water*, 15, 2464. DOI: <https://doi.org/10.3390/w15132464>



ABSTRACT

Although in water deficient regions, agricultural runoff, drainage water or surplus irrigation water is often used, there are constraints related to its quality to be considered (salinity, nutrients and pollutants). Thus, it is necessary to treat surplus irrigation water considering low energy supply systems available for farmers. This work focuses on a nature-based water treatment system, consisting of two prototypes of anaerobic bioreactors, with horizontal or vertical flow. To enhance the circular economy strategy, two different wastes (coarse sand and almond pruning) were used as bioreactor components. The aim of the research was to monitor the quality of the water (pH, electrical conductivity, suspended solids, chemical oxygen demand, alkalinity, bicarbonate, carbonate and nitrogen contents), before and after the treatment. All the parameters studied (except chemical oxygen demand) were reduced by the treatments, but with large variations. Furthermore, there was 100% nitrogen reduction in the horizontal water flow treatment with filter bed formed by coarse sand and almond pruning. It was observed that the variation in the concentration of some parameters was associated with the type of filter bed (i.e., the C/N ratio of the residue) and with the design for water circulation flow. Although the findings are promising, further research is needed to achieve reductions in all studied parameters.

1. Introduction

Worldwide water resources are increasingly coming under pressure, leading to water scarcity and a deterioration in water quality. The expected growth of the human population [1,2] entails an increase in global demand for resources such as food or water, 60% and 55%, respectively, by 2050 [3–5]. Future projections consider that a lack of water will affect 60% of the world's population by 2025 [6,7]. However, global water scarcity is caused not only by the physical scarcity of the resource, but also by the progressive deterioration of water quality; so, this reduces the quantity of water that is safe to use [8]. In 2015, 60% of surface waters in the European Union (EU) had a poor ecological status, mainly due to point pollution (e.g., wastewater) or non-point pollution (e.g., agriculture) [9,10]. Agriculture is the largest water user worldwide, and it accounts for 70 to 95 percent of total freshwater withdrawals, depending on the degree of the country's development [3,8].

Currently, water scarcity affects more than 40% of the global population [11], and in the EU, 29% of its territory was affected by water scarcity in 2019 [12]. In this context, non-conventional water resources are becoming more prominent [6]. To improve the worldwide water supply and sanitation infrastructure, it is estimated that USD 6.7 trillion are needed [4].

As a result of the increasing reuse and recirculation of water, water quality tends to deteriorate, and this restricts its future uses [13]. The reuse of wastewater for irrigation is widespread to improve the circular economy of water in urban settlements [14]. By 2023, it is expected that global water reuse will achieve 1.66% of total water use, with 32% of reclaimed water used for irrigating [15]. In 2006, EU countries reused 964 million m³ year⁻¹, and Spain had the best share, 347 million m³ year⁻¹ [16].

Although agricultural runoff, drainage water or surplus irrigation water are often used in water-deficient regions, there are some constraints to be considered, such as salts, pathogens, emerging contaminants and nutrients because of fertilizer use [8,9,14,17]. Nitrogen (N) is an essential nutrient for crop yields and food production,

but its excessive presence in aquatic ecosystems can trigger eutrophication processes. In Europe, for the period 2016–2019, water categorized as eutrophic included 81% of marina waters, 31% of coastal waters, 36% of rivers and 32% of lakes [18]. This poses problems for crop yield, ecosystems sustainability and human health [19–21]. Therefore, its repeated use should be carried out when an adequate quality is ensured. If not, agricultural drainage water (marginal water) must be treated, which implies addressing the difficulty of installing treatment plants in rural settings covering large or scattered agricultural areas.

To overcome this issue, and in relation to the European Green Deal [22], the EU Action Plan: “Towards a Zero Pollution for Air, Water and Soil” aims to reduce soil, water and air pollution, improving soil quality by reducing nutrient losses and chemical pesticides use by 50%. Additionally, in March 2020, the European Commission announced the adoption of the circular economy action plan (CEAP) [23,24] and prioritized the reduction, reuse, recycling and alternative management of waste materials. The CEAP represents a new economic and production paradigm that requires a shift in mindset, recognizing waste as a potential resource rather than a burden to be managed and discarded in landfills, as in the previous linear economy [25]. In addition, the Water Framework Directive [26] aims to ensure the sustainable use of water resources and its quality by 2027. Materials in suspension, substances that contribute to eutrophication and substances which have an unfavorable influence on the oxygen balance, among others, are a main concern. Moreover, the Nitrates Directive is an important instrument to achieve and proposes the use of eco-agricultural practices and nature-based solutions for water treatment and soil remediation [18].

In such a way, green treatment technology (constructed wetlands, waste stabilization ponds and infiltration land) is being used to model nature works mainly for wastewater remediation [27–31]. Nature-based solutions have more benefits compared to those of traditional wastewater treatments, such as a low maintenance requirement, cost effectivity, removal efficiency [30,31] and extensive design possibilities based on the element to be removed (water level and flow movement, phytoremediation, phycoremediation, substrate, aerobic or anaerobic conditions,

whether it is energetically self-sufficient or not and nutrient recovery, among others). Bioreactors are one of the most used treatments since pollution removal is conducted due to retention on adsorbent material (biofilter) and microorganisms that accumulate on the adsorbent [32]. The surface of the biofilter is key for determining the biomass growth rate and biomass retention capacity [7,33,34]. Accordingly, the selection of adsorbent will determine the efficiency of the adsorption process [7]. A wide range of adsorbent materials, both inorganic and organic ones (agricultural waste, among others), have been studied for wastewater treatments, confirming its effectiveness for removing pollutants [33–35]. The use of waste can enhance the circular economy and avoid the costs associated with management [34]. Moreover, it can be a helpful practice as the increase in food production will lead to an increase in food waste. Agricultural waste, such as pruning residues, due to its porous and multi-hierarchical lignocellulosic composition, have intrinsic mesoporous structure, exceptional optical and mechanical characteristics and a high capacity for water transportation, which offers them interesting opportunities for water treatment [7].

Several authors consider that technosols can be designed to provide ecosystem services like a natural soil does and to recover a degraded ecosystem, including aquatic ones [36–43]. Technosols, have been successfully used to improve the surface runoff water quality in mining areas, urban stormwater and wastewater [7,33,34,44–48]. However, their ability to treat irrigation water has not been studied as much, especially when macrophytes are not involved [28].

Based on the previous ideas, the aim of this research was to study a nature-based treatment free of emergent vegetation by using residues as the adsorbent and the design of pilot biofilter systems to improve the quality of agricultural water. The physical and chemical parameters (pH, electrical conductivity, suspended solids, chemical oxygen demand, alkalinity and bicarbonate, carbonate and total nitrogen contents) of low-quality irrigation water before and after the treatments were determined to check the effectiveness of the treatments designed.

2. Materials and Methods

2.1. Irrigation water source

The irrigation water has its origin in the Main Irrigation Channel of Elche's reservoir (Alicante, Spain). Elche's reservoir is in the north of the city and receives water from Vinalopó river. This river is fed by natural waters and treated water from wastewater treatment plants situated along its basin. The irrigation channel of Elche's reservoir begins at the dam reservoir and runs in the same directions as Vinalopó river does, crossing the city of Elche from the north to the south.

The experiment was conducted over twenty weeks. Water was collected weekly (Figure 1) (UTM geographical coordinates X: 701,170.5 m; Y: 4,239,112.38 m), and fed into the biofilters systems. Irrigation water samples were analyzed immediately.



Figure 1. Sampling location map (National Geographic Institute of Spain.)

2.2 Bioreactor designs

Water pilot treatment plants were inspired by the performance of nature-based solutions using wastes as the adsorbent material. They were located inside the greenhouse of the University Miguel Hernández of Elche (Alicante, Spain) and were kept under controlled conditions. Two types of anaerobic bioreactors were designed,

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one with subsurface water and horizontal flow, and the other with subsurface water and vertical flow (Figure 2).



Figure 2. Bioreactors diagrams. At the top: anaerobic bioreactor with subsurface water and horizontal flow. At the bottom: anaerobic bioreactor with subsurface water and vertical flow. (a) irrigation water in polyethylene deposits; (b) peristaltic pump; (c) biofilter; (d) effluent recovered in polyethylene deposits.

Both biofilters were made of fiberglass-reinforced polyester (Figure 2, part c). The horizontal bioreactor size was 120 cm × 15 cm × 35 cm (L × W × H), and the vertical bioreactor of 15 cm × 15 cm × 60.5 cm (L × W × H), and they had three sections. The first and last one (10 cm × 15 cm × 27 cm) were the water inlet zone and the water

outlet zone, which were full of volcanic gravel (diameter approximately between 3–5 cm) and worked as pre-treatment and homogenization areas prior to the introduction of water to the anaerobic treatment. The middle section (length 100 cm) held the natural adsorbent, and both horizontal treatments had two layers. The bottom one contained wastes (22 cm) and the top one contained coarse sand (4 cm) to control and reduce the evapotranspiration of subsurface flow. The inlet point was 24 cm high, and the outlet point 20 cm high from the bottom of the bioreactor.

The vertical bioreactor had one section with two layers. The bottom one contained the wastes (48 cm high), and the top one contained sand (high 4 cm). The inlet point was situated at the top of the bioreactor, and the outlet point was 45 cm high from the bottom. Both types of bioreactors maintained the anaerobic conditions, and water (inlet and outlet) was disposed in polyethylene deposits.

The wastes used were selected for treatments based on their availability in the area (considering circular economy and zero waste strategy) and their adsorption potentiality. Inorganic residue was collected from the extractive activities of limestone deposits and fine gravel/coarse sand (2–3 mm) (G). This was composed mainly of calcium carbonate (over 99%), and to a lesser extent, magnesium carbonate, and the bed had a porosity of 41.8%. Further, an organic residue of almond tree pruning (A) was collected from agricultural areas close to Elche (Alicante, Spain). Almond tree pruning was subjected to conditioning processes consisting of air drying at room temperature and chopping (5 cm size). The porosity was 69.6%, and its characterization is provided in Table 1, and methods of analysis were previously published [49,50].

Table 1. Almond tree pruning characterization: organic matter content (OM), pH, electrical conductivity (EC) and bulk density (ρ_b), mean value (M) and standard deviation (SD). [49,50]

Residue	OM (%)		pH (units)		EC ($\mu\text{S cm}^{-1}$)		ρ_b (g cm^{-3})	
	M	SD	M	SD	M	SD	M	SD
G	0	0	9.90	0.03	107.85	17.62	1.55	0.05
A	93.2	0.6	4.66	0.007	665	0.80	0.36	0.006

Therefore, by combining the wastes and bioreactors design, four treatments were studied:

- Horizontal water flow with filter of G (HG).
- Horizontal water flow with filter of G and A (HA).
- Vertical water flow with filter of G (VG).
- Vertical water flow with filter of G and A (VA).

The constant supply of irrigation water to the bioreactors was achieved using peristaltic pumps (inlet point) from polyethylene deposits, keeping the flow rate in all the treatments (2.3 L day^{-1}) and the hydraulic retention time (4 days) the same. Bioreactors were covered with a black mesh of 1 mm situated over them (5 cm) to reduce evapotranspiration (0.5 mm m^{-2}) and protect from insect access and seed germination. Influent water in the deposits was replaced weekly to avoid water degradation. The effluent, as well, was taken weekly and directly from the source point as it arrived for an hour to ensure that we had enough water to analyze. Therefore, the bioreactors were used for substrate adsorption and microbial degradation as removal mechanisms.

2.3 Water characterization methods

Influent (I) and effluent water (E) -EHG, EHA, EVG and EVA- from each treatment was analyzed weekly: pH, electrical conductivity (EC), total suspended solids (SS), chemical oxygen demand (COD), total alkalinity and bicarbonate, carbonate and total nitrogen contents (N). Analysis of water samples was based on the APHA standard methods [51]. The pH was measured (method 4500-H⁺ and 2580) by using a CRISON GLP 21 pH-meter, and electrical conductivity (EC) was measured with a CRISON GLP 31 conductivity meter (method 2510). SS values were obtained after filtering the samples with 47 mm glass microfiber filters and heating them in an

oven (J.P SELECTA CONTEM) at 105 °C (method 2540 D). The COD was tested using a digestion vials reagents kit, a thermoreactor (HI 839800-02) at 150 °C and a multiparameter photometer (HI 83300) (all from HANNA INSTRUMENTS (method 5220). Alkalinity, bicarbonates and carbonates contents were measured according to the methods, 4500-CO₂ and 2320 D. The N content was measured using the HANNA kit (HI94767). The persulfate method was used to determine the total nitrogen content via the oxidation of all nitrogenous compounds to nitrate with the HANNA reactor (HI839800) at 105 °C and HANNA multiparameter photometer (HI83399).

Weekly changes in irrigation water characteristics were calculated as the percentage of variation according to Equation (1) [52]:

$$\text{Variation (\%)} = (1 - (C_e/C_i)) \times 100 \quad (1)$$

C_e: the value of the analyzed parameter in the bioreactor outlet water (effluent);
C_i: the value of the analyzed parameter in the bioreactor inlet water (influent). When the result of variation is positive, there is a reduction of the analyzed parameter; on the contrary, when it is negative, there is an increment.

2.4 Statistical analysis

Descriptive statistics were used to calculate the mean and standard deviation for each individual water test (five repetitions per each treatment). Analysis of variance (ANOVA) and Tukey's multiple comparisons test were conducted using SPSS Statistics (v.26).

3. Results and Discussion

3.1 Irrigation water characterization

Table 2 provides the mean value of the parameters analyzed in the influent (I) in the horizontal bioreactors (HG and HA) and in the vertical bioreactors (VG and VA).

Table 2. Irrigation water (influent) characteristics used for each type of bioreactor (horizontal and vertical), mean value (M) and standard deviation (SD)

Parameter	Units	Horizontal		Vertical	
		M	SD	M	SD
pH	(units)	8.25	0.09	8.27	0.11
EC	(mS cm ⁻¹)	17.45	1.55	18.26	0.78
SS	(mg L ⁻¹)	41.38	8.50	40.37	8.60
COD	(mg L ⁻¹ O ₂)	96.84	61.99	100.29	60.79
Alkalinity	(mg CaCO ₃ L ⁻¹)	250.69	18.16	260.12	14.85
Bicarbonates	(mg HCO ₃ ⁻ L ⁻¹)	150.15	10.76	155.60	8.78
Carbonates	(mg CO ₃ ⁻² L ⁻¹)	2.66	0.50	2.96	0.88
Nitrogen	(mg N L ⁻¹)	15.40	5.22	20.15	9.22

As it was expected, the inlet water characteristics were similar in both treatments; although, the water derived from the deposits used to fill the horizontal bioreactors and vertical bioreactors was obtained from the same source (time needed to prepare the systems and refill the deposits). So, there are slightly variations in the composition of the inlet water.

3.2. Effluent characterization

pH, EC, SS, COD, alkalinity, bicarbonates, carbonates and N data obtained weekly are provided in a graphic format (Figures 3 and 4) and in detail in Appendix A (Tables 1–8).



Figure 3. pH, EC, SS and COD results of horizontal and vertical water flow bioreactors. **(a)** Weekly pH (units) of horizontal water flow bioreactors. **(b)** Weekly pH (units) of vertical water flow bioreactors. **(c)** Weekly EC (mS cm⁻¹) of horizontal water flow bioreactors. **(d)** Weekly EC (mS cm⁻¹) of vertical water flow bioreactors. **(e)** Weekly SS concentration (mg L⁻¹) of horizontal water flow bioreactors. **(f)** Weekly SS concentration (mg L⁻¹) of vertical water flow bioreactors. **(g)** Weekly COD concentration (mg L⁻¹) of horizontal water flow bioreactors. **(h)** Weekly COD concentration (mg L⁻¹) of vertical water flow bioreactors.

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Figure 4. Alkalinity, bicarbonates, carbonates and N results of horizontal and vertical water flow bioreactors. **(a)** Weekly alkalinity concentration (mg L^{-1}) of horizontal water flow bioreactors. **(b)** Weekly alkalinity concentration (mg L^{-1}) of vertical water flow bioreactors. **(c)** Weekly bicarbonates concentration (mg L^{-1}) of horizontal water flow bioreactors. **(d)** Weekly bicarbonates concentration (mg L^{-1}) of vertical water flow bioreactors. **(e)** Weekly carbonates concentration (mg L^{-1}) of horizontal water flow bioreactors. **(f)** Weekly carbonates concentration (mg L^{-1}) of vertical water flow bioreactors. **(g)** Weekly N concentration (mg L^{-1}) of horizontal water flow bioreactors. **(h)** Weekly N concentration (mg L^{-1}) of vertical water flow bioreactors.

All of the treatments showed a pH in the effluent (Figure 3a,b) lower than the pH of the influents (Table 2). The maximum pH value (8.48) was reached in the EHA in the fifth week, and the minimum (5.06) one was obtained in the EHA in the first week (Appendix Table 1). The contribution of almond pruning residue leads to greater fluctuations in the pH of the effluent (Figure 3a,b). Acidification in the first week of the EHA are due to the contribution of the highly soluble compounds from the almond pruning that can acidify water, e.g., (dissolved organic matter). According to Rodríguez-Espinosa et al. [50], the pH of the aqueous extract of almond pruning shows a value of 4.66 (Table 1). However, in the EHA, as the weeks passed, the pH values increased, obtaining the same as that in the EHG in week 20 (Appendix Table 1). However, the changes in the pH in the VA treatment, after an initial reduction, increased; although, at week 20, the lowest pH value of all effluents was observed (8.01). This may be associated with the type of bioreactor. The mean pH of EHG and EVG, both only with an inorganic bed, were similar and quite stable over time.

All the effluents showed a mostly higher EC than the incoming water did (Appendix Table 2). However, some differences were observed between the types of bioreactor (Figure 3c,d). Both horizontal effluents achieved lower EC during weeks 2 and 3, and only the EVA among vertical effluents maintained reached a lower EC than the inlet water did in weeks 1, 4 and 20. EC may be influenced by the type of bioreactor and, in general, an increment in the salinity was noticed in all the effluents. This means that these treatments have low efficiency, reducing the salinity of low-quality water.

The values obtained for SS in the outlet waters in the EHA and the EVA were generally higher than those in the inlet water (Figure 3e,f). The use of organic waste in these cases favored the increment of the SS. The SS in the EHA was very high throughout the experiment, except for the last week (43.58 mg L^{-1}), when it was close to the inlet value (41.38 mg L^{-1}), as it is showed in the Appendix (Table 3). In the VA treatment, there was an initial contribution to the SS that was stabilized from week 6, even reaching a lower concentration than the inlet water had until the last week (Figure 3e,f). The SS in the outlet water was always under the value of the inlet water in the EHG (except in week 4). The SS in the EVG was below the inlet water during all 20 weeks. Although, the SS concentration in the EVA reached the lowest value

(22.07 mg L⁻¹) in week 16 (Appendix Table 3). Therefore, the SS was better controlled by the vertical bioreactors to facilitate precipitation and sedimentation processes and favoring the diminution of the SS in the outlet water.

None of the four bioreactors achieved a weekly lower COD than that of the inlet water (Figure 3g,h). A contribution of oxidizable organic matter released from the organic waste (A) can be observed in both type of bioreactors (Appendix Table 4). However, the concentration of the COD in the EVA was better, and even in week 20, the COD concentration was lower (346.75 mg L⁻¹) than the achieved in the EHG (396.25 mg L⁻¹). The inorganic bioreactors reached lower COD values comparing with the values of those containing almond pruning (Figure 3g,h). During experimentation, the COD reached similar values in the four treatments. In fact, this parameter is related to the biological activity of bioreactors and also dead matter coming from the biomass formed in the bioreactors.

Figure 4a,b shows the weekly alkalinity concentrations of the effluents. The weekly alkalinity concentration was always lower than the initial one (inlet waters) in the EHG and EVG, and they were the most stable systems to control this parameter. Although, the alkalinity concentration in the EVA fluctuated, from week 14, the results were below those of the influent water (Table 2). Inorganic bioreactors obtained the best values (109.36 mg L⁻¹ in EHG and 162.19 mg L⁻¹ in EVG), although they are composed of fine gravel/coarse sand composed mainly by calcium carbonate (Appendix Table 5).

The trend in the bicarbonate content of the effluents (Figure 4c,d) is like that shown for alkalinity (Figure 4a,b). Inorganic bioreactors achieved weekly concentrations lower (Appendix Table 6) than the initial ones (Table 2). Despite the high initial contribution of bicarbonates from the EHA and EVA effluents, due to the organic waste and the acidity of this residue, the VA system stabilized it, and from week 15, it showed a concentration lower than that of the influent (Appendix Table 6).

Table 3. Variation in the parameters analyzed (%) in horizontal and vertical bioreactors from weeks 1 to 20.

pH	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20
EHG	-0.6	3	2.6	2.8	0.7	1.4	0	-0.5	0.3	-1.6	-0.8	1.2	2.3	1.3	0.6	1.7	1.7	2.4	1.6	0.8
EHA	38.2	9.7	8.4	1.4	-2.8	4.3	-1.3	0.3	-0.4	-2.6	1.4	2.9	3.2	3.3	3.5	3.6	1.5	2.7	2.7	0.8
EVG	1.1	1.4	-0.6	-0.2	2.5	1.9	2.7	1.8	2.4	1.1	0.3	2.1	0	0.7	1.3	1.9	6.8	-1.7	2.6	3.6
EVA	2.2	6.5	2	5	2.5	4.1	6.8	8.4	6.1	4.9	6.4	4.8	1.7	1.7	2.3	1.9	0.7	0	2.3	6.5
EC	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20
EHG	-24.8	10.4	0.7	-3.2	-16	-14.3	-14.9	-14.5	-14.9	-13.4	-11.7	-15	-8.8	-13.6	-5.1	-11.6	-9.8	-8.6	-5.3	-13.0
EHA	-39.6	8.2	0.4	-11.5	-14.8	-6.8	-8.4	-5.3	-11.1	-15.8	-9.4	-10.5	-7.3	-13.5	-2.8	-8.2	-6.7	-8.9	-5.5	-11.8
EVG	1.0	-2	-1.1	-1.6	-2.6	-1.1	-2.8	-3.7	-2.9	-1.8	-2.4	-0.1	-8.2	-6.8	-4.8	-5.5	-1.5	-2.7	-1.7	-0.2
EVA	0.3	-0.7	-3.3	0.7	-2	0	-1.6	0.9	-3.0	-1.6	-2.7	-0.1	-6.6	-0.7	-5.1	-1.3	-0.4	-2.5	-2.4	0.1
SS	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20
EHG	54.8	31.6	22	0.2	-80	-2.8	30.6	19.1	22.0	25.3	39.6	15.0	26.4	31	47.2	23	7.7	36.1	49.4	7.7
EHA	-81.1	-1650.8	-1080.3	-994.1	-607.2	-499.2	-416.3	-651.1	-354.4	-93.6	-114.4	-148.0	-49.4	-134.2	-162.8	-104.3	-93.6	-14.8	1.7	-22.2
EVG	25.8	37.8	43.5	47.9	29.6	44.7	37.9	42.5	39.9	36.8	58.2	55.5	21.9	27.0	44.1	-13.3	8.3	23.8	23.1	-6.6
EVA	-452.6	-354.4	-273.9	-108.2	-10.4	-50.2	18.9	36.2	17.5	36.7	41.1	48.6	24.1	12.3	31.7	24.9	-9.7	21.9	0.3	15.8
COD	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20
EHG	-695.3	-281.3	-401.9	-378	-508.6	-376.3	-390.3	-434.1	-344.4	-420.3	-315.9	-2.1	-192.3	-390.2	-303.1	-401.7	-268.4	-395.7	-344.9	-323.8
EHA	-34561.8	-7253.6	-4156.6	-3088.8	-2122.1	-1048.8	-951.0	-846.4	-689.4	-711.6	-545	-52.3	-314.2	-501.1	-424.2	-508	-371.3	-445.7	-344.1	-364.4
EVG	-454.7	-233.2	-310.5	-246.2	-1.8	-141.8	-322.1	-233	-273.5	-183.1	-350.6	-292.9	-303.5	-204.0	-242.7	-351.3	-444.2	-275.5	-415.6	-316
EVA	-1896.4	-1490.1	-1217.2	-410.6	-34.4	-137.7	-376.1	-259.8	-315.7	-247.1	-350.9	-265.1	-279.1	-258.5	-222.8	-281.7	-396.5	-298.6	-361.5	-391.8
Alkal	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20
EHG	26.8	37.9	47.2	39.5	50.2	33.2	55.6	54.4	48.5	51.7	58.2	55	57.1	50.8	51.2	53.8	51.6	53.7	51.2	51.4
EHA	-310.3	-348.3	-264.4	-385.3	-309.5	-281.6	-316.8	-274	-296.4	-229.5	-189.1	-171.4	-187.4	-133.3	-123.3	-112.9	-109.1	-77.0	-54.8	-42.4
EVG	20.6	19.2	32.4	36.7	36.2	36.8	26.3	34.1	35	29.7	30.2	29.5	29.3	29.8	27.3	36.5	34.5	32.2	19.2	12
EVA	-184.8	-201.8	-221.6	-80.1	-89.5	-65.7	-42	-30.9	-9.8	-16.7	-4.2	-3.4	4	-9.9	19.1	17	18.9	24.5	16.2	7
Bicarb.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20
EHG	26.5	37.1	46.8	39.1	50	33	55.3	54.4	48.5	51.9	58.2	54.8	56.8	50.6	51.1	53.5	51.4	53.3	50.9	51.2
EHA	-316.8	-357.8	-270	-387.5	-305.6	-286.2	-315.6	-274.7	-296.8	-227.7	190.5	-173.9	-189.8	-135.7	-125.4	-115.1	-110.2	-78.8	-56.2	-43
EVG	20.3	18.9	32.4	36.7	35.8	36.6	25.7	33.7	34.4	29.4	29.9	28.9	29.1	29.5	27.1	36.2	33.7	32.6	17.9	10.5
EVA	-186.3	-204.9	-223.6	-81.8	-91.1	-67.6	-44.2	-32.8	-11.4	-18	-5.9	-4.6	3.4	-10.5	18.6	16.8	18.7	24.6	15	4.7
Carbo.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20
EHG	43.5	67.9	65.3	59.8	59.5	48.5	78.2	57.9	51.4	38.7	56.2	64.6	71.1	62.9	57.9	67.1	64.4	73.4	66	63
EHA	99.7	41.9	17.2	-287.3	-519.7	-41.8	-417.2	-226.5	-270.3	-379.2	-100.9	-46.8	-68.8	-25.1	-18.3	-11.6	-47.2	6.2	14.2	-12.3
EVG	43.6	34.9	33.2	38.8	60	51.9	56.2	63.1	43.9	42.4	57.2	43.9	44.7	41.4	55.3	77.5	9.1	54.9	55.7	
EVA	-82.8	10	-64.1	34	-11	29.2	61.6	69.6	68.6	54.6	60.5	57.4	33.9	24.4	45.6	33.1	30	24.5	50	72.5
N	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20
EHG	29.2	0	88.9	56	95.6	68.8	37.5	27.6	68	27	44.2	16.7	82.8	25.7	-36.4	-106.9	-37.8	6.3	9.1	-36.8
EHA	0	-100	-3.7	40	24.4	53.1	-4.2	-37.9	-4	24.3	44.2	-83.3	58.6	51.4	21.2	13.8	56.8	96.9	60.6	100
EVG	34.5	40	5.4	37.2	-16.7	51.7	0	-45.5	-31	31.1	12.5	3	-15.8	-165.2	41.4	55.9	47.5	20.5	-106.1	36.2
EVA	44.8	48	40.5	60.5	-50	75.9	68.6	75.8	41.4	51.4	87.5	18.2	47.4	-63	36.8	-7.4	67.8	43.6	-33.3	-24.6

Note(s): Alkal.: alkalinity; Bicarb.: bicarbonates; Carbo.: carbonates.

Figure 4e,f shows the concentration of carbonates determined in all the treatments over the 20 weeks in each effluent. Inorganic bioreactors showed lower carbonate concentrations than the incoming water did (Table 2). In the organic bioreactors, an initial contribution of carbonates was observed, which was greatly exacerbated in the case of EHA (Appendix Table 7). However, in the organic vertical system (VA), from week 6, the carbonate concentration was lower than the concentration presented in the low-quality irrigation water, and it reached the lowest value among all treatments in the first week (0.01 mg L^{-1}).

Regarding the most important parameters of water quality, N concentration is one of the most relevant due to the possible eutrophication that can be caused by inorganic N in water (lakes and coastal areas). The results in the effluents are shown in Figure 4g,h and in Appendix Table 8. All the treatments reached lower N concentrations than the inlet water did for several weeks (Table 2), but fluctuations in N reduction are seen every 2–3 weeks. This variability is associated with changes in the microbial activity and the removal capacity associated with the increment of biomass and the needs of N for this increase (Appendix Table 8). The HA treatments showed fewer fluctuations in the N concentration. In fact, from week 17, this treatment reached a substantial reduction of N, reaching an almost total reduction in the last week. At this point, the microbial activity was very consolidated, and in the last weeks, the inlet water shows a lower N concentration, so that the need for N by the microbial population (sized for a higher N input) may not be met; so, there is a higher N demand. Probably, this means that this treatment would be the best to control N.

Table 3 provides the weekly variation, in percentages, for each parameter analyzed. In all treatments, a pH variation was observed, reducing the pH of the effluents (0.8%, 0.8%, 3.6% and 6.5% in EHG, EHA, EVG and EVA, respectively) at the end of the 20 weeks. In the systems with organic wastes, although there were fluctuations (increase and reduction), the pH reduction was predominant, which may be due to the action of anaerobic microorganisms' metabolisms [53]. The inorganic vertical system achieved higher percentages of pH reduction, reaching its maximum at week 17 with 6.8%. The highest percentages of pH reduction were obtained in the EHA (38.2% in week 1) and

EVA (8.4% in week 8) effluents, mainly due to the initial contribution of the most soluble organic acids from the organic waste. VA achieved the greatest reduction.

The trend of the EC was associated with the type of flow: water circulation, horizontal or vertical (Table 3). In the horizontal systems, there was a very high contribution of EC during the first week (-24.8% in EHG and -39.6% in EHA), but both systems reached positive variations in the second and third weeks. However, from the third week, the percentages of reduction, although fluctuating, remained negative. For the vertical systems, though they also obtained negative percentages (except for the first week), the EVA one obtained an EC variation percentage of 0.1 in the last week, which was compared to -0.2% for the EVG one. In general, salinity was affected negatively, with slight increments in the effluents.

Table 3 shows how the variation in the SS in the effluents depends to a greater extent on the type of absorbent (inorganic or a combined organic+inorganic bed). Thus, EHG and EVG showed positive SS variation over the 20 weeks, except in weeks 5 and 6 (EHG) and in weeks 16 and 20 (EVG). EHG and EVG reached maximum SS variation percentages of 54.8% and 58.2%, respectively. The bioreactors with organic waste showed greater difficulties in reducing the SS, especially with horizontal water flow. EHA had a high initial SS input (up to -1650.8%), so that its variation percentages up to week 17 showed very high negative values. EVA managed to reach positive percentages of variation from week 7, ending with the best percentage of variation (15.8%) in the last week. Particulate matter from the bed of the bioreactors was responsible for this increment, mainly in the bioreactors with the presence of almond waste.

None of the systems achieved a positive weekly variation in the COD percentage (Table 3). These results agree, in some way, with the results obtained for the SS presented in the effluents. The biological activity after the first few weeks can help to maintain a higher COD in the effluents regarding the values of influents.

The inorganic systems showed positive variations in alkalinity (reducing the alkalinity) during all the weeks (Table 3). In fact, EHG reached its maximum positive variation in week 11 (58.2%), and EVG reached its maximum positive variation in week 6 (36.8%). EHG maintained high percentages of variation until week 20 (51.4%); however, EVG at week 20 obtained a 12% variation. High initial alkalinity was observed in the organic

treatments with the presence of almond pruning; although, EVA continued to have a positive variation from week 13 (except for week 14), and at week 20, this was 7%. The same trend of variation was observed for bicarbonates (Table 3).

High percentages of variation were obtained with carbonates (Table 3). The systems with only inorganic waste showed positive variations in all the weeks, obtaining the highest percentages of variation in week 7 (78.2%) for EHG and in week 17 (77.5%) for EVG. Regarding the bioreactors with almond waste, EVA started with negative variations, but from week 5, the values were positive, ending in week 20 with the maximum value of reduction (72.5%). However, EHA started with positive reduction percentages (99.7% at week 1), but from week 4 (except for weeks 18 and 19), the percentages were negative.

Biological nitrogen removal is based on the process of the oxidation of ammonium to nitrate (nitrification) and the denitrification of nitrate to nitrogen gas and the efficiency of these processes. Increased dissolved oxygen contents can negatively affect nitrogen removal [54]. So, maintaining anaerobic conditions would facilitate N removal. Although the reactors are anaerobic, the best anaerobic conditions prevail in the deeper layers [21]. A priori, by checking the great N results (reduction of 100%) of the EHA reactors at week 20 (Table 3), which were better than the others, we came to think that the absence of oxygen contributed to N removal [55,56]. However, EHG and EVA reached high values of N reduction at weeks 5 (95.6%) and 11 (87.5%), respectively.

The results of previous studies indicate that the pH can influence N removal processes. Although Wu et al. [57] concluded that alkalinity enhances a higher denitrification rate, Feng et al. [58] showed that the N removal was higher when reactors use acid-treated carriers. As mentioned before, the pH of the aqueous extract of almond pruning shows a value of 4.66 [50]. In these pilot bioreactors, the best nitrogen reduction values were obtained in the presence of almond residue. Moreover, this waste facilitates the microbial biomass growth due to its porous structure.

The C/N ratio is also a determinant for denitrification processes; so, at a low C/N ratio, denitrification is reduced [57], and the opposite is also true. According to the results obtained by Rodríguez-Espinosa et al. [59], almond pruning residues have a high C/N ratio (C/N = 89), which could facilitate nitrogen removal (denitrification). As a

consequence, microorganisms need an extra N supply (coming, in this case, from inlet water) to process N from almond tree pruning. Therefore, this result is in line with the conclusions obtained by the authors of the above-mentioned reference.

4. Conclusions

Water quality assurance is starting to be of interest mainly in water-deficient regions. Technologies based on nature-based solutions are a valid option to improve the quality of such water resources, as well as to promote the circular economy when using waste as adsorbent materials. However, the changes in water quality parameters are not the same for all of them, and the design and construction of pilot plants to improve water quality should be considered for each case.

For most of the studied parameters in this work (pH, SS, COD, alkalinity, bicarbonates, carbonates and N), the type of waste used in the bioreactors has a large influence. However, the design and flow of water (horizontal or vertical circulation) is important. In general, the vertical flow regime was favorable for reducing the parameters analyzed. The exception may be salinity, which was not strictly affected by the treatments, and this is an issue for the future study of treatment systems, and the same is true for the COD, which was increased.

The most important result was that the N content was reduced and reached almost a total diminution in water in the treatment EHA. In general, the C/N ratio, in this case of the almond residue, is the key for N reduction.

Therefore, bioreactors can be helpful to improve the characteristics of irrigation water. In view of the many design possibilities, future studies should be carried out to achieve reductions in all the studied parameters, and a combination of several systems can favor the treatment of the low-quality water by using nature-based solutions.

LOW-QUALITY IRRIGATION WATER TREATED
USING WASTE BIOFILTERS

Appendix A

Table 1. Mean value (M) and standard deviation (SD) of pH (units of pH) in horizontal and vertical flow bioreactors.

Horizontal	Week 1		Week 2		Week 3		Week 4		Week 5		Week 6		Week 7		Week 8		Week 9		Week 10	
	M	SD	M	SD	M	SD	M	SD	M	SD	M	SD	M	SD	M	SD	M	SD	M	SD
I	8.18	0.012	8.44	0.012	8.35	0.006	8.36	0.006	8.25	0.006	8.29	0.017	8.13 a	0.012	8.12 a	0.010	8.15	0.015	8.10	0.006
EHG	8.23	0.012	8.19	0.013	8.13	0.008	8.13	0.006	8.19	0.008	8.17	0.006	8.13 a	0.013	8.16	0.019	8.13	0.006	8.23	0.0010
EHA	5.06	0.006	7.62	0.008	7.64	0.008	8.24	0.006	8.48	0.006	7.93	0.006	8.24	0.006	8.09 a	0.013	8.19	0.017	8.31	0.013
F	1 × 10 ⁵ ***		5906 ***		9400 ***		1588 ***		2057 ***		1100 ***		133 ***		19.3 ***		19.4 ***		2820 ***	
	Week 11		Week 12		Week 13		Week 14		Week 15		Week 16		Week 17		Week 18		Week 19		Week 20	
I	8.15	0.021	8.25	0.010	8.29	0.010	8.30	0.021	8.26	0.012	8.31	0.017	8.27	0.006	8.28	0.013	8.29	0.0010	8.25	0.013
EHG	8.21	0.019	8.15	0.006	8.11	0.006	8.19	0.005	8.21	0.005	8.17	0.006	8.12 a	0.021	8.08	0.006	8.16	0.006	8.18 a	0.005
EHA	8.04	0.006	8.01	0.008	8.03	0.017	8.03	0.005	7.98	0.006	8.01	0.008	8.14 a	0.008	8.05	0.008	8.06	0.008	8.18 a	0.008
F	119 ***		888 ***		532 ***		466 ***		1440 ***		653 ***		138 ***		723 ***		817 ***		63.0 ***	
Vertical	Week 1		Week 2		Week 3		Week 4		Week 5		Week 6		Week 7		Week 8		Week 9		Week 10	
	M	SD	M	SD	M	SD	M	SD	M	SD	M	SD	M	SD	M	SD	M	SD	M	SD
I	8.12	0.010	8.15	0.015	8.10	0.006	8.15 a	0.021	8.25	0.010	8.29	0.010	8.30	0.021	8.26	0.012	8.31	0.017	8.27	0.006
EVG	8.03	0.008	8.04	0.029	8.14	0.013	8.17 a	0.005	8.05 a	0.006	8.14	0.013	8.08	0.006	8.11	0.005	8.11	0.006	8.17	0.010
EVA	7.94	0.006	7.63	0.013	7.94	0.013	7.74	0.036	8.04 a	0.017	7.96	0.017	7.74	0.021	7.57	0.017	7.80	0.008	7.86	0.008
F	522 ***		759 ***		396 ***		407 ***		399 ***		613 ***		1080 ***		3531 ***		1940 ***		2820 ***	
	Week 11		Week 12		Week 13		Week 14		Week 15		Week 16		Week 17		Week 18		Week 19		Week 20	
I	8.28 a	0.013	8.29	0.010	8.25 a	0.013	8.26	0.006	8.27	0.012	8.26	0.006	8.23	0.006	8.26 a	0.010	8.53	0.006	8.57	0.012
EVG	8.26 a	0.006	8.12	0.005	8.25 a	0.006	8.20	0.006	8.16	0.005	8.10 a	0.008	7.67	0.006	8.40	0.006	8.31	0.006	8.27	0.006
EVA	7.75	0.017	7.89	0.012	8.11	0.006	8.12	0.006	8.08	0.005	8.10 a	0.008	8.17	0.013	8.26 a	0.008	8.33	0.008	8.01	0.010
F	2230 ***		1909 ***		336 ***		592 ***		609 ***		577 ***		4862 ***		264 ***		1309 ***		3620 ***	

Note(s): F values followed by ***, ** and * indicate significant differences at $p = 0.001, 0.01$ and 0.05 . F values followed by ns indicates no significant differences. In the columns, mean values followed by a letter in common are statistically equal to $p = 0.05$.

Table 2. Mean value (M) and standard deviation (SD) of EC (mS cm⁻¹) in horizontal and vertical flow bioreactors.

Horizontal	Week 1		Week 2		Week 3		Week 4		Week 5		Week 6		Week 7		Week 8		Week 9		Week 10	
	M	SD	M	SD	M	SD	M	SD	M	SD	M	SD	M	SD	M	SD	M	SD	M	SD
I	11.27	0.059	17.65	0.008	17.64	0.099	18.32	0.046	17.50	0.039	17.54	0.072	17.42	0.101	17.48	0.064	16.77	0.061	17.4	0.102
EHG	14.07	0.993	15.82	0.045	17.53	0.021	18.91	0.078	20.29	0.085	20.04	0.008	20.02	0.055	20.01	0.025	19.27	0.148	19.73	0.041
EHA	15.73	0.047	16.20	0.084	17.58	0.015	20.44	0.048	20.08	0.029	18.73	0.051	18.88	0.050	18.42	0.070	18.63	0.057	20.15	0.058
F	5455 ***		1219 ***		3.80 ns		1357 ***		3018 ***		2397 ***		1303 ***		1518 ***		702 ***		1703 ***	
	Week 11		Week 12		Week 13		Week 14		Week 15		Week 16		Week 17		Week 18		Week 19		Week 20	
I	17.76	0.078	17.42	0.095	17.64	0.024	16.99	0.070	18.07	0.043	18.05	0.034	18.37	0.086	18.62	0.056	18.71	0.053	18.49	0.176
EHG	19.84	0.028	20.03	0.019	19.20	0.177	19.30 a	0.061	18.99	0.081	20.14	0.140	20.16	0.158	20.23 a	0.096	19.70 a	0.141	20.90 a	0.141
EHA	19.43	0.083	19.26	0.049	18.93	0.119	19.28 a	0.161	18.57	0.010	19.53	0.140	19.60	0.148	20.28 a	0.050	19.73 a	0.054	20.68 a	0.150
F	1059 ***		1280 ***		180 ***		620 ***		300 ***		345 ***		206 ***		725 ***		161 ***		289 ***	
Vertical	Week 1		Week 2		Week 3		Week 4		Week 5		Week 6		Week 7		Week 8		Week 9		Week 10	
	M	SD	M	SD	M	SD	M	SD	M	SD	M	SD	M	SD	M	SD	M	SD	M	SD
I	17.65	0.008	16.77 a	0.061	17.40	0.102	17.76 a	0.078	17.42	0.095	17.64 a	0.024	16.99	0.070	18.07 a	0.043	18.05	0.034	18.37 a	0.086
EVG	17.47	0.108	17.11	0.107	17.60	0.021	18.04	0.067	17.87 a	0.041	17.84	0.070	17.46	0.031	18.73	0.154	18.56 a	0.015	18.71 a	0.069
EVA	17.60	0.166	16.89 a	0.033	17.98	0.067	17.64 a	0.109	17.77 a	0.010	17.65 a	0.057	17.27	0.013	17.90 a	0.087	18.59 a	0.054	18.67 a	0.139
F	1.45 ns		21.2 ***		68.0 ***		22.4 ***		61.7 ***		16.8 ***		112 ***		69.5 ***		259 ***		13.1 **	
	Week 11		Week 12		Week 13		Week 14		Week 15		Week 16		Week 17		Week 18		Week 19		Week 20	
I	18.62	0.056	18.71	0.053	18.49	0.176	18.69	0.062	18.94	0.017	19.14 a	0.065	19.21	0.026	18.95	0.070	19.03	0.083	19.41	0.039
EVG	19.06 a	0.080	18.73	0.125	20.00	0.164	19.96	0.008	19.85 a	0.071	20.19 a	0.257	19.50	0.025	19.47 a	0.048	19.34 a	0.031	19.45	0.062
EVA	19.12 a	0.042	18.73	0.053	19.72	0.021	18.82	0.050	19.90 a	0.019	19.40	0.031	19.29	0.026	19.42 a	0.026	19.48 a	0.124	19.39	0.057
F	79.6 ***		0.16 ns		133 ***		923 ***		611 ***		50.7 ***		134 ***		124 ***		27.4 ***		1.36 ns	

Note(s): F values followed by ***, ** and * indicate significant differences at $p = 0.001, 0.01$ and 0.05 . F values followed by ns indicates no significant differences. In the columns, mean values followed by a letter in common are statistically equal to $p = 0.05$.

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Table 3. Mean value (M) and standard deviation (SD) of SS (mg L⁻¹) in horizontal and vertical flow bioreactors.

Horizontal	Week 1		Week 2		Week 3		Week 4		Week 5		Week 6		Week 7		Week 8		Week 9		Week 10	
	M	SD	M	SD	M	SD	M	SD	M	SD	M	SD	M	SD	M	SD	M	SD	M	SD
I	51.96	3.18	35.64	1.14	31.31 a	8.29	29.49 a	2.69	35.13	4.47	30.78 a	2.55	41.08	0.88	34.98	0.84	36.7	0.07	44.55	0.58
EHG	23.50	6.18	24.39	3.22	24.43 a	2.36	29.43 a	0.05	63.24	5.17	31.66 a	0.40	28.52	1.92	28.31	2.18	28.63	2.74	33.26	4.44
EHA	94.08	3.57	624.00	2.31	369.56	15.90	322.65	18.07	248.39	14.47	184.44	10.90	212.05	1.88	262.69	4.60	166.78	4.63	86.24	8.68
F	248 ***		82,946 ***		1431 ***		1030 ***		629 ***		748 ***		15,774 ***		8098 ***		2491 ***		98.0 ***	
Horizontal	Week 11		Week 12		Week 13		Week 14		Week 15		Week 16		Week 17		Week 18		Week 19		Week 20	
	M	SD	M	SD	M	SD	M	SD	M	SD	M	SD	M	SD	M	SD	M	SD	M	SD
I	53.12	6.22	35.60 a	0.79	41.64	0.73	42.39	1.13	47.99	2.93	42.42 a	1.05	42.55 a	1.01	57.98	2.55	56.73 a	1.03	35.67 a	0.55
EHG	32.09	1.07	30.25 a	0.84	30.65	6.28	29.27	0.11	25.35	1.59	32.68 a	0.18	39.29 a	0.34	37.05	2.80	28.70	2.44	32.91 a	0.29
EHA	113.90	2.62	88.28	14.10	62.22	6.80	99.30	6.81	126.11	10.89	86.68	9.87	82.39	27.97	66.58	2.12	55.75 a	0.58	43.58	4.95
F	464 ***		61.7 ***		35.8 ***		349 ***		258 ***		101 ***		8.82 **		147 ***		412 ***		14.8 ***	
Vertical	Week 1		Week 2		Week 3		Week 4		Week 5		Week 6		Week 7		Week 8		Week 9		Week 10	
	M	SD	M	SD	M	SD	M	SD	M	SD	M	SD	M	SD	M	SD	M	SD	M	SD
I	34.98	0.69	36.70 a	0.07	44.55	0.58	53.12	6.22	35.60 a	0.79	41.64	0.73	42.39	1.13	47.99	2.93	42.42	1.05	42.55	1.01
EVG	25.97	1.69	22.82 a	1.06	25.18	1.88	27.67	1.30	25.06	2.66	23.04	2.27	26.34	0.67	27.60 a	0.58	25.51	1.07	26.90 a	2.67
EVA	193.26	4.25	205.36	13.72	166.57	5.44	110.58	2.95	39.31 a	6.50	62.54	3.45	34.39	0.84	30.62 a	0.50	35.01	4.82	26.93 a	1.99
F	4967 ***		655 ***		2109 ***		441 ***		13.1 **		266 ***		318 ***		158 ***		33.9 ***		80.7 ***	
Vertical	Week 11		Week 12		Week 13		Week 14		Week 15		Week 16		Week 17		Week 18		Week 19		Week 20	
	M	SD	M	SD	M	SD	M	SD	M	SD	M	SD	M	SD	M	SD	M	SD	M	SD
I	57.98	2.55	56.73	1.03	35.67	0.55	37.93	0.20	43.64	3.34	29.37	1.18	30.02 a	1.42	32.43	0.28	31.92 a	7.47	29.89 a	4.43
EVG	24.25	1.63	25.22	0.51	27.86 a	1.32	27.68	2.11	24.41	3.08	33.29	2.36	27.53 a	6.24	24.72 a	5.45	24.54 a	4.28	31.88 a	1.92
EVA	34.15	1.47	29.19	0.94	27.08 a	0.87	33.25	1.44	29.82	1.29	22.07	0.91	32.95 a	1.61	25.34 a	3.64	31.83 a	6.36	25.18 a	5.98
F	318 ***		1598 ***		96.9 ***		48.1 ***		52.8 ***		50.1 ***		2.03 ns		5.11 *		1.88 ns		2.4 ns	

Note(s): F values followed by ***, ** and * indicate significant differences at $p = 0.001, 0.01$ and 0.05 . F values followed by ns indicates no significant differences. In the columns, mean values followed by a letter in common are statistically equal to $p = 0.05$.

Table 4. Mean value (M) and standard deviation (SD) of COD (mg L⁻¹) in horizontal and vertical flow bioreactors.

Horizontal	Week 1		Week 2		Week 3		Week 4		Week 5		Week 6		Week 7		Week 8		Week 9		Week 10	
	M	SD	M	SD	M	SD	M	SD	M	SD	M	SD	M	SD	M	SD	M	SD	M	SD
I	43	5.20	80	3.77	67 a	10.11	72	6.35	70	2.31	80	0.00	75	1.73	69	0.01	81	1.73	89	10.97
EHG	338	0.02	306	0.01	335 a	0.82	342	15.84	426	22.00	381	15.01	365	10.81	369	36.37	358	24.54	461	30.60
EHA	14,731	94.37	5901	16.52	2841	515.40	2280	208.01	1556	35.22	919	121.25	783	0.01	653	12.73	636	4.04	718	2.50
F	94,705 ***		4.5 × 10 ⁶ ***		106 ***		400 ***		4173 ***		145 ***		12,693 ***		689 ***		1487 ***		1132 ***	
	Week 11		Week 12		Week 13		Week 14		Week 15		Week 16		Week 17		Week 18		Week 19		Week 20	
	M	SD	M	SD	M	SD	M	SD	M	SD	M	SD	M	SD	M	SD	M	SD	M	SD
I	85	2.31	351 a	7.53	120	8.66	87	10.39	97	0.02	88	13.00	104	0.58	87	5.20	103	8.66	94	1.73
EHG	354	26.56	359 a	8.10	349	10.11	427	17.90	391	3.56	440	11.84	381	92.68	429	33.20	456 a	25.40	396	26.29
EHA	548	10.53	535	22.52	495	9.24	523	42.15	509	8.66	534	9.81	488	25.12	472	0.82	445 a	10.98	434	2.63
F	790 ***		206 ***		1638 ***		285 ***		6150 ***		1636 ***		51.2 ***		474 ***		576 ***		597 ***	
Vertical	Week 1		Week 2		Week 3		Week 4		Week 5		Week 6		Week 7		Week 8		Week 9		Week 10	
	M	SD	M	SD	M	SD	M	SD	M	SD	M	SD	M	SD	M	SD	M	SD	M	SD
I	69	0.01	81	1.73	89	10.97	85	2.31	351 a	7.53	120	8.66	87	10.39	97	0.02	88	13.00	104	0.58
EVG	383	27.43	268	9.54	363	10.69	294	75.93	357 a	0.50	289 a	2.31	367	0.50	323 a	32.33	328 a	31.48	293	11.55
EVA	1378	37.53	1280	20.80	1166	36.69	434	35.22	472	0.96	284 a	19.63	414	15.88	349 a	6.93	365 a	24.45	359	22.81
F	2592 ***		9486 ***		2378 ***		52.1 ***		959 ***		240 ***		1042 ***		211 ***		154 ***		323 ***	
	Week 11		Week 12		Week 13		Week 14		Week 15		Week 16		Week 17		Week 18		Week 19		Week 20	
	M	SD	M	SD	M	SD	M	SD	M	SD	M	SD	M	SD	M	SD	M	SD	M	SD
I	87	5.20	103	8.66	94	1.73	106	1.15	97	1.73	78	1.41	65	1.29	74	0.58	66	5.20	71	7.51
EVG	390 a	11.30	403	6.40	377 a	28.58	322	3.20	331	7.23	352	4.08	351	15.64	276 a	28.87	338 a	36.11	293	17.63
EVA	390 a	16.79	374	1.5	355 a	8.66	380	1.15	312	15.02	298	25.12	320	8.54	293 a	4.62	302 a	13.57	347	6.08
F	843 ***		2789 ***		333 ***		19,382 ***		722 ***		389 ***		930 ***		209 ***		174 ***		637 ***	

Note(s): F values followed by ***, ** and * indicate significant differences at $p = 0.001, 0.01$ and 0.05 . F values followed by ns indicates no significant differences. In the columns, mean values followed by a letter in common are statistically equal to $p = 0.05$.

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Table 5. Mean value (M) and standard deviation (SD) of alkalinity (mg L⁻¹) in horizontal and vertical flow bioreactors.

Table 5. Mean value (M) and standard deviation (SD) of alkalinity (mg L⁻¹) in horizontal and vertical flow bioreactors.

Horizontal	Week 1		Week 2		Week 3		Week 4		Week 5		Week 6		Week 7		Week 8		Week 9		Week 10	
	M	SD	M	SD	M	SD	M	SD	M	SD	M	SD	M	SD	M	SD	M	SD	M	SD
I	213.11	1.17	264.47	0.17	265.40	0.90	208.32	0.15	248.33	0.15	253.55	1.21	261.01	0.10	244.50	0.58	217.00	2.66	240.00	1.13
EHG	156.10	0.64	164.27	0.80	140.22	0.34	125.99	0.30	123.66	2.37	169.26	11.18	115.97	0.59	111.40	1.62	111.67	0.77	115.99	1.86
EHA	874.33	1.95	1185.71	0.58	967.23	0.60	1011.05	1.21	1016.84	1.82	967.56	0.62	1087.99	0.65	914.37	1.24	860.11	0.62	790.81	2.48
F	3.4 × 10 ⁵ ***		3.9 × 10 ⁶ ***		1.9 × 10 ⁶ ***		1.8 × 10 ⁶ ***		3.1 × 10 ⁵ ***		18,195 ***		4.2 × 10 ⁵ ***		5 × 10 ⁵ ***		2.4 × 10 ⁵ ***		1.4 × 10 ⁵ ***	
	Week 11		Week 12		Week 13		Week 14		Week 15		Week 16		Week 17		Week 18		Week 19		Week 20	
	M	SD	M	SD	M	SD	M	SD	M	SD	M	SD	M	SD	M	SD	M	SD	M	SD
I	261.43	0.65	262.68	0.32	262.03	1.68	246.50	1.73	257.91	2.21	259.70	0.34	251.17	9.51	260.85	0.32	265.47	1.13	270.33	1.54
EHG	109.36	0.41	118.25	0.81	112.50	0.06	121.26	0.86	125.93	0.82	120.00	1.15	121.47	0.00	120.74	0.29	129.65	0.40	131.27	2.26
EHA	755.85	0.63	712.91	0.62	753.20	1.24	575.08	0.00	576.11	3.57	552.95	1.73	525.10	0.60	461.77	2.32	411.00	1.15	384.98	1.13
F	1.4 × 10 ⁶ ***		1 × 10 ⁶ ***		3.1 × 10 ⁵ ***		1.8 × 10 ⁵ ***		35.122 ***		1.3 × 10 ⁵ ***		5616 ***		63,407 ***		85,661 ***		22,125 ***	
Vertical	Week 1		Week 2		Week 3		Week 4		Week 5		Week 6		Week 7		Week 8		Week 9		Week 10	
	M	SD	M	SD	M	SD	M	SD	M	SD	M	SD	M	SD	M	SD	M	SD	M	SD
I	244.50	0.58	217.00	2.66	240.00	1.13	261.43	0.65	262.68	0.32	262.03	1.68	246.50	1.73	257.91	2.21	259.70	0.34	251.17	9.51
EVG	194.05	0.20	175.39	2.31	162.19	0.22	165.47	0.40	167.48	0.60	165.50	0.58	181.61	0.45	170.00	0.00	168.74	0.29	176.70	0.80
EVA	696.33	1.17	654.82	1.68	771.88	0.00	470.96	1.17	497.76	3.43	434.28	0.34	349.95	1.12	337.73	0.55	285.04	2.29	293.00	0.10
F	5.3 × 10 ⁵ ***		55,542 **		9.9 × 10 ⁵ ***		1.5 × 10 ⁵ ***		28,388 ***		67,609 ***		19,423 ***		16,304 ***		8262 ***		458 ***	
	Week 11		Week 12		Week 13		Week 14		Week 15		Week 16		Week 17		Week 18		Week 19		Week 20	
	M	SD	M	SD	M	SD	M	SD	M	SD	M	SD	M	SD	M	SD	M	SD	M	SD
I	260.85	0.32	265.47	1.13	270.33	1.54	270.72	2.22	272.64	0.00	276.00	0.00	276.24	2.26	280.16	11.31	269.00	1.15	258.00	2.31
EVG	182.10	0.12	187.16	1.06	191.00	1.15	190.06	0.02	198.13	0.00	175.35	1.13	181.00	3.46	190.00	0.00	217.47	2.26	227.00	8.08
EVA	271.92	0.25	274.42	0.16	259.59	1.13	297.39	1.20	220.60	0.00	229.00	1.15	224.00	6.93	211.40	1.18	225.39	0.00	240.00	0.00
F	1.6 × 10 ⁵ ***		11,356 ***		4472 ***		5885 ***		4.3 × 10 ³ ***		11,649 ***		419 ***		206 ***		1432 ***		41.1 ***	

Note(s): F values followed by ***, ** and * indicate significant differences at $p = 0.001, 0.01$ and 0.05 . F values followed by ns indicates no significant differences. In the columns, mean values followed by a letter in common are statistically equal to $p = 0.05$.

Table A6. Mean value (M) and standard deviation (SD) of bicarbonates (mg L⁻¹) in horizontal and vertical flow bioreactors.

Horizontal	Week 1		Week 2		Week 3		Week 4		Week 5		Week 6		Week 7		Week 8		Week 9		Week 10	
	M	SD	M	SD	M	SD	M	SD	M	SD	M	SD	M	SD	M	SD	M	SD	M	SD
I	127.97	0.57	157.73	0.22	158.78	0.54	124.50	0.09	148.63	0.31	151.76	0.80	157.08	0.06	147.01	0.35	130.43	1.55	144.59	0.66
EHG	94.06	0.76	99.04	0.50	84.44	0.19	75.81	0.15	74.25	1.39	101.74	6.70	70.26	0.19	67.03	0.99	67.15	0.45	69.62	1.15
EHA	533.34	1.19	721.22	0.30	587.47	0.36	607.00	0.98	602.86	0.86	586.15	0.32	652.83	0.53	550.90	0.93	517.59	0.56	473.85	1.71
F	3.1 × 10 ⁵ ***		3.6 × 10 ⁶ ***		1.9 × 10 ⁶ ***		1.0 × 10 ⁶ ***		3.6 × 10 ⁵ ***		18,642 ***		3.7 × 10 ⁵ ***		4.1 × 10 ⁵ ***		2.4 × 10 ⁵ ***		1.2 × 10 ⁵ ***	
	Week 11		Week 12		Week 13		Week 14		Week 15		Week 16		Week 17		Week 18		Week 19		Week 20	
	M	SD	M	SD	M	SD	M	SD	M	SD	M	SD	M	SD	M	SD	M	SD	M	SD
I	157.14	0.33	157.15	0.05	156.77	1.01	147.20	1.03	154.44	1.32	155.12	0.25	150.40	5.69	155.88	0.23	158.72	0.80	161.87	0.92
EHG	65.66	0.22	71.02	0.50	67.71	0.05	72.77	0.50	75.57	0.48	72.09	0.68	73.07	0.01	72.78	0.18	77.97	0.23	78.93	1.39
EHA	456.44	0.50	430.40	0.49	454.34	0.95	346.89	0.05	348.05	2.25	333.66	0.95	316.21	0.30	278.67	1.36	247.97	0.73	231.46	0.72
F	1.2 × 10 ⁶ ***		8.5 × 10 ⁵ ***		2.6 × 10 ⁵ ***		1.8 × 10 ⁵ ***		33,592 ***		1.5 × 10 ⁵ ***		5694 ***		66,589 ***		70,420 ***		21,167 ***	
Vertical	Week 1		Week 2		Week 3		Week 4		Week 5		Week 6		Week 7		Week 8		Week 9		Week 10	
	M	SD	M	SD	M	SD	M	SD	M	SD	M	SD	M	SD	M	SD	M	SD	M	SD
I	147.01	0.35	130.43	1.55	144.59	0.66	157.14	0.33	157.15	0.05	156.77	1.01	147.20	1.03	154.44	1.32	155.12	0.25	150.40	5.69
EVG	117.16	0.12	105.71	1.41	97.71	0.17	99.49	0.22	100.91	0.35	99.46	0.35	109.39	0.23	102.35	0.02	101.71	0.16	106.19	0.52
EVA	420.91	0.76	397.72	1.07	467.92	0.08	285.76	0.75	300.24	2.20	262.75	0.35	212.26	0.73	205.14	0.36	172.84	1.40	177.46	0.08
F	4.8 × 10 ⁵ ***		56,969 ***		1.0 × 10 ⁶ ***		1.5 × 10 ⁵ ***		24,450 ***		65,361 ***		19,651 ***		16,878 ***		834 ***		475 ***	
	Week 11		Week 12		Week 13		Week 14		Week 15		Week 16		Week 17		Week 18		Week 19		Week 20	
	M	SD	M	SD	M	SD	M	SD	M	SD	M	SD	M	SD	M	SD	M	SD	M	SD
I	155.88	0.23	158.72	0.80	161.87	0.92	162.14	1.29	163.46	0.07	165.54	0.07	165.69	1.36	167.97	6.78	158.57	0.68	152.02	1.29
EVG	109.20	0.12	112.78	0.62	114.80	1.09	114.26	0.06	119.18	0.02	105.69	0.70	109.77	2.08	113.22	0.10	130.15	1.35	136.09	4.85
EVA	165.00	0.13	166.03	0.04	156.35	0.71	179.15	0.73	133.01	0.02	137.80	0.67	134.77	4.19	126.73	0.65	134.71	0.07	144.92	0.02
F	1.3 × 10 ⁵ ***		9676 ***		3126 ***		6195 ***		9.5 × 10 ⁵ ***		11,418 ***		396 ***		210 ***		1213 ***		30.4 ***	

Note(s): F values followed by ***, ** and * indicate significant differences at $p = 0.001$, 0.01 and 0.05 . F values followed by ns indicates no significant differences. In the columns, mean values followed by a letter in common are statistically equal to $p = 0.05$.

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Table 7. Mean value (M) and standard deviation (SD) of carbonates (mg L⁻¹) in horizontal and vertical flow bioreactors.

Horizontal	Week 1		Week 2		Week 3		Week 4		Week 5		Week 6		Week 7		Week 8		Week 9		Week 10	
	M	SD	M	SD	M	SD	M	SD	M	SD	M	SD	M	SD	M	SD	M	SD	M	SD
I	1.94	0.1377	3.47	0.3173	3.00	0.0102	2.46	0.0018	2.75	2.7481	2.80	0.0596	2.05	0.0008	2.06	0.0049	1.87	0.0718	1.74	0.0311
EHG	1.10	0.3475	1.11	0.0092	1.04	0.0162	0.99	0.0283	1.11	0.0505	1.44	0.1141	0.45	0.5160	0.87	0.0012	0.91	0.0182	1.07	0.0108
EHA	0.01	0.0001	2.01	0.0544	2.48	0.0015	9.53	0.2380	17.03	0.2505	3.97	0.0550	10.61	0.1324	6.72	0.1672	6.92	0.1765	8.35	0.1918
F	81.2 ***		163 ***		33,501 ***		4358 ***		8307 ***		983 ***		1262 ***		4098 ***		3416 ***		5128 ***	
	Week 11		Week 12		Week 13		Week 14		Week 15		Week 16		Week 17		Week 18		Week 19		Week 20	
	M	SD	M	SD	M	SD	M	SD	M	SD	M	SD	M	SD	M	SD	M	SD	M	SD
I	2.25	0.0646	2.97	0.2359	2.96	0.0190	3.05	0.0214	2.78	0.0239	3.17	0.0371	2.71	0.1027	3.12	0.0368	3.10	0.1080	2.92	0.0166
EHG	0.98	0.0295	1.05	0.0065	0.85	0.0107	1.13	0.0228	1.17	0.0230	1.04	0.0237	0.97	0.0127	0.83	0.0020	1.05	0.0171	1.08	0.0097
EHA	4.52	0.1152	4.36	0.1110	5.00	0.1887	3.81	0.0501	3.29	0.0663	3.54	0.1042	3.99	0.0569	2.92	0.0531	2.66	0.0275	3.28	0.0333
F	2105 ***		488 ***		1426 ***		6567 ***		2676 ***		1705 ***		1985 ***		4625 ***		1097 ***		11,286 ***	
Vertical	Week 1		Week 2		Week 3		Week 4		Week 5		Week 6		Week 7		Week 8		Week 9		Week 10	
	M	SD	M	SD	M	SD	M	SD	M	SD	M	SD	M	SD	M	SD	M	SD	M	SD
I	2.06	0.0050	1.87	0.0718	1.74	0.0311	2.25	0.0646	2.97	0.2359	2.96	0.0190	3.05	0.0214	2.78	0.0239	3.17	0.0371	2.71	0.1027
EVG	1.16	0.0010	1.22	0.0001	1.16	0.0290	1.38	0.0214	1.19	0.0199	1.42	0.0050	1.33	0.0383	1.29	0.0169	1.17	0.0174	1.52	0.0329
EVA	3.76	0.0432	1.68	0.0402	2.86	0.0755	1.49	0.0356	3.30	0.1074	2.10	0.1363	1.17	0.0426	0.85	0.0211	1.00	0.0052	1.23	0.0158
F	11,045 ***		200 ***		1186 ***		462 ***		230 ***		375 ***		3466 ***		9507 ***		10,292 ***		622 ***	
	Week 11		Week 12		Week 13		Week 14		Week 15		Week 16		Week 17		Week 18		Week 19		Week 20	
	M	SD	M	SD	M	SD	M	SD	M	SD	M	SD	M	SD	M	SD	M	SD	M	SD
I	3.12	0.0368	3.10	0.1088	2.92	0.0166	2.89	0.0614	2.75	0.0719	2.72	0.0712	2.72	0.0223	2.83	0.1141	5.32	0.0229	5.16	0.1125
EVG	1.80	0.0458	1.33 a	0.0250	1.64 a	0.3716	1.60	0.0417	1.61	0.0211	1.22	0.0081	0.61	0.0279	2.57	0.0000	2.40	0.0250	2.29	0.0816
EVA	1.23	0.0158	1.32 a	0.0531	1.93 a	0.0169	2.18	0.0088	1.50	0.0197	1.82	0.0331	1.91	0.0340	2.13	0.0676	2.66	0.0000	1.42	0.0187
F	3040 ***		836 ***		39.0 ***		897 ***		963 ***		1108 ***		5597 ***		83.7 ***		27,339 ***		2342 ***	

Note(s): F values followed by ***, ** and * indicate significant differences at $p = 0.001, 0.01$ and 0.05 . F values followed by ns indicates no significant differences. In the columns, mean values followed by a letter in common are statistically equal to $p = 0.05$.

Table 8. Mean value (M) and standard deviation (SD) of total nitrogen (mg L⁻¹) in horizontal and vertical flow bioreactors.

Horizontal	Week 1		Week 2		Week 3		Week 4		Week 5		Week 6		Week 7		Week 8		Week 9		Week 10	
	M	SD	M	SD	M	SD	M	SD	M	SD	M	SD	M	SD	M	SD	M	SD	M	SD
I	12	0.82	5.5	2.89	13.5 a	1.73	12.5	9.81	22.5 a	1.73	16 a	5.77	12	4.62	14.5	1.73	12.5	1.73	18.5	8.66
EHG	8.5	6.35	5.5	4.04	1.5	0.58	5.5	6.35	1 b	1.15	5 b	5.77	7.5	6.35	10.5	7.51	4	4.62	13.5	4.04
EHA	12	5.77	11	3.46	14 a	5.77	7.5	1.73	17 c	2.31	7.5 ab	2.89	12.5	6.35	20	8.08	13	6.93	14	9.24
F	0.66 ns		3.3 ns		16.4 ***		1.12 ns		155 ***		5.32 *		0.89 ns		2.19 ns		4.24 ns		3.59 ns	
	Week 11		Week 12		Week 13		Week 14		Week 15		Week 16		Week 17		Week 18		Week 19		Week 20	
	M	SD	M	SD	M	SD	M	SD	M	SD	M	SD	M	SD	M	SD	M	SD	M	SD
I	21.5	4.04	9	1.15	29 a	12.70	17.5	1.73	16.5 ab	1.73	14.5 a	2.89	18.5	2.89	16 a	2.31	16.5 a	4.04	9.5 a	1.73
EHG	12 a	3.46	7.5	2.89	5 b	4.62	13	3.46	22.5 a	5.20	30	5.77	25.5	14.43	15 a	1.15	15 a	4.62	13 b	0.00
EHA	12 a	3.46	16.5	10.97	12 ab	13.86	8.5	9.81	13 b	3.46	12.5 a	0.58	8	5.77	0.5	0.58	6.5	0.58	0.00 c	0.00
F	8.95 **		2.15 ns		4.89 *		2.18 ns		6.60 *		26.2 ***		3.72 ns		129 ***		9.18 **		181 ***	
Vertical	Week 1		Week 2		Week 3		Week 4		Week 5		Week 6		Week 7		Week 8		Week 9		Week 10	
	M	SD	M	SD	M	SD	M	SD	M	SD	M	SD	M	SD	M	SD	M	SD	M	SD
I	14.5	1.73	12.5	1.73	18.5	8.66	21.5	4.04	9 a	1.15	29	12.70	17.5 a	1.73	16.5 a	1.73	14.5 ab	2.89	18.5	2.89
EVG	9.5	5.20	7.5	0.58	17.5	2.89	13.5 a	2.89	10.5 a	0.58	14	13.86	17.5 a	4.04	24 b	3.46	19 a	3.37	12.75	4.50
EVA	8	4.62	6.5	6.35	11	3.46	8.5 a	0.58	13.5	1.73	7	6.93	5.5	2.89	4 c	4.62	8.5 b	5.20	9	6.93
F	2.71 ns		2.84 ns		2.09 ns		20.6 ***		13.5 ***		3.78 ns		20.8 ***		33.7 ***		7.14 *		3.59 ns	
	Week 11		Week 12		Week 13		Week 14		Week 15		Week 16		Week 17		Week 18		Week 19		Week 20	
	M	SD	M	SD	M	SD	M	SD	M	SD	M	SD	M	SD	M	SD	M	SD	M	SD
I	16 a	2.31	16.5	4.04	9.5 a	1.73	11.5 a	1.73	43.5	7.51	34 a	3.46	29.5	9.81	19.5 a	0.58	16.5 a	7.51	34.5 a	0.58
EVG	14 a	6.63	16	1.15	11 a	1.15	30.5 b	1.73	25.5	12.12	15	5.77	15.5 a	4.04	15.5 a	1.73	34 b	11.55	22	5.77
EVA	2	2.31	13.5	0.58	5	2.31	18.75 c	0.50	27.5	8.66	36.5 a	10.97	9.5 a	1.73	11	3.46	22 ab	5.77	43 a	6.93
F	12.6 ***		1.72 ns		12.1 **		177 ***		4.19 ns		10.0 **		10.9 **		14.1 **		4.31 ns		16.4 ***	

Note(s): F values followed by ***, ** and * indicate significant differences at $p = 0.001, 0.01$ and 0.05 . F values followed by ns indicates no significant differences. In the columns, mean values followed by a letter in common are statistically equal to $p = 0.05$.

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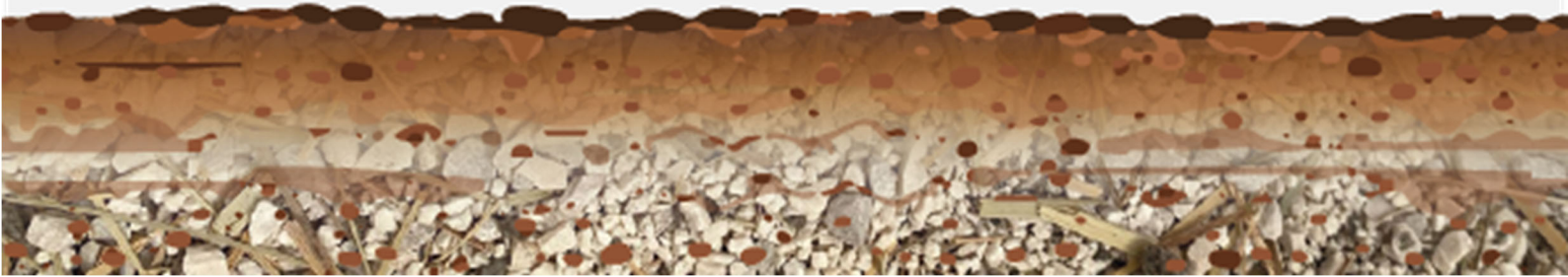
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CAPÍTULO 10: DISCUSIÓN



10.1 Discusión

El propósito general de esta disertación es contribuir a aumentar el conocimiento sobre las propiedades y riesgos del uso de residuos, para asentar las bases de cómo pueden ser utilizados para la formulación de tecnosuelos, y potenciar la producción de servicios ambientales, también llamados ecosistémicos, como son el aporte de los nutrientes requeridos para asegurar la producción agrícola a la par que la salud del entorno agrario. De forma general, los resultados obtenidos (**Capítulos 4 – 9**) indican que los tecnosuelos pueden ser un gran aliado para llevar a buen término las estrategias del *European Green Deal*. Los artículos (**Capítulos 4 – 9**), como se ha indicado, se transcriben manteniendo el formato con el que fueron publicados. Llegados a este punto, discutiremos los hallazgos más representativos que se han evidenciado.

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Los suelos degradados ven limitada su capacidad de proveer servicios ecosistémicos (UN-HABITAT y WHO, 2020), como la producción de alimentos, la descontaminación, y la regulación de los ciclos hidrológicos, entre otros (Munafò *et al.*, 2013; Brevik *et al.*, 2018). La mayoría de estos servicios ecosistémicos se desarrollan directamente sobre el suelo y están influenciados por el estado funcional de sus propiedades físicas, químicas y biológicas. Las guías y directrices dadas por EC (2020), consideran que un suelo sano es aquel que muestra una capacidad continuada de proveer servicios ecosistémicos. Definir este concepto no es sencillo, y algunos autores consideran que requiere mayor discusión (Ling y Zhang, 2019). Para contribuir a ello, aportamos la siguiente definición: la salud del suelo está asociada con su habilidad para auspiciar la salud humana (**Capítulo 4**). Consideración que concuerda con el relevante papel que desempeñan los suelos en salvaguardar la salud de las personas (Montanarella y Panagos, 2021).

A pesar de que la modificación del suelo debido a las actividades humanas es contemporánea a nuestra presencia en la Tierra, el uso inicial del término *technosols* en referencias científicas (Rossiter y Burghardt, 2003; Lehman, 2006) y su inclusión en la clasificación WRB (IUSS, 2006), es bastante reciente. Sin embargo, desde 2005 a 2020, los tecnosuelos suscitan un mayor interés para la comunidad científica, ya que se aprecia una tendencia creciente tanto del número de publicaciones como de sus citas, principalmente en el período comprendido entre el 2013 y 2020 (**Capítulo 4**).

Aunque los suelos construidos artificialmente, o mejorados y transformados técnicamente, son incluidos expresamente en la definición de *Technosols* como grupo de referencia de suelos del sistema WRB (IUSS, 2015), independientemente de su uso (agrícola, urbano, etc.), la interpretación de esta definición puede conllevar cierta discusión. Esta tesis trata de aclarar este aspecto, y tras recopilar varias definiciones previamente publicadas (**Capítulo 4**), observamos que, aunque la consideración de *Technosols* en WRB engloba suelos que han sido modificados inintencionadamente por los humanos (Santos *et al.*, 2016), también se utiliza para los suelos técnicamente diseñados para una misión específica (Arranz-González, 2011; Rivas-Pérez *et al.*, 2016, Deeb *et al.*, 2020). Contribuyendo a esta discusión aportamos una nueva definición funcional de *technosols* o tecnosuelos, por la que consideramos que son suelos

diseñados con la intención de proveer los mismos o nuevos servicios ecosistémicos que los suelos naturales, para asegurar la salud de las personas y de los ecosistemas, así como la mejora de la productividad o la mitigación de los efectos negativos del cambio climático (**Capítulo 4**).

La descripción de los *technosols*, en la que su funcionalidad debe ser contrastada, se alcanza tras comprobar que la mayoría de las referencias consultadas elaboran tecnosuelos para estudiar su viabilidad para el crecimiento y desarrollo de las plantas (Fourvel *et al.*, 2019; Barredo *et al.*, 2020; Ugolini *et al.*, 2020), para almacenar más carbono orgánico que los suelos (Rees *et al.*, 2019), para la gestión del agua y mejora de la biodiversidad (González-Méndez y Chávez-García, 2020), así como para contrarrestar los efectos del cambio climático (Macías y Camps Arbestain, 2010), entre otras. De hecho, pueden llegar a desarrollar posteriores procesos pedogenéticos, mineralizar la materia orgánica, formar agregados, así como funcionar hidro-estructuralmente tal y como lo hacen los suelos naturales (Seré *et al.*, 2010; Deeb *et al.*, 2016; Deeb *et al.*, 2017; Shchepeleva *et al.*, 2017; Shchepeleva *et al.*, 2019).

Los tecnosuelos han sido muy estudiados en el ámbito de la actividad minera, para la recuperación de espacios degradados por estas actuaciones (**Capítulo 4**). Los objetivos perseguidos se enmarcan tanto para conocer la evolución de los suelos afectados por actividades mineras como para la formulación de suelos técnicos que suplan deficiencias o favorezcan la descontaminación, empleando principalmente residuos de la propia actividad extractiva (Moreno-Barriga *et al.*, 2017; Zornoza *et al.*, 2017; Santos *et al.*, 2019). El segundo uso que suscita mayor interés es el que implica su incorporación en áreas urbanas para ampliar o mejorar las zonas verdes, utilizando residuos municipales (Barredo *et al.*, 2020; Deeb *et al.*, 2020; Ugolini *et al.*, 2020). Curiosamente, la funcionalidad de los tecnosuelos elaborados con fines agrícolas ha sido minoritariamente estudiada (**Capítulo 4**).

Por otra parte, debido a la importancia de asegurar la existencia de suelo agrícola, que pueda atender la demanda de alimentos de la creciente población mundial (**Capítulo 4 y 5**), la Unión Europea insta a reducir la ocupación de espacio por sellado del

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suelo, reduciendo la tasa de ocupación y recuperando suelos sellados, por ejemplo, de antiguas áreas industriales abandonadas (EC, 2021a).

La recuperación de suelos implica volver a desarrollar terrenos que habían sido previamente afectados para un fin económico determinado, con la mejora ecológica para su uso como zona verde, por ejemplo, y la naturalización mediante la eliminación de estructuras y superficies sellantes (EEA, 2016). Sin embargo, estos suelos también deben recuperar su funcionalidad para la provisión de servicios ambientales (**Capítulo 5**). Algunos autores consideran que el uso de suelos recuperados para zonas verdes, que puedan ser utilizados para la agricultura urbana, contribuye a incrementar los servicios ecosistémicos, sin embargo, en Europa esta práctica es minoritaria (EC, 2012; Tobias *et al.*, 2018).

Esto puede ser debido a diversos factores que limitan el futuro uso de los suelos recuperados, como el tamaño de la zona a recuperar (entre 1 y 20 hectáreas es adecuado para zona verde), el estado del suelo (grado de contaminación, fertilidad), y el uso previo, si estaba sellado o no (Song *et al.*, 2019; Pecina *et al.*, 2021; Pytel *et al.*, 2021). Aspectos que están directamente relacionados con el coste económico de la recuperación, ya que los suelos contaminados o sellados conllevan mayores costes de remediación al tener que eliminar la capa sellante, excavar, retirar o descontaminar el suelo y rellenar (**Capítulo 5**). En consecuencia, el nuevo uso de un suelo recuperado suele coincidir con el inicial (Pytel *et al.*, 2021). Sin embargo, si finalmente se decide asumir el coste económico de la recuperación de un suelo, que se encuentre altamente contaminado o que haya albergado actividades con alto riesgo de contaminación, para su reconversión a zonas verdes, residenciales o a zonas agrícolas, la seguridad de las personas y de los ecosistemas debe quedar garantizada. En este sentido, algunos autores sugieren que esta reconversión no se produzca en suelos altamente contaminados, pero de ser así, deben ser previamente remediados o recubiertos con una capa de suelo en buen estado (mínimo 50 cm) (Deeb *et al.*, 2020; Pecina *et al.*, 2021; Sobocká *et al.*, 2021).

Es indudable pues, que durante el proceso de recuperación de los suelos sellados se requiere el aporte de nuevo suelo con una adecuada calidad. Los tecnosuelos formulados con residuos podrían ser una opción válida para recuperar los servicios ecosistémicos perdidos (Lal *et al.*, 2021), formulando nuevos suelos sin necesidad de extraer suelos naturales para tal función, como la de generar un suelo con la calidad suficiente para recuperar las funciones edáficas (**Capítulo 5**). Llegados a este punto, hay cierta discusión de si los suelos a los que se les retira la capa sellante pueden llegar a ser funcionales. Algunos autores consideran que si es posible tanto añadiendo nuevo suelo como sin añadirlo ya que por sí mismos pueden recuperar su calidad y fertilidad (Tobias *et al.*, 2018; Maienza *et al.*, 2021). Por lo tanto, es inevitable preguntarse si estos suelos recuperados podrían llegar a ser funcionales para la provisión de alimentos. Renella (2020) concluye que los suelos a los que se les retira la capa sellante, sin ningún tratamiento posterior, pueden por ellos mismos mejorar su fertilidad física y química. Hasta tal punto, que pueden aumentar la biomasa microbiana y la actividad bioquímica superando a la de los suelos agrícolas. En este caso, el tiempo para alcanzar un estado satisfactorio puede llegar a ser un factor limitante porque se requiera una remediación previa en un plazo corto de tiempo.

Además, para que los suelos puedan ser agrícolamente eficientes, requieren del aporte de nutrientes, disponibles en forma soluble en la disolución del suelo, para ser absorbidos por las plantas. Tal y como se menciona en la Introducción, las diversas estrategias que emanan del Pacto Verde Europeo o *European Green Deal* (EC, 2020c; EC, 2020d; EC, 2021a) así como las prácticas de agricultura ecológica, abogan por la reducción de la pérdida de nutrientes potenciando el uso de residuos orgánicos como fertilizantes. Los residuos mediante procesos de transformación en el medio edáfico pueden aportar nutrientes; sin embargo, poder ajustar la curva de necesidad nutricional de los cultivos con los aportes nutricionales de los residuos, es complicado. Foereid (2019) considera que no todos los nutrientes presentes en los fertilizantes y productos utilizados como abonos y enmiendas del suelo de origen orgánico están inmediatamente disponibles para las plantas, ni tampoco cuando podrían estarlo (**Capítulos 6 y 7**). Además, la contribución inicial de elementos solubles desde los

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residuos orgánicos ha sido escasamente estudiada, así como los posibles riesgos por la presencia de nutrientes que sean metales pesados (Parr y Colacicco, 1987; Alloway, 2013; Jamroz *et al.*, 2020).

Como aproximación necesaria para conocer el potencial de los residuos para formular tecnosuelos, llevamos a cabo la caracterización fisicoquímica (**Capítulo 6**) de los residuos de poda de almendro, turba, poda de olivo, acículas de pino, hoja de palmera, compost de lodos de depuradora y poda de vid. Los resultados obtenidos permiten indicar que poseen densidades aparentes bajas (entre 0,23 y 0,40 g cm⁻³), presentan porcentajes de materia orgánica muy elevados (entre 90 y 94%, excepto el compost de lodo de depuradora que tiene un 59%), así como un contenido en humedad de entre 6,3 y 9,3 (excepto el compost de lodos de depuradora que alcanza el 26%). El pH de los residuos orgánicos estudiados en el **Capítulo 6** es ácido, entre 4,66 y 5,94, excepto el compost de lodo de depuradora que obtiene un pH de 7,34. Además, presentan valores considerables de conductividad eléctrica, entre 665 y 4358 $\mu\text{S cm}^{-1}$. Sobre la base de investigaciones precedentes, la incorporación de los residuos estudiados en el suelo contribuiría a reducir la densidad aparente del suelo, a aumentar el contenido en materia orgánica y humedad, así como influiría en el pH (Repullo *et al.*, 2012; Almendro-Candel *et al.*, 2018; Oueriemmi *et al.*, 2021), incluso en mayor medida que los fertilizantes inorgánicos (Golabi *et al.*, 2017). Por ende, incrementan el secuestro de carbono, participan el ciclo de los nutrientes y su biodisponibilidad en el suelo (Papafilippaki *et al.*, 2015; Gómez-Muñoz *et al.*, 2016; Golabi *et al.*, 2017; Oueriemmi *et al.*, 2021). Cabe mencionar que la conductividad eléctrica de los residuos, se debe tener presente para su adecuada elección, la poda de almendro y las acículas de pino son los que muestran menor conductividad eléctrica, por tanto, menor aporte de sales al menos inicialmente.

Además, el estudio de su composición elemental (**Capítulo 6**) indica que poseen grandes cantidades de nutrientes (Na, K, Ca, Mg, Fe, Mn, Cu y Zn). Ordenando los residuos sobre la base de la cantidad total de nutrientes que poseen, obtenemos la siguiente secuencia: Compost de lodos de depuradora > poda de olivo > acícula de pino > hoja de palmera > sarmiento > poda de almendro > turba. Curiosamente, todos los

residuos estudiados tienen más nutrientes en su composición elemental en materia seca que la turba comercial utilizada habitualmente como sustrato vegetal. Los nutrientes con mayor concentración en la composición elemental de los residuos son: Ca > K > Fe > Mg > Na > Zn > Mn > Cu, siendo el orden esperado sobre la base de la cantidad requerida de dichos nutrientes por las plantas. El compost de lodo de depuradora es el residuo que presenta mayor cantidad de Ca ($64.245 \text{ mg kg}^{-1}$) seguido de las acículas de pino ($14.059 \text{ mg kg}^{-1}$). La poda de olivo muestra la mayor concentración de K (6.889 mg kg^{-1}) seguido de la hoja de palmera (6.858 mg kg^{-1}) y el compost la mayor de Fe ($18.989 \text{ mg kg}^{-1}$) y de Mg (5.815 mg kg^{-1}).

Para determinar si estos nutrientes pueden estar rápidamente disponibles para las plantas en la solución acuosa del suelo, estudiamos su presencia en el extracto acuoso de cada residuo (**Capítulo 6**). La relevancia de los residuos orgánicos, de acuerdo a la cantidad total de nutrientes obtenidos en el extracto acuoso es: hoja de palmera > poda de olivo > sarmiento > compost de lodo de depuradora > turba > acícula de pino > poda de almendro. A su vez, los nutrientes más solubles son K > Ca > Mg > Na > Fe > Zn > Mn > Cu. En la hoja de palmera el que es más soluble es el K y aporta (4.892 mg kg^{-1}), seguido de la poda de olivo (4.688 mg kg^{-1}). En cuanto al Ca, se detecta en mayor cantidad en el extracto acuoso de la hoja de palmera (4.330 mg kg^{-1}) con mucha diferencia respecto a los demás residuos cuyo contenido en Ca soluble se encuentra entre 963 y 353 mg kg^{-1} . Lo mismo ocurre con el Mg soluble procedente de la poda de palmera (1.662 mg kg^{-1}). No obstante, la hoja de palmera también muestra la mayor cantidad de Na soluble (807 mg kg^{-1}) de entre todos los residuos estudiados.

Por lo tanto, comparando los resultados de las concentraciones de nutrientes de cada residuo en su composición elemental frente al extracto acuoso, consideramos que no hay una relación directa (**Capítulo 6**). Es decir, la presencia de los nutrientes en la composición elemental no indica que pueden estar en el extracto acuoso en la misma proporción, no mantienen el mismo orden en función de la composición total, de la cantidad presente en el residuo. Esta circunstancia es sumamente evidente en el caso del compost de lodo de depuradora, debido a que durante el proceso de compostaje se han lavado los nutrientes más solubles (Foereid, 2019; Jamroz *et al.*, 2020). No obstante,

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la aplicación de este residuo podría ser interesante para el suministro de nutrientes a largo plazo.

Sin embargo, en los residuos de poda, esta diferencia en los contenidos de nutrientes se observa en menor medida. Las acículas de pino son el residuo de procedencia vegetal con mayor variación y podría ser debido a un mayor contenido de materia orgánica muy estable, ya que las acículas de pino pueden llegar a tener un 60% de materia lignificada (Rovira y Vallejo, 2002). Esta consideración también se podría aplicar a la hoja de palmera (66,3% celulosa + hemicelulosa y 22,53% de lignina según Ghori *et al.*, 2018). Aunque siendo el residuo con mayor cantidad de nutrientes rápidamente solubles la naturaleza hidrofílica de sus fibras podría ser un factor determinante (Ghori *et al.*, 2018).

Para ampliar el conocimiento al respecto, esta tesis aporta el cálculo y análisis del índice de solubilidad de cada nutriente respecto de la cantidad en la composición elemental (**Capítulo 6**). Así pues, la hoja de palmera es el residuo cuyos nutrientes obtienen los mayores índices de solubilidad: 74% Mg, 73% Na, 71% K, 67% Zn, 66% Mn, 63% Ca, 21% Cu y 2% Fe. Por añadidura, los índices de solubilidad obtenidos del Ca, Fe y Zn captan nuestra atención. El Ca es el nutriente con mayor cantidad en la composición elemental del total de los residuos estudiados, sin embargo, en el extracto acuoso pasa a la segunda posición en la mayoría de los residuos, y su índice de solubilidad es de los más bajos (entre 1 y 14%) en todos los residuos (excepto en la hoja de palmera, como se ha comentado previamente). Esto podría ser debido al papel estructural del Ca como constituyente de las paredes celulares (Cavalli *et al.*, 2018). La misma tendencia se observa para el Fe, siendo el nutriente con menores índices de solubilidad en todos los residuos (entre 0 y 8%). Los resultados más llamativos son los obtenidos por el Zn que, a pesar de ser un micronutriente, alcanza valores muy altos de su índice de solubilidad en todos los residuos de procedencia vegetal (entre 35 y 90%). Algunos autores consideran que el Zn es poco soluble y está condicionado por el pH (Oliver y Gregory, 2015). La poda de almendro es el residuo con el menor pH (4,66) de entre los estudiados y el que mayor índice de solubilidad obtiene (90%). Esta relación entre el pH y la solubilidad del Zn se comprueba con las matrices de correlación (**Capítulo 6**),

obteniendo una asociación significativamente alta con el contenido de Zn en el extracto acuoso.

El nitrógeno es el nutriente más crítico para las plantas, en términos de la cantidad requerida y su potencial impacto en la salud de los ecosistemas. Por eso le dedicamos un artículo, con la intención de estudiar la mineralización del nitrógeno procedente de los residuos de poda (**Capítulo 7**). Las estrategias de la Unión Europea (EC, 2019; EC, 2020c) tratan de reducir las pérdidas de nutrientes en un 50%, pero los cultivos toman solo entre el 40 y 50% del nitrógeno disponible, tanto si procede de fuentes orgánicas como inorgánicas (Mosier *et al.*, 2001). Por lo que la sincronización entre la necesidad de nitrógeno de los cultivos y los aportes de nitrógeno es vital y comienza por conocer la capacidad de mineralización neta del nitrógeno de cada residuo orgánico que se aplique al suelo y en las condiciones ambientales concretas del medio, así como según el sistema de manejo y gestión del suelo.

Las plantas toman el nitrógeno del suelo cuando se encuentra en sus formas minerales (excepto las leguminosas), por lo que la disponibilidad del nitrógeno procedente de residuos orgánicos dependerá de su presencia en formas inorgánicas (amonio y nitratos, principalmente) o de los procesos de mineralización de la materia orgánica por parte de la biomasa microbiana del suelo (Jat *et al.*, 2018). Uno de los principales indicadores del potencial de mineralización de la materia orgánica es la relación C/N, y cuando se sitúa entre 20-30 se favorece la mineralización ya que se potencia el metabolismo aeróbico y anaeróbico (Thuriès *et al.*, 2001; Puyuelo *et al.*, 2011; Repullo *et al.*, 2012; Gomez-Muñoz *et al.*, 2016).

Así pues, calculamos la relación C/N de los siguientes residuos orgánicos: restos de poda de almendro, turba, paja de heno, poda de olivo, piel de granada, acícula de pino, hoja de palmera, compost de lodo de depuradora y restos de poda de vid (**Capítulo 7**). Los residuos de poda y la turba contienen los menores valores de nitrógeno, entre 4,3 g kg⁻¹ (materia seca, m.s) de la paja y 9,3 g kg⁻¹ (m.s) de la hoja de palmera. Por el contrario, el compost es el que dispone de mayor cantidad de nitrógeno (22,6 g kg⁻¹ m.s). De tal forma, la relación C/N de los residuos de poda y recolección se sitúa entre 44 (hoja de

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palmera) y 99 (paja de heno). Al obtener valores de C/N altos, para que se produzca la mineralización se requiere un aporte adicional de nitrógeno, que en los sistemas agrícolas procede del nitrógeno mineralizado que se encuentra en el suelo o por aporte de fertilizantes. En cualquier caso, las bacterias preferirán el nitrógeno inorgánico ya disponible en el suelo, que lo inmovilizarán para atender sus necesidades metabólicas, entrando en competencia por dicho nutriente con las plantas. Este descenso del contenido en nitrógeno disponible en el suelo puede derivar en carencias nutricionales para los cultivos. Así pues, la mineralización bacteriana de la materia orgánica queda relegada hasta encontrar nuevas fuentes de nitrógeno, por ejemplo, con el aporte de fertilizantes. En cambio, el compost es el único residuo de entre los estudiados que tiene una relación C/N baja (C/N = 12), así que se podría activar la mineralización, pero puede ser rápida con el consiguiente riesgo de lixiviación o arrastre de los nutrientes.

Además del riesgo de inmovilización o lixiviación y pérdida del nitrógeno, y aunque los beneficios ambientales de la aplicación de residuos orgánicos al suelo son considerables y han sido comentados anteriormente, esta práctica también puede entrañar otros riesgos ambientales (Oliver y Gregory, 2015; Deeb *et al.*, 2020; FAO, 2022b). A priori, los residuos de poda son residuos con reducido riesgo de toxicidad, debido a la presencia de sustancias contaminantes o patógenos. No obstante, un exceso en el contenido de nutrientes, principalmente de los considerados también como metales pesados, puede implicar un desequilibrio en el suelo tras su aplicación que afectaría al desarrollo de los cultivos, así como a la salud de los ecosistemas y de las personas (Guerra *et al.*, 2011; Jivan y Ajay, 2011; FAO 2022b).

En el **Capítulo 8**, ampliamos la investigación con dos residuos más (paja de heno y piel de granada) y analizamos la concentración de otros metales pesados (Cd, Cr, Ni y Pb) en todos los residuos.

El contenido de metales pesados en los residuos de poda o de recolección agrícola, está principalmente asociado a la adición previa de fertilizantes en los suelos donde fueron cultivados y al contenido basal de dichos contaminantes en los suelos (bien sea de origen natural o por incorporaciones previas). Los resultados alcanzados (**Capítulo 8**)

indican que ninguno de los residuos de poda o de recolección agrícola, muestra concentraciones de Cd, Cr, Ni y Pb por encima del límite de detección analítico empleado (límite que está muy por debajo de los valores indicados como máximos permitidos por la legislación actual). Además, comparando las concentraciones de metales pesados en la composición elemental de los residuos de poda de almendro, paja de heno, poda de olivo, piel de granada, acícula de pino, hoja de palmera y poda de viñedos con los límites que establece la normativa para los sustratos de cultivo, enmiendas y fertilizantes (RD 865/2010; EU 2019/1009), ninguno sobrepasa dichos umbrales. Así pues, estos residuos orgánicos podrían ser una fuente extra de micronutrientes esenciales sin significar un riesgo en cuanto el aporte de elementos traza contaminante.

Por el contrario, el compost de lodo de depuradora es el residuo que presenta las mayores concentraciones de los metales estudiados (Cu: 79,7 mg kg⁻¹, Zn: 249,5 mg kg⁻¹, Cd: 0,686 mg kg⁻¹, Cr: 2,4 mg kg⁻¹, Ni: 6,2 mg kg⁻¹ y Pb: 10,8 mg kg⁻¹). Sin embargo, estos datos (**Capítulo 8**) son significativamente inferiores a los publicados por referencias previas (Alonso *et al.*, 2006; Milik *et al.*, 2017), ya que el contenido en metales pesados en las aguas residuales, y por ende en los fangos obtenidos de su depuración, depende del grado de actividad industrial desarrollado en cada localidad. A pesar de la presencia de metales pesados en el compost de lodo de depuradora, todas sus concentraciones se sitúan dentro del rango permitido por la legislación que regula la aplicación de lodos de depuradora en la agricultura (CD 86/278/EEC; RD 1310/1990).

De los datos obtenidos (**Capítulo 8**), se aprecian unos contenidos de Cd (0,629 mg kg⁻¹) y Cr (2,8 mg kg⁻¹) en la turba comercial (en materia seca), que se utiliza como sustrato de jardinería. Su origen se debe a la posible presencia de metales pesados en las turberas, donde sus concentraciones pueden ser elevadas (Borgulat *et al.*, 2018; Sypalov *et al.*, 2020). El rango habitual de Cr en las turberas se encuentra entre 0,18 y 1,89 mg kg⁻¹ (Sypalov *et al.*, 2020), siendo inferior a nuestro resultado. En el caso de que todo el Cr fuera Cr(VI) habría que contemplar el límite de 2 mg kg⁻¹ m.s establecido en el reglamento EU 2019/1009 sobre productos fertilizantes. El resultado del Cd en la turba está próximo al valor límite estipulado para el Cd (máximo permitido 0,7 mg kg⁻¹ en el RD 865/2010 sobre sustratos de cultivo).

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En cuanto al extracto acuoso de los residuos estudiados (**Capítulo 8**), excepto para el compost de lodo de depuradora, los metales pesados Cd, Cr, Ni y Pb no muestran resultados por encima del límite de detección. En el extracto acuoso del compost de lodo de depuradora, que sí presentaba concentraciones de todos los metales pesados en su composición elemental por encima de los límites de detección, se ha obtenido solamente 0,38 mg kg⁻¹ de Pb soluble. En relación al índice de solubilidad, la tendencia es similar a la observada en el **Capítulo 6**, donde el Zn alcanza elevados índices de solubilidad para los residuos de poda, seguido del Cu. El índice de solubilidad del Pb en el compost de lodo de depuradora es bajo (4%).

Así pues, las aplicaciones de los residuos a los suelos estarán limitadas no solo por la concentración de nutrientes y metales pesados en su composición elemental y extracto acuoso, sino también por su concentración previa en los suelos donde se vayan a incorporar, limitando así la cantidad y la frecuencia de las aplicaciones de residuos. Tras consultar los umbrales de concentración de metales pesados en los suelos agrícolas (CD 86/278/EEC; RD 1310/1990; Van der Voet *et al.*, 2013), el compost de lodo de depuradora es el único residuo, de entre los estudiados, con una concentración de Cu y Zn en su composición elemental (en materia seca) a la que habría que prestar atención si se aplica en suelos ácidos para no superar los límites permitidos de concentración en el suelo (según el CD 86/278/EEC), ya que la acidez del suelo aumenta la solubilidad de los metales pesados y su absorción por las plantas (**Capítulo 8**).

Por lo tanto, calculamos la posible contribución en metales pesados al suelo con una aplicación de 30.000 kg ha⁻¹ de cada uno de los residuos y consideramos la frecuencia de aplicación para no incumplir los límites máximos estipulados por el RD 1310/1990. Aunque solo aplica al lodo de depuradora, tomaremos como referencia los valores límites para las cantidades anuales de metales pesados que se podrán introducir en los suelos basándose en una media de diez años (Cu: 12, Zn: 30, Cd: 0.15, Cr: 3, Ni: 3 y Pb: 15 kg ha⁻¹ año), al no disponer de un marco normativo armonizado para los demás residuos (**Capítulo 8**).

La concentración de los metales pesados en la composición elemental es el factor limitante para su aplicación en el suelo. El compost de lodo de depuradora, en nuestro caso, si se aplica cuatro veces al año, supera los límites en el caso de Zn y Cr. Siguiendo con lo comentado para los valores límites para las cantidades anuales de metales pesados que se podrán introducir en los suelos basándose en una media de diez años, la concentración de Cd en la turba no permite que se aplique más de siete veces al año. En cuanto a los residuos de poda o de recolección agrícola (excepto la piel de granada, donde la concentración de Zn no permite su aplicación más de ocho veces al año) se requieren entre 32 y 100 aplicaciones de 30.000 kg ha⁻¹ al año para superar los límites críticos de metales pesados, según el residuo escogido. Por lo tanto, hay residuos cuya aplicación no presenta restricciones en cuanto a los límites establecidos, sin embargo, para otros residuos conviene ser cauteloso.

Adicionalmente, calculamos la cantidad de residuo orgánico (considerando su humedad) que hay que aportar al campo para cubrir la demanda de nitrógeno de diversos cultivos (cereales, frutales, tubérculos, caña de azúcar, tomates y hortalizas) de acuerdo con las referencias bibliográficas (**Capítulo 7**). Los cultivos que más nitrógeno requieren para asegurar la producción agrícola son la caña de azúcar (200-300 kg ha⁻¹), las hortalizas (190 kg ha⁻¹) y los cereales (100-300 kg ha⁻¹), según indican diversos autores (Lloyd *et al.*, 1997; Furtado da Silva *et al.*, 2020; IFA, 2022). Así pues, para los cálculos consideramos el valor inferior, de estos intervalos, de la necesidad nutricional de cada uno de los cultivos. Wang *et al.* (2022), consideran que aplicar nitrógeno en cantidades superiores a 300 kg ha⁻¹ es excesivo, ya que conllevaría una reducción del nitrógeno disponible y de la actividad microbiana. Basados en las referencias bibliográficas, definimos dos posibles escenarios posibles de mineralización de la materia orgánica: 10% y 15% de su paso total en seco (Jat *et al.*, 2018), para un ciclo de cultivo (aproximadamente 6 meses), asumiendo que todo el nitrógeno se aporta únicamente desde los residuos orgánicos. Los resultados obtenidos para el escenario menos favorable de mineralización del nitrógeno (10%) muestran que se tienen que añadir, en peso de residuo húmedo, entre 240 y 530 tons ha⁻¹ de residuos de poda o recolección a cultivos de caña de azúcar, entre 230 y 490 tons ha⁻¹ de residuos de poda o recolección

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a cultivos de hortalizas y entre 120 y 260 tons ha⁻¹ de residuos de poda o recolección a los cultivos de cereales. En cuanto al compost de lodo de depuradora, es el residuo que se puede aplicar en menor cantidad, concretamente 120 tons ha⁻¹ para cubrir la demanda nutricional de nitrógeno de la caña de azúcar y de los vegetales, y alrededor de 60 tons ha⁻¹ para los cultivos de cereales.

Por el contrario, si comparamos con la cantidad de fertilizante comercial, por ejemplo, con urea con un contenido del 46% de nitrógeno, habría que añadir a los cultivos 435 kg ha⁻¹ para la caña de azúcar, 413 kg ha⁻¹ a las hortalizas y 217 kg ha⁻¹ a los cereales (**Capítulo 7**). Si consideramos 150 kg ha⁻¹ como el aporte óptimo de nitrógeno, observamos que se requiere añadir residuos de poda o de recolección entre 400 a 1,000 veces más que el fertilizante de urea.

Concluyendo, sobre la base de los retos logísticos y ambientales que implican la aplicación de tan elevadas cantidades de residuos orgánicos, y para asegurar la calidad y la producción agrícola, se propone combinar el abonado orgánico con el uso de fertilizantes sintetizados, ya que puede incrementar la disponibilidad de nitrógeno en el suelo al facilitar su mineralización (Parr y Colacicco, 1987; Chatzistathis *et al.*, 2021; Wang *et al.*, 2022).

Hasta ahora se han planteado las ventajas ambientales en entornos agrícolas y urbanos que pueden proveer los tecnosuelos elaborados a partir de residuos. Con la intención de ampliar el estudio a otros servicios ambientales desde un punto de vista experimental, se construyeron plantas piloto de tratamiento de aguas de riego que utilizan como material adsorbente residuos orgánicos e inorgánicos (**Capítulo 9**), como función que podrían realizar tecnosuelos basados en estos materiales. Se inspiran en el funcionamiento de las soluciones basadas en la naturaleza, como humedales artificiales o biorreactores dónde los suelos tienen un papel fundamental en la capacidad depuradora de las aguas. Estos sistemas de depuración plantean grandes ventajas frente a los tratamientos tradicionales, como son un reducido mantenimiento, bajos costes para su funcionamiento y una alta eficiencia depuradora. La reducción de la carga de nutrientes del agua de riego se realiza físicamente por adsorción gracias a los residuos

empleados, y bioquímicamente por el consumo de nutrientes por parte de la actividad biológica que se desarrolla intrínsecamente en los biorreactores.

Discutimos los resultados más relevantes obtenidos (**Capítulo 9**) tras analizar las propiedades fisicoquímicas del influente (I) y de los efluentes (E) tras su tratamiento con los biorreactores de flujo de agua horizontal: con adsorbente de grava (EHG) o con adsorbente de grava y poda de rama de almendro (EHA); o con flujo de agua vertical: con adsorbente de grava (EVG) o con adsorbente de grava y poda de rama de almendro (EVA). En todos los parámetros estudiados se pudo apreciar una reducción de la concentración semanal (excepto la de la DQO) en las aguas de riego tras ser tratadas con los biorreactores, si bien hay ciertas variaciones que procedemos a interpretar.

Comenzando con el pH del agua de riego todos los tratamientos consiguieron reducir su pH (**Capítulo 9**), donde el residuo orgánico desempeñó un importante papel. La acidificación del EHA durante las primeras semanas de muestreo (38,2% de reducción en la semana 1) fue posiblemente debida a la contribución de los componentes altamente solubles de la poda de rama de almendro, como son la materia orgánica disuelta y al metabolismo de los microorganismos anaeróbicos. De acuerdo con los resultados obtenidos en el **Capítulo 6**, el pH del extracto acuoso de la poda de rama de almendro tiene un pH de 4,66, lo que concuerda con los resultados obtenidos. Sin embargo, conforme pasaron las semanas el pH de EHA fue aumentando hasta obtener valores próximos a los de EHG en la semana 20. En los biorreactores verticales, la presencia de la poda de rama de almendro también facilitó la reducción del pH (alcanzado el mayor porcentaje de reducción (8,4%) en la semana 8), pero de forma más homogénea en el tiempo, lo que debe ser debido al tipo de biorreactor.

En cuanto a la CE (**Capítulo 9**), aunque en algunas semanas la conductividad eléctrica de los efluentes fue menor a la del influente (semana 2 y 3 en EHG y EHA; y semana 1, 4 y 20 del EVA), de forma general se apreció un aumento de la CE en todos los efluentes. Esto indica que los tratamientos utilizados tuvieron una baja eficiencia para la reducción de la salinidad.

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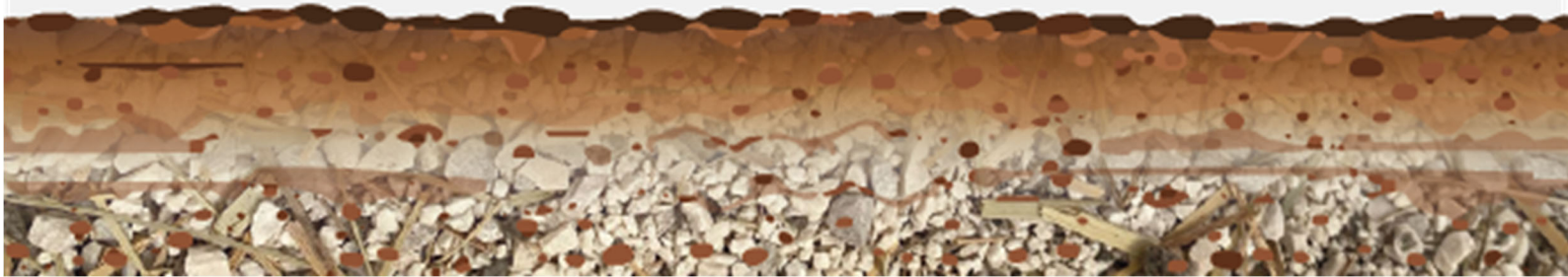
Los valores obtenidos de SS en los EHA y EVA (**Capítulo 9**) fueron generalmente mayores que los del agua de riego, debido a la contribución de SS por parte del residuo orgánico. Aunque cabe mencionar que estos aportes iniciales fueron controlados por los sistemas de depuración, alcanzando concentraciones menores a las del agua de riego en la última semana de EHA y a partir de la semana 6 en el EVA. Los tratamientos con residuo inorgánico (EHG y EVG) consiguieron concentraciones de SS inferiores a la del influente, aunque los SS fueron mejor controlados con los biorreactores verticales ya que favorecerían su precipitación y sedimentación (máxima reducción la semana 11 obteniendo un 58,2% en EVG).

Por otro lado, ninguno de los biorreactores consiguió mantener una reducción de la DQO (**Capítulo 9**) respecto de la concentración del agua de riego (I). De hecho, se produjo un aporte de materia orgánica oxidable liberada por el residuo orgánico tanto en los biorreactores de flujo horizontal como en los de flujo de agua vertical. Con el paso de las semanas se obtuvieron valores de DQO similares en todos los tratamientos debido a la actividad biológica de la población microbiana y a la materia orgánica muerta procedente de dicha biomasa.

Las gráficas de la concentración semanal de la alcalinidad (**Capítulo 9**) fueron muy similares a las de los bicarbonatos. Los sistemas con grava (EHG y EVG) fueron los que controlaron ambos parámetros de forma más estable, de hecho, la concentración de alcalinidad y de bicarbonatos fue siempre inferior a la del influente. EHG obtuvo su máximo porcentaje de reducción de la alcalinidad y bicarbonatos la semana 11 (58,2%). Los biorreactores orgánicos mostraron un aporte de las concentraciones, aunque el sistema vertical consiguió reducirlas por debajo de la del agua de riego. Observando las concentraciones de carbonatos, aunque hay ciertas fluctuaciones, de forma general, los sistemas inorgánicos consiguieron valores inferiores a las del influente (EHG alcanzó su máxima reducción 78,2% la semana 7). La contribución de carbonatos procedente del residuo orgánico fue alta en el sistema horizontal, sin embargo, en el vertical se consigue su reducción.

Finalmente, se estudió la concentración de N en las aguas (**Capítulo 9**), ya que es uno de los nutrientes que están asociados a los procesos de eutrofización por la presencia de N inorgánico en lagos y áreas costeras. La reducción biológica del nitrógeno se basa en los procesos de oxidación del amonio a nitrato (nitrificación) y la desnitrificación de nitrato a gas nitrógeno. Todos los tratamientos consiguieron reducir la concentración de N del agua de riego, aunque se observaron fluctuaciones cada 2-3 semanas. Esto pudo ser debido a los cambios en la actividad microbiana y a la capacidad de eliminación asociada con el incremento de la biomasa y las necesidades de N para dicho crecimiento. Además, posiblemente las condiciones anaerobias en todos los sistemas y el pH del residuo orgánico favorecieron la reducción. En los sistemas con residuo orgánico, la relación C/N de la poda de rama de almendro (C/N = 89) (**Capítulo 7**) también potenció la reducción de la carga contaminante. La presencia de N procedente del residuo implica que los microorganismos necesiten un aporte de N extra (del agua de riego) para su metabolismo. De hecho, desde la semana 17, EHA alcanzó reducciones sustanciales del N, llegando a la total reducción (100%) en la última semana. Esto posiblemente se debió a que en ese momento la actividad microbiana se encontraba consolidada, y durante las últimas semanas la concentración de N en el agua de riego fue menor, por lo que las necesidades de N de la población microbiana (dimensionada para mayores aportes de N) no fueron cubiertas. Probablemente, este tratamiento fue el más eficiente para el control del N en las aguas.

CAPÍTULO 11: CONCLUSIONES



11.1 Conclusiones

A continuación, aportamos las conclusiones más relevantes obtenidas que contribuyen a la investigación:

- 1) Los suelos técnicos formulados a partir de residuos pueden ser incluidos en el grupo de referencia de los *Technosols* de la WRB y por las referencias consultadas. Es un concepto relativamente reciente, pero suscita interés científico, debido a la necesidad de suelo de calidad para atender las necesidades alimentarias de la creciente población mundial y de las actuaciones establecidas en el marco del *European Green Deal*. Se añade su gran potencial para la provisión de servicios ambientales y su capacidad para poder funcionar como lo hacen los suelos naturales. Los *technosols* han sido desarrollados principalmente en el ámbito

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minero y el urbano, así pues, esta tesis provee un avance en el conocimiento de la viabilidad de generar tecnosuelos con utilidad agrícola.

- 2) Los suelos degradados (sellados, compactados o contaminados) experimentan una reducción en su capacidad para proveer servicios ecosistémicos, como la producción de alimentos. La Unión Europea insta a los países miembros a recuperar estos suelos para no comprometer la seguridad alimentaria y evitar la ocupación de más suelo. Tras eliminar la capa sellante, remediar la contaminación y la compactación, los suelos pueden recuperar su funcionalidad ecosistémica, y el uso de tecnosuelos puede facilitar la transformación, incluso hacia su futura utilidad agrícola.

- 3) Los residuos estudiados poseen propiedades fisicoquímicas adecuadas y un alto contenido en nutrientes (Na, K, Ca, Mg, Fe, Mn, Cu y Zn), que sugieren su posible uso para formular tecnosuelos. Además, implica un destacado potencial agrícola. En general, los residuos que muestran mayores concentraciones de nutrientes solubles, con altos índices de solubilidad, son: restos de poda de hoja de palmera, de poda de sarmiento y de poda de olivo. Por otro lado, los residuos orgánicos y de poda contienen cantidades bajas de nitrógeno en su composición elemental implicando que su relación C/N es alta, lo que dificulta la mineralización. Por ello, se evidencia que la combinación de fuentes de nutrientes orgánicas como inorgánicas puede ser recomendable. En definitiva, si se necesita un rápido aporte de nutrientes para una determinada fase de crecimiento vegetal, podemos escoger los residuos de poda que tengan mayor concentración soluble de los nutrientes requeridos y menor relación C/N. Esto facilita el establecimiento de un plan de fertilización en el que se incorporen residuos orgánicos como fuente nitrogenada, ya que podremos discernir qué residuo interesa más según su contenido en nutrientes y su relación C/N.

- 4) Todos los residuos estudiados cumplen con los límites estipulados por la normativa reguladora de los sustratos de cultivo, enmiendas y fertilizantes. Además, en cuanto a la normativa que regula los límites de metales pesados en los suelos agrícolas, cabría prestar atención al compost de lodo de depuradora si se aplica sobre suelos ácidos, no así para los residuos de poda y recolección. En cuanto al extracto acuoso de los residuos estudiados, excepto para el compost de lodo de depuradora (que obtiene un índice de solubilidad bajo para el Pb), los metales pesados Cd, Cr, Ni y Pb no muestran resultados por encima del límite de detección. Las concentraciones de Cu y Zn en el extracto acuoso de todos los residuos, a pesar de que obtienen mayores índices de solubilidad, cumplen con los límites de la normativa reguladora de los sustratos de cultivo, enmiendas y fertilizantes. Por lo tanto, hay residuos cuya aplicación no presenta restricciones en cuanto a los límites establecidos, sin embargo, para otros residuos conviene ser cauteloso.

- 5) El tratamiento de las aguas de riego con los biorreactores estudiados fue efectivo para la reducción de la mayoría de los parámetros, a excepción de la salinidad y la DQO que no se vieron prácticamente afectadas. El mayor potencial de mejora de las propiedades fisicoquímicas de las aguas marginales y de baja calidad que se usan para riego, puede ser la reducción de su contenido en N, lo que contribuiría a prevenir los procesos de eutrofización. En nuestro experimento, se consiguió una reducción del 100% del N la última semana de muestreo en el efluente sometido al tratamiento horizontal con residuo orgánico, donde la relación C/N del residuo pudo ser clave. Concluyendo, los biorreactores que utilizan residuos pueden ser una solución muy útil para mejorar la calidad de las aguas y la economía circular en línea con las estrategias del *Green Deal*.

- 6) Se requiere seguir investigando sobre la formulación de *technosols* a partir de residuos, dada la amplia variedad de residuos, factores y condiciones ambientales y de gestión del medio, rural o urbano, para la provisión de servicios ecosistémicos.

11.2 Perspectivas futuras

Los resultados obtenidos sientan un precedente para futuras investigaciones sobre la gestión de los residuos, desde el punto de vista del aporte de nutrientes rápidamente solubles y los riesgos asociados al exceso de nutrientes y elementos traza. Se ha tratado de plantear, a nivel bibliográfico y de experimentación, los principales factores que influyen en la disponibilidad de los nutrientes (relación C/N, propiedades fisicoquímicas, procesos de transformación de los residuos, etc.). Sin embargo, debido a la amplia variedad de otros factores como la diversidad de cultivos y por lo tanto de sus necesidades nutricionales, de su composición elemental y de su solubilidad, los diversos escenarios posibles (mezclas de diversos residuos para la formulación de tecnosuelos, tipos de suelos y estado del suelo, condiciones ambientales, entre otras), conviene seguir ampliando los esfuerzos investigadores al respecto.

Consideramos que podrían ir encaminados hacia la experimentación de la supervivencia, la comprobación de la disponibilidad y absorción efectiva de los nutrientes por las plantas, los beneficios aportados a los cultivos (productividad, crecimiento, entre otros), el análisis de nutrientes en lixiviados, atendiendo a todas las variables mencionadas. De tal forma que podamos determinar la adecuada dosificación de los residuos orgánicos junto con la fertilización inorgánica para evitar las pérdidas de nutrientes a la par que potenciar la producción agrícola. En definitiva, procuramos ampliar el conocimiento para que el agricultor pueda escoger con rigor el mejor plan de fertilización de sus cultivos empleando en la medida de lo posible los residuos que genera su explotación para conseguir reducir a cero la producción de residuos, en línea con la estrategia europea *Zero Waste* (EC, 2014).

En este sentido, se están desarrollando nuevas investigaciones que sumarán conocimiento a los resultados aquí presentados y en los que aporte los conocimientos

adquiridos para la realización de esta tesis, considerada un paso para asentar sólidamente las bases de formulación de tecnosuelos.

Concluyendo, el futuro de esta investigación es el desarrollo de un sistema integral de gestión de residuos orgánicos de las áreas agrícolas, de acuerdo con los objetivos de las estrategias desarrolladas por el Pacto Verde Europeo y con la intención de potenciar la provisión de servicios ecosistémicos, tanto en el propio medio rural, pero fundamentalmente en medios urbanos y periurbanos muy afectados por la actividad antrópica.

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«Yo puedo hacer cosas que tú no puedes, tú puedes hacer cosas que yo no puedo;
juntos podemos hacer grandes cosas»

Santa Teresa de Calcuta.

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TESIS DOCTORAL

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