GREYWATER REUSE: DECENTRALIZED TREATMENT WITH FORWARD OSMOSIS AND HYDROPONIC SYSTEMS

Esther Mendoza

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Doctoral Thesis

Greywater reuse: decentralized treatment with forward osmosis and hydroponic systems

Esther Mendoza

2024

Doctoral Thesis

Greywater reuse: decentralized treatment with forward osmosis and hydroponic systems

Annex I-VII

Esther Mendoza

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The results of this PhD thesis, which is a compendium of previously published articles in scientific journals, are presented here as chapters.

Esther Mendoza, Giuliana Ferrero, Yness March Slokar, Xavier Amores, Arianna Azzellino and Gianluigi Buttiglieri. "Water management practices in Euro-Mediterranean hotels and resorts." *International Journal of Water Resources Development* 39, no. 3 (2022): 485-506. (IF$_{2022}$: 3.1, Q1) https://doi.org/10.1080/07900627.2021.2015683

Esther Mendoza, Gianluigi Buttiglieri, Gaetan Blandin and Joaquim Comas. "Exploring the limitations of forward osmosis for direct hydroponic fertigation: Impact of ion transfer and fertilizer composition on effective dilution." *Journal of Environmental Management* 305 (2022): 114339. (IF$_{2022}$: 8.7, Q1) https://doi.org/10.1016/j.jenvman.2021.114339

Esther Mendoza, Albert Magrí, Gaëtan Blandin, Àlex Bayo, Josephine Vosse, Gianluigi Buttiglieri, Jesús Colprim and Joaquim Comas. "Second-Generation Magnesium Phosphates as Water Extractant Agents in Forward Osmosis and Subsequent Use in Hydroponics." *Membranes* 13, no. 2 (2023): 226. (IF$_{2023}$: 4.3, Q2) https://doi.org/10.3390/membranes13020226

Esther Mendoza, Gaetan Blandin, Marc Castaño-Trias, Lucas Leonel Alonso, Joaquim Comas and Gianluigi Buttiglieri. "Rejection of organic micropollutants from greywater with forward osmosis: A matter of time." *Journal of Environmental Chemical Engineering* 11, no. 5 (2023): 110931. (IF$_{2023}$: 7.7, Q1) https://doi.org/10.1016/j.jece.2023.110931

Esther Mendoza, Josephine Vosse, Arianna Azzellino, Lucia Helena Santos, Sofia Semitsoglou-Tsiapou, Joaquim Comas and Gianluigi Buttiglieri. “From shower to table: fate of organic micropollutants in hydroponic systems for greywater treatment and lettuce cultivation.” *Blue-Green Systems* 6, no. 1. (2024): 70-89. (IF$_{2022}$: 4.6, Q1) https://doi.org/10.2166/bgs.2024.051

Other publications and book chapters derived from this PhD thesis (but not presented in the document):

Esther Mendoza, Joaquim Comas, Gianluigi Buttiglieri, Heinz Gattringer and Johannes Kisser. “vertECO®: A vertical ecosystem for wastewater treatment”. *Nature-Based Solutions for Wastewater Treatment. A series of factsheets and case studies.* IWA Publishing (2021). ISBN: 9781789062267. https://iwaponline.com/ebooks/book/834/Nature-Based-Solutions-for-Wastewater-TreatmentA

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Esther Mendoza, Gianluigi Buttiglieri and Mónica Genestar. "El Hotel Samba de Lloret de Mar cumple diez años como laboratorio de pruebas del ICRA para evaluar tecnologías innovadoras de ahorro de agua”. *Tecnoaqua.* (2022). https://www.tecnoaqua.es/noticias/20221021/icra-investigacion-agua-sostenibilidad-turismo-hotel-samba

List of acronyms

BOD	Biochemical oxygen demand
COD	Chemical oxygen demand
CTA	Cellulose triacetate
DI	Deionized
DAP	Diammonium phosphate
DS	Draw solution
ECP	External concentration polarization
EDC	Endocrine disrupting compound
FDFO	Fertilizer-drawn forward osmosis
FO	Forward osmosis
FS	Feed solution
GW	Greywater
ICP	Internal concentration polarization
K_{OW}	Octanol-water partitioning coefficient
LOD	Limit of detection
LOQ	Limit of quantification
MBR	Membrane bioreactor
MgP	Magnesium phosphate
NBS	Nature-based solutions
OMP	Organic micropollutants
PFAS	Perfluorinated alkylated substances
PhAC	Pharmaceutical active compound
RO	Reverse osmosis
RSF	Reverse solute flux
TFC	Thin-film composite
TOC	Total organic carbon
TP	Transformation product
TSS	Total suspended solids
WHO	World Health Organization
WW	Wastewater
WWTP	Wastewater treatment plant

Summary

In response to the pressing challenges on freshwater resources posed by climate change and population growth, alongside with inadequate water management practices, a transition towards a circular economy paradigm is crucial. This transition holds significant relevance in water-scarce areas, often reliant on tourism, a sector acknowledged both for its substantial water consumption and its rapid global expansion. Consequently, it is imperative to reduce the demand for freshwater, especially in tourism applications. Within this scope, water reuse emerges as a fundamental strategy in addressing water scarcity while aligning with circular economy principles. Within the spectrum of water reuse possibilities, greywater (GW) represents the fraction of domestic wastewater (WW) without toilet waste, thus categorized as low-strength WW. Particularly light GW (sourced from baths, showers and bath sinks) constitutes the predominant fraction of GW, characterized by its minimal contamination levels, rendering it an exceptional candidate for reuse. However, concerns persist regarding the presence of contaminants, notably organic micropollutants (OMP), which pose risks to both the environment and human health.

Decentralized water treatment systems present a promising solution for addressing water reuse needs, especially in water-scarce regions and in isolated areas. In this context, membrane technologies and nature-based solutions (NBS) could play a major role in combining safe water reuse with low energy costs. Forward osmosis (FO) membrane process, which relies on osmotic gradient difference as driving force, emerges as a promising technology for the recovery of water from WW, offering advantages over traditional membrane processes in contaminant rejection and fouling mitigation with lower energy requirements. Notably, the fertilizer-drawn forward osmosis (FDFO) approach, which utilizes fertilizer salts as draw solutions, enables the direct application of the reclaimed water for irrigation purposes, enhancing FO efficiency by avoiding the draw solution recovery. Alternatively, hydroponic systems have the capacity of growing food crops and have showcased effectiveness as NBS for water treatment. Additionally, these systems offer multiple co-benefits, emerging among the most sustainable options for the transition towards the circular economy.

This thesis aims to explore the feasibility of FO and hydroponics as decentralized systems for the treatment and on-site reuse of GW, with a focus on ensuring safe reuse, through a comprehensive investigation covering five scientific articles. Initially, article 1 focused on evaluating water management practices in Mediterranean coastal hotels through a questionnaire answered by 80 hotels (covering the whole range of star categories, ages and sizes) situated across the Euro-Mediterranean basin and Turkey. The findings showed a prevalent utilization of water-saving devices; however, limited implementation of water reuse practices was adopted, despite a notable level of environmental awareness among the hotel establishments, indicating significant room for improvement.

Articles 2, 3 and 4 analyzed the performance of FO, and particularly the potential of the FDFO to produce a safe and ready to use diluted draw solution for hydroponics. Article 2 assessed process performance under

osmotic equilibrium conditions, showing the capability of FO to achieve adequate nutrient concentrations for direct application in hydroponic systems, but highlighting the challenges related to fertilizer losses, affecting both technical and economic feasibility of FDFO applications. Article 3 demonstrated the feasibility of three magnesium phosphate salts (i.e., struvite, hazenite and cattiite) recovered from WW as draw solutions in FO, and the subsequent utilization in hydroponic systems. After their dissolution using nitric acid, all three salts were successfully used in FO, achieving a draw dilution suitable for hydroponics. Proper plant development was achieved for lettuces in hydroponic regime growing in the diluted draw solution after nutrient adjustment with KNO_3, where hazenite showed the best results. Article 4 analyzed the performance of FO for GW treatment, utilizing either fertilizers (KNO_3 and $(NH_4)_2HPO_4$) or NaCl in the draw solutions, and focused on the analysis of the behaviors of a mix of 23 OMP. The high rejection rates obtained for most GW constituents resulted in excellent quality of the diluted draw solution for reuse applications. While remarkably high rejections were obtained for the tested OMP (average 98.5%), concerns were raised over the decreased rejection with recirculation time, necessitating further research into process optimization and safety.

Article 5 investigated the capability of hydroponic systems for GW treatment and edible crop production, by evaluating the growth of lettuces in synthetic GW alongside a mixture of 20 OMP. The condition supplemented with commercial nutrient solution yielded lettuces of comparable size to the control, indicating that adequately supplemented GW holds promise as growing media for crop production. Only the effluent of this condition met the physicochemical quality requirements outlined in the European water reuse legislation (EU 2020/741), underpinning the fundamental role of optimal plant growth in the success of GW treatment with hydroponics. The study elucidated the pathway of OMP from GW to the edible tissues (leaves), underscoring the variations in OMP removal, influenced by experimental conditions and physicochemical properties of the OMP. Human health risk assessment identified potential risks associated with the ingestion of lettuce for only two compounds (atenolol and epoxy-carbamazepine), but the importance of considering cumulative risks was underscored, as was the need of system optimization to enhance pollutant removal.

Overall, this thesis contributes to the growing body of knowledge on decentralized water treatment and reuse, offering insights into the potential of FO and hydroponic systems for addressing water scarcity challenges while increasing circularity in water management practices. However, there is a big room for improvement on the exploration and optimization of decentralized treatment technologies to enhance pollutant removal, particularly concerning OMP, to ensure the safety of reuse applications.

Resum

Davant els desafiaments urgents en la gestió dels recursos hídrics deguts al canvi climàtic i al creixement demogràfic, agreujats per pràctiques inadequades de gestió, la transició cap a un paradigma d'economia circular resulta cabdal. Aquesta transició cobra una rellevància molt important en regions amb escassetat d'aigua, sovint dependents del turisme, un sector reconegut tant pel seu substancial consum d'aigua com per la seva ràpida expansió global. En conseqüència, és imperatiu reduir la demanda d'aigua dolça, especialment en usos turístiques. En d'aquest context, la regeneració i la reutilització de les aigües residuals esdevé com una estratègia fonamental per abordar l'escassetat d'aigua alineant-se amb els principis de l'economia circular.

Les aigües grises *(GW - greywater)* representen la fracció de les aigües residuals *(WW - wastewater)* domèstiques sense contribució dels vàters, classificant-se així com a aigües residuals de baixa intensitat. Particularment, les 'aigües grises febles o lleugeres' (provinent de banyeres, dutxes i lavabos) constitueixen la fracció predominant de les aigües grises, caracteritzades pels seus nivells mínims de contaminació, la qual cosa les converteixen en una opció excepcional per a la seva reutilització. No obstant això, encara hi ha preocupacions respecte a la possible presència de contaminants, especialment els microcontaminants orgànics *(OMP - organic micropollutants)*, que plantegen riscos tant per al medi ambient com per a la salut humana.

Els sistemes descentralitzats de tractament d'aigua suposen una solució prometedora per abordar les necessitats de reutilització, especialment en regions amb escassetat d'aigua i en àrees aïllades. En aquest context, les tecnologies de membrana i les solucions basades en la naturalesa *(NBS – nature-based solutions)* poden exercir un paper important a l'hora de combinar la reutilització segura de les aigües residuals amb baixos costos energètics. El procés d'osmosi directa *(FO – forward osmosis)*, que es basa en la diferència de gradient osmòtic entre dues solucions com a força motriu, emergeix com una tecnologia prometedora per a la regeneració i recuperació de les aigües residuals, oferint avantatges sobre els processos de membrana tradicionals en quant al rebuig de contaminants i mitigació de l'embrutiment de les membranes amb menors requisits energètics. Especialment, utilitzar sals de fertilitzants com a solucions d'extracció a l'osmosi directa *(FDFO – fertilizer-drawn forward osmosis)* permet l'aplicació directa de l'aigua recuperada per a finalitats de reg, millorant així l'eficiència de la FO perquè evita la recuperació de la solució d'extracció. Alternativament, els sistemes hidropònics tenen la capacitat de produir cultius comestibles i han demostrat la seva eficàcia com a NBS per al tractament i regeneració d'aigües. A més, aquests sistemes ofereixen múltiples cobeneficis, convertint-se en una de les opcions més sostenibles per a la transició cap a l'economia circular.

L'objectiu d'aquesta tesi és explorar la viabilitat de l'osmosi directa i des sistemes hidropònics com a sistemes descentralitzats per al tractament i reutilització in situ d'aigües grises, enfocats a garantir una reutilització segura, a través d'una recerca integral que ha permès publicar cinc articles científics. En primer lloc, l'Article 1 es va centrar en avaluar les pràctiques de gestió de l'aigua en hotels de la costa mediterrània a través d'un qüestionari respost per 80 hotels situats a la conca Euromediterrània i Turquia (incloent tota la gamma de categories d'hotels respecte a estrelles, antiguitat i grandària). Els resultats van mostrar una utilització prevalent de dispositius d'estalvi d'aigua; no obstant això, es va observar que la implementació de pràctiques de reutilització de l'aigua és limitada, malgrat un notable nivell de consciència ambiental entre els establiments hotelers, la qual cosa indica un important marge de millora.

Els articles 2, 3 i 4 van analitzar el rendiment de l'osmosi directa i, en particular, el potencial de la FDFO per a produir una solució d'extracció diluïda segura i apta pel seu ús directe en sistemes hidropònics. L'Article 2 va avaluar el procés en condicions d'equilibri osmòtic, mostrant la capacitat de la FO per aconseguir concentracions adequades de nutrients per a l'aplicació directa en sistemes hidropònics, encara que es van destacar limitacions relacionades amb les pèrdues de fertilitzants, les quals afectarien tant la viabilitat tècnica com econòmica de les aplicacions de FDFO. L'Article 3 va demostrar la viabilitat de tres sals de fosfat de magnesi (estruvita, hazenita i cattiita) recuperades de les aigües residuals com a solucions d'extracció en FO i la seva posterior aplicació en sistemes hidropònics. Després de la seva dissolució amb àcid nítric, les tres sals es van utilitzar amb èxit en FO, aconseguint una dilució de la solució d'extracció adequada per a sistemes hidropònics. Es va aconseguir un creixement adequat dels enciams en règim hidropònic quan van ser conreades amb les solucions d'extracció diluïdes després de l'ajust de nutrients amb KNO_3, amb la hazenita mostrant els millors resultats. L'Article 4 va analitzar la capacitat de la FO per al tractament d'aigües grises, utilitzant fertilitzants (KNO_3 i $(NH_4)_2HPO_4$) o NaCl com a solucions d'extracció, i es va centrar en l'anàlisi del comportament d'una mescla de 23 OMP. Les altes taxes de rebuig obtingudes per a la majoria dels constituents de dels OMP presents a les aigües grises van resultar en una excel·lent qualitat de la solució d'extracció diluïda per a reutilització. Si bé es van obtenir rebutjos molt alts de OMP (amb una mitjana del 98,5%), van sorgir preocupacions a l'observar que el rebuig disminuïa amb el temps de recirculació, la qual cosa requereix una recerca addicional sobre l'optimització i la seguretat del procés.

L'Article 5 va investigar la capacitat dels sistemes hidropònics per al tractament d'aigües grises i la producció de cultius comestibles, avaluant el creixement d'enciams en aigua gris sintètica (amb diferents concentracions de fertilitzants) juntament amb una mescla de 20 OMP. La condició suplementada amb una solució nutritiva comercial va produir enciams de grandària comparable al control, la qual cosa indica que les aigües grises adequadament suplementades tenen potencial per a la producció de cultius. Tan sols l'efluent d' aquesta condició va complir amb els requisits de qualitat fisicoquímica descrits en la legislació europea de reutilització d'aigua (UE 2020/741), la qual cosa recolza el paper fonamental del creixement òptim de les plantes en l'èxit del tractament d'aigües grises amb sistemes hidropònics. L'estudi va elucidar la ruta dels OMP des de l'aigua gris als teixits comestibles (fulles), destacant les variacions en l'eliminació de

OMP, influenciades per les condicions experimentals i per les propietats fisicoquímiques dels OMP. L'avaluació de riscos per a la salut humana va identificar riscos potencials associats amb la ingestió d'enciam per a només dos compostos (atenolol i epoxi-carbamazepina), malgrat que es va destacar també la importància de considerar els riscos acumulatius, així com la necessitat d'optimitzar el sistema per augmentar l'eliminació de contaminants.

En línies generals, aquesta tesi contribueix al conjunt creixent de coneixements sobre el tractament descentralitzat i la reutilització de l'aigua, oferint idees sobre el potencial de la FO i dels sistemes hidropònics per abordar els desafiaments de l'escassetat d'aigua i al mateix temps augmentar la circularitat en les pràctiques de gestió de l'aigua. Malgrat tot, existeix encara un gran marge de millora en la recerca i optimització de tecnologies de tractament descentralitzat per augmentar l'eliminació de contaminants, particularment pel que fa als OMP, per garantir la seguretat de les aplicacions de reutilització.

Resumen

Ante los desafíos apremiantes en los recursos hídricos debidos al cambio climático y al crecimiento demográfico, agravado con prácticas inadecuadas de gestión del agua, la transición hacia un paradigma de economía circular resulta crucial. Esta transición cobra una relevancia significativa en regiones con escasez de agua, a menudo dependientes del turismo, un sector reconocido tanto por su sustancial consumo de agua como por su rápida expansión global. En consecuencia, es imperativo reducir la demanda de agua dulce, especialmente en aplicaciones turísticas. Dentro de este contexto, la regeneración y reutilización de las aguas residuales surge como una estrategia fundamental para abordar la escasez de agua alineándose con los principios de la economía circular.

El agua gris *(GW - greywater*) contiene aguas residuales *(WW - wastewater*) domésticas sin contribución de los inodoros, clasificándose así como agua residual de baja intensidad. Particularmente, el agua gris ligera (proveniente de bañeras, duchas y lavabos) constituye la fracción predominante de toda el agua gris, caracterizada por sus niveles mínimos de contaminación, lo que la convierte en una opción excepcional para su reutilización. Sin embargo, persisten preocupaciones respecto a la presencia de contaminantes, especialmente los microcontaminantes orgánicos *(OMP - organic micropollutants*), que plantean riesgos tanto para el medio ambiente como para la salud humana.

Los sistemas descentralizados de tratamiento de agua suponen una solución prometedora para abordar las necesidades de reutilización, especialmente en regiones con escasez de agua y áreas aisladas. En este contexto, las tecnologías de membrana y las soluciones basadas en la naturaleza (*NBS - nature-based solutions*) pueden desempeñar un papel importante a la hora de combinar una reutilización segura del agua

con bajos costes energéticos. El proceso de ósmosis directa *(FO – forward osmosis)*, que se basa en la diferencia de gradiente osmótico entre dos soluciones como fuerza motriz, emerge como una tecnología prometedora para la regeneración y recuperación de agua de las aguas residuales o grises, ofreciendo ventajas sobre los procesos de membrana tradicionales en cuanto al rechazo de contaminantes y la mitigación del ensuciamiento con menores requisitos energéticos. Especialmente, utilizar sales de fertilizantes como soluciones de extracción en FO *(FDFO – fertilizer-drawn forward osmosis)* permite la aplicación directa del agua recuperada para fines de riego, mejorando así la eficiencia de la FO al evitar la necesidad de la recuperación de la solución de extracción. Alternativamente, los sistemas hidropónicos tienen la capacidad de producir cultivos comestibles y han demostrado su eficacia como NBS para el tratamiento de agua. Además, estos sistemas ofrecen múltiples cobeneficios, convirtiéndose en una de las opciones más sostenibles para la transición hacia la economía circular.

El objetivo de esta tesis es explorar la viabilidad de la ósmosis directa y de los sistemas hidropónicos como sistemas descentralizados para el tratamiento y reutilización in situ de agua gris, enfocada en garantizar una reutilización segura, a través de una investigación integral plasmada en cinco artículos científicos. En primer lugar, el artículo 1 se centró en evaluar las prácticas de gestión del agua en hoteles de la costa mediterránea a través de un cuestionario respondido por 80 hoteles ubicados en la cuenca Euromediterránea y Turquía (incluyendo toda la gama de categorías de hoteles respecto a las estrellas, antigüedad y tamaño). Los hallazgos mostraron una utilización prevalente de dispositivos de ahorro de agua; sin embargo, la implementación de prácticas de reutilización del agua era limitada, a pesar de un notable nivel de conciencia ambiental entre los establecimientos hoteleros, lo que indica un importante margen de mejora

Los artículos 2, 3 y 4 analizaron el rendimiento de la osmosis directa y, en particular, el potencial de la FDFO para producir una solución de extracción diluida segura y lista para usar directamente en sistemas hidropónicos. El artículo 2 evaluó el proceso en condiciones de equilibrio osmótico, mostrando la capacidad de la FO para alcanzar concentraciones adecuadas de nutrientes para la aplicación directa en sistemas hidropónicos, aunque se destacaron los desafíos relacionados con las pérdidas de fertilizantes, que afectarían tanto a la viabilidad técnica como económica de las aplicaciones de FDFO. El artículo 3 demostró la viabilidad de tres sales de fosfato de magnesio (estruvita, hazenita y cattiita) recuperadas de WW como soluciones de extracción en FO y su posterior aplicación en sistemas hidropónicos. Después de su disolución con ácido nítrico, las tres sales se utilizaron con éxito en FO, logrando una dilución de la solución de extracción adecuada para sistemas hidropónicos. Se logró un crecimiento adecuado de lechugas en régimen hidropónico cultivadas con las soluciones de extracción diluidas después del ajuste de nutrientes con KNO_3, mostrando la hazenita los mejores resultados. El artículo 4 analizó la capacidad de la FO para el tratamiento de GW, utilizando fertilizantes (KNO_3 y $(NH_4)_2HPO_4$) o NaCl como soluciones de extracción, y se centró en el análisis del comportamiento de una mezcla de 23 OMP. Las altas tasas de rechazo obtenidas para la mayoría de los constituyentes del agua gris resultaron en una excelente calidad de la solución de extracción diluida para reutilización. Si bien se obtuvieron rechazos muy altos de OMP (promedio 98,5%), se plantearon preocupaciones sobre la disminución del rechazo con el tiempo de recirculación, lo que requiere una investigación adicional abordando la optimización y la seguridad del proceso.

El artículo 5 investigó la capacidad de los sistemas hidropónicos para el tratamiento de agua gris y la producción de cultivos comestibles, evaluando el crecimiento de lechugas en agua gris sintética (con diferentes concentraciones de fertilizantes) junto con una mezcla de 20 OMP. La condición suplementada con una solución nutritiva comercial produjo lechugas de tamaño comparable al control, lo que indica que el agua gris adecuadamente suplementado tiene potencial como medio para la producción de cultivos. Solo el efluente de esta condición cumplió con los requisitos de calidad fisicoquímica descritos en la legislación europea de reutilización de agua (UE 2020/741), lo que respalda el papel fundamental del crecimiento óptimo de las plantas en el éxito del tratamiento de agua gris con sistemas hidropónicos. El estudio elucidó la ruta de los OMP desde el agua gris a los tejidos comestibles (hojas), destacando las variaciones en la eliminación de OMP, influenciadas por las condiciones experimentales y por las propiedades fisicoquímicas de los OMP. La evaluación de riesgos para la salud humana identificó riesgos potenciales asociados con la ingestión de lechuga para solo dos compuestos (atenolol y epoxi-carbamazepina), aunque se destacó la importancia de considerar los riesgos acumulativos, así como la necesidad de optimizar el sistema para aumentar la eliminación de contaminantes.

En líneas generales, esta tesis contribuye al creciente conjunto de conocimientos sobre el tratamiento descentralizado y la reutilización del agua, ofreciendo ideas sobre el potencial de la FO y los sistemas hidropónicos para abordar los desafíos de la escasez de agua y al mismo tiempo aumentar la circularidad en las prácticas de gestión del agua. Sin embargo, existe todavía un gran margen de mejora en la investigación y optimización de tecnologías de tratamiento descentralizado para aumentar la eliminación de contaminantes, particularmente en lo que respecta a los OMP, para garantizar la seguridad de las aplicaciones de reutilización.

1. General introduction

1.1. Water resources in tourism sector and future perspectives

Access to water sources faces challenges in both quality and availability of freshwater supplies. Water consumption has rapidly increased over the last decades due to population growth and urbanization, which has consequently limited the availability of freshwater resources [1]. As a result, over two billion people currently face water stress [2]. Furthermore, pollution poses risks on freshwater resources, ecosystems and humans [3,4]. Anthropogenic activities related to industrial, agricultural, or urban sectors contribute to the pollution of water bodies like rivers, lakes, groundwater, or oceans with the input of different contaminants, such as nutrients, heavy metals and organic compounds [5,6]. In addition, climate change is a major factor influencing the status of the freshwater resources [7], as alterations in the occurrence and intensity of precipitation events, as well as the temperature rising, have increased the frequency of extreme events such as floods and droughts, carrying economic and environmental repercussions [8]. Projections show an increase in water stress in in regions vulnerable to desertification, characterized by infrequent and inconsistent precipitation patterns [9]. One of those areas is the Mediterranean region, with Spain at the top of European countries facing risks related to desertification and water shortage [10,11].

Conversely, touristic activities are of particular importance in coastal areas as the Mediterranean region, which receives around 300 million tourists every year, comprising more than 20% of global arrivals [12,13]. Tourism has certainly become one of the most rapidly expanding sectors on a global scale [14], and with identified large water consumption [15] particularly in coastal, island, and arid or semi-arid regions, with greater influx of tourists and fewer rainfall events during summer. For example, in Spain, where domestic activities contribute approximately 12% of water usage, tourism can drive more than half of the total water demand in touristic areas [16,17], being the principal source of demand in certain coastal municipalities [18]. Tourism drives water consumption through both direct and indirect uses, including the maintenance of water features like swimming pools and fountains, along with the irrigation of green areas. Consequently, tourists consume between 200 to 900 liters of water per day, up to three times more than their typical usage at home [15, 16, 17].

Given the escalating influx of tourists, it is imperative to mitigate freshwater demand and enhance water management practices in tourist cities, especially within hotel establishments (major water consumers) in water-stressed areas [20]. There is a big room for improvement, as research indicates that while hotels have implemented water-saving measures to some extent, they have yet to widely adopt other sustainable practices, such as the use of alternative water sources for non-potable purposes, like irrigation or toilet flushing [20–22]. Therefore, adaptation and resilience measures are essential to ensure sustainable water management in response to the escalating challenges.

1.2. The circular economy paradigm

Circular economy can be defined as a model of production and consumption which aims to transform our current linear system into a regenerative and sustainable one by maximizing the value and utility of materials and resources, while minimizing environmental impacts and waste generation [23,24]. This model proposes a closed-loop system, where resources and products remain as long as possible through recycling, reusing and regenerating, which shifts to a "cradle to cradle" approach. The circular economy has several benefits and can contribute to mitigate climate change effects [25].

At institutional level, the European Union has recognized the urgent need for sustainable development, and consequently has promoted the transition towards a circular economy paradigm, by creating the *Circular Economy Action Plan* [26] in 2020, adopted in 2021. The plan provides a future-oriented agenda for a cleaner and competitive Europe, by promoting initiatives to prevent food waste, increasing resource efficiency and endorsing the reuse and recycling of materials in diverse sectors as construction, fertilizers or water [27]. Applying circular economy principles related to the promotion of innovation in different sectors has the potential to create 700,000 new jobs by 2030 in the European Union [28]. This encourages member states to implement strategies, plans and measures included in the *Circular Economy Action Plan* [26].

In what refers to water, it is tremendously important to embrace the principles of circular economy to improve numerous aspects related to its management. In this sense, the circular economy perspective encompasses water management and conservation through the whole cycle, while encouraging water reuse [29]. Certainly, 66% of the surveyed circular economy initiatives by OECD identified the water and sanitation sector as key for the circular economy, only behind the waste sector [30]. At domestic level, the use of water saving devices, the installation of green roofs for rain harvesting [31,32], or the use of reclaimed greywater for toilet flushing [33–35] are some examples of practices that increase circularity in water management [36]. Moreover, it is of particular importance to include circular economy approaches towards water in agriculture, estimated to represent 87% of global water consumption, with 60% of global freshwater withdrawals dedicated to irrigation, being the largest water consumer worldwide [37,38]. In this case, the implementation of precision irrigation techniques [39], as well as the use if impaired sources, such as rainwater or treated wastewater (WW) [40,41] are necessary to cope with the growing demand for food and water while increasing circularity. In addition, reclaimed water and other non-conventional water sources may provide valuable compounds for the crops, mainly nitrogen and phosphorus, which are essential nutrients for their development and, consequently, resulting in smaller fertilizer needs. One of the most critical resources, in fact, is phosphorus, an essential element for life expected to deplete within this century [42], and therefore considered a critical raw material in the European Union [43]. In contrast to traditional phosphate rock mining, struvite production from the precipitation of magnesium, phosphate and ammonium ($MgNH_4PO_4 \cdot 6H_2O$) from WW streams, offers a promising path. The use of precipitated fertilizers from WW not only mitigates water pollution but also implies the recycling of indispensable nutrients, thereby diminishing the demand for energy-intensive synthetic fertilizers, contributing to sustainable agriculture. Recent studies have demonstrated that struvite can produce the same yields and product quality than conventional fertilizers [44–46]. The production of struvite is increasing, with the European Union alone generating 1,350 tons annually, where a significant proportion (64 to 71%) is recovered from municipal WW sources [47].

1.3. Water reuse

Water reuse is an essential practice to cope with the challenges related to water scarcity, while embracing circular economy principles. Despite water reuse being practiced since ancient times, legislation or guidelines for the implementation of this practice were developed only during the last four decades and in a limited number of regions, thus this practice remains far from ubiquitous [48]. Recent innovations in WW treatment technologies as well as the numerous advantages of this practice resulted in a notable increase in the global volume of reused water, [49] estimated to be 40.7×10^9 m^3/year by 2020, representing around 11% of the total volume of generated WW [50]. In the European Union, approximately 10^9 m^3 of treated WW are reused annually [51], regardless of the potential for a sixfold increase. Although the European Commission has been exploring best options to optimize water reuse since 2012 [52], it was in 2020 when the water reuse legislation from the European Union (EU 2020/741) [53] was released, coming into effect in June 2023. The European regulation on *minimum requirements for water reuse* attempts to ensure the safety of reclaimed water for agricultural irrigation purposes, while simultaneously promoting the principles of the circular economy and climate change adaptation. The legislation establishes four quality classes based on the type of crop to which the reclaimed water is to be applied. In contrast, some countries have embraced more elaborated water reuse legislation guidelines, extending the spectrum of applications beyond agricultural use. Spain serves as an example in this regard, as outlined in the Royal Decree 1620/2007 [54], which specifies 14 distinct quality classes for the application of treated water. These classes encompass a diverse array of scenarios, including industrial, urban, environmental and recreational applications in addition to agricultural irrigation. This approach has placed Spain at the head of European countries in water reuse [55].

1.3.1. Greywater

There is a growing interest in the on-site treatment and reuse of greywater (GW), focused on its use for non-potable purposes such as toilet flushing and irrigation [56], particularly in regions grappling with water scarcity [57]. Greywater, defined as the portion of domestic wastewater excluding toilet waste, includes water generated in bathtubs, showers, hand basins, laundry machines and kitchen sinks [58]. GW constitutes from 50% to 80% of the total domestic WW volume, which ranges from 15 to 200 liters per person per day [57,59–61]. Consequently, the reuse of GW has shown the potential of significantly reducing the demand for freshwater resources [59,62] and increases the resilience and adaptability of local water systems while being economically viable [63,64]. GW is an attractive candidate for reuse due to its classification as low-strength WW, with reduced levels of nitrogen, solids, organic matter and pathogens in comparison with the whole fraction of domestic WW [60,65,66], potentially simplifying treatment processes and reducing the risks posed by more polluted WW streams [67]. Hence, GW was reported to stand between medium strength raw WW and secondary [68] or tertiary effluent [69]. Notably, the majority of GW (approximately 60%), is derived from bathroom uses, which produce comparatively less contaminated water than other GW sources [57]. This is the so-called light GW (Table 1), which mainly contains non-ionic, anionic and amphoteric surfactants, fragrances, flavors, solvents and preservatives from cleaning products [58,60]. Because of the lower pollutant loads, light GW is easier to treat and reuse in decentralized scenarios [63].

Table 1. Average and range values of light GW (from bath tubs, showers and hand basins) obtained from diverse studies [21,57,69–73].

parameter	unit	average	lowest value	highest value
EC	µS/cm	859.5±413.5	318.0	1565
pH		7.5±0.8	6.6	10.0
turbidity	NTU	56.2±44.3	18.1	122.0
COD	mg O_2/L	384.9±173.5	139.0	587.0
BOD_5	mg O_2/L	175.3±99.2	39.0	309.5
TOC	mg C/L	92.8±37	23.0	120.0
TSS	mg/L	114.3±91.9	19.0	280.0
NO_3	mg N/L	3±3.5	0.2	12.3
PO_4	mg P/L	9.1±13.9	0.3	40.8
Cl	mg/L	170.3±89.2	23.6	284.0
Na	mg/L	133.4±14.8	38.3	151.0
NH_4	mg N/L	2±2.7	0.9	28.0
K	mg/L	8.5±2.1	7.0	11.9

Despite its potential, GW reuse in the legislation is often not explicitly mentioned, regulated, or even allowed in most regions. The same criteria are generally applied for GW reuse as for WW, with few specific regulations on GW existing, as in Australia, Japan or Jordan [74]. Additionally, the WHO published the guidelines on *Safe use of wastewater, excreta and greywater* in 2006 [75], focused on reducing the risks associated with GW application in agricultural irrigation, where the emphasis was on microbial parameters rather than on physicochemical ones [76]. In Europe, the technical committee of The European Committee for Standardization published the norm *EN 16941-2:2021. On-site non-*

potable water systems - Part 2: Systems for the use of treated greywater [77]. This norm sets the principles for the installation of systems for the separation, treatment and reuse of GW, as well as the quality requirements for the different uses of the reclaimed GW, where toilet flushing, garden irrigation and laundry are proposed.

Among the different scenarios for light GW reuse, touristic accommodations are of particular interest, with hotels typically featuring a higher proportion of bathrooms in comparison to residential structures. An illustrative example is Hotel Samba, located in Lloret de Mar (Spain), where GW is collected from baths, showers and toilet sinks, and subsequently treated and reused for toilet flushing [22]. This practice achieves an 80% reduction in water consumption per guest per night, resulting in substantial yearly municipal water savings of 13,500 to 15,000 m^3 [12]. Additionally, the use of GW for irrigation is remarkably compelling because it contains essential nutrients for plant growth [78], potentially reducing the need for synthetic fertilizers [79]. Previous studies reported increased growth and nutrient content for above-ground and below-ground crops (Swiss chards and carrots) irrigated with GW, although the potential of increasing soil salinity with the time was highlighted, and thus recommended to combine GW with freshwater irrigation [80]. Similarly, improved plant growth was reported for several edible crops (spinach, green pepper, potatoes and madumbes) irrigated with raw GW [81] or for tomato crops irrigated with laundry GW [82].

1.3.2. Safety implications on the use of reclaimed greywater

Safety guarantees of water reuse are of the utmost importance to protect public health and the environment, and the scientific community has raised several related concerns [83]. The health risks associated with GW arise from three principal sources: chemical (organic and inorganic), physical and pathogenic [81]. Main concerns around GW reuse are typically related with the exposure to pathogens (usually fecal microorganisms), and consequently, disinfection is required to reduce or eliminate their presence in reclaimed GW [63]. In this line, it was recommended to include disinfection with residual Cl_2 concentration higher 1 mg/L, and with a water storage time of less than 48 hours for the application of treated GW for toilet flushing in hotels [84]. The application of GW for food-crop irrigation was reported to exhibit a higher microbiological risk than toilet flushing, with kitchen and laundry GW posing higher risks than bathroom GW [56]. Another study pointed out the need of special attention on the risk of microbial contamination during irrigation and harvesting, while highlighting the potential of treated WW for the growth of leafy edibles [85]. Studies on the presence of heavy metals in reclaimed GW indicated minimal risks for its application for toilet flushing, clothes washing or irrigation [70,86]. While risks associated with pathogen exposure, heavy metals, salinity and sodicity are more debated, those related to emerging contaminants, a key hazard to environmental health [87], remain understudied [83]. Certainly, water reuse legislations and guidelines are primarily centered on monitoring coliforms, BOD_5, turbidity and TSS, but most of them do not include or only include a limited number of organic micropollutants and emerging pathogens [88,89], which are commonly found in GW streams [60,71,90].

1.3.3. Organic micropollutants in greywater

Organic micropollutants (OMP) constitute a diverse group of compounds such as pharmaceutical active compounds (PhACs), endocrine disrupting compounds (EDCs), plasticizers, industrial chemicals, or pesticides. Ubiquitously present in water bodies, OMP have become a point of concern for water reuse applications [91,92]. These compounds originate in diverse anthropogenic sources: domestic [62,93], industrial WW [94], or agricultural runoff [95,96]. Conventional treatment methods struggle to effectively remove OMP [97], with reported removal rates from 12 to 100%, depending on the compound [4], necessitating advanced technologies with multibarrier approaches to increase their elimination from WW [90]. In addition, when OMP go through processes like oxidation, hydrolysis, or microbiological degradation [98] may form transformation products (TPs). The TPs often have distinct properties compared to their parent compounds [58], sometimes being more toxic [99] and resistant to biodegradation [100], making them more abundant in the environment than the corresponding parent compounds [101].

GW can contain a broad array of OMP, at concentrations sometimes even higher than the whole fraction of domestic WW [102]. The potential presence of 900 different compounds in GW was reported, from which 10% were categorized as priority pollutants [58]. A recent review about OMP in GW gathered a list of 350 OMP found in different GW sources [90], where surfactants were detected at the highest concentrations, followed by personal care products, preservatives, UV filters and PhACs. The presence of persistent OMP in GW carries several risks for the aquatic environment, due to direct discharge into natural waters and agricultural runoff. OMP can be mutagenic/carcinogenic/toxic to reproduction, they have endocrine disrupting potential or can induce resistance to antibiotics [90,103–105]. As regards to human health, although the main risks related to reclaimed water reuse seem to be those linked to pathogens, the detection of an increasing number of OMP, and the need to expand water reuse could lead to the emergence of greater or unknown risks. Moreover, although several OMP are commonly found at harmless concentrations, cumulative exposure could enhance risks. The use of reclaimed GW or WW for irrigation, in fact, can act as a source of OMP in the soil [106]. Afterwards, OMP can travel from the soil to plant roots and translocate to various parts of the plants, including edible portions, and thus entering the food chain [83,107–109]. Human Health Risk Assessment (HHRA) methods, widely employed to estimate adverse health effects from contaminants, provide the magnitude and probability of such effects in humans exposed to those contaminants [110]. Several studies applying HHRA have indeed raised concerns regarding the potential risks associated with consuming crops irrigated with reclaimed water due to the presence of OMP [111,112]. In contrast, negligible risks were reported in other studies evaluating ingestion of various crops irrigated with raw or treated WW [108,113–117]. Consequently, understanding the occurrence, risks and implications associated with OMP, including for GW reuse, is needed, aiming to promote safe reuse of water and integrate findings into water reuse legislations [118].

1.3.4. Decentralized systems for greywater treatment and reuse

Two predominant scenarios stand out in water supply and treatment: centralized and decentralized. In the conventional centralized approach, water undergoes treatment at a central facility before distribution through a network and user-generated wastewater goes back to a centralized treatment plant, where targeted pollutants are removed before discharge into adjacent water bodies or reuse [11]. In contrast, decentralized scenarios integrate centralized supply systems with on-site water treatment and reuse systems [11]. The escalating costs associated with centralized systems, particularly in water transport and logistics, have promoted the development of decentralized systems, recognized as an emerging solution for a more sustainable WW management [119,120]. On-site collection, treatment and reuse of WW aims at saving freshwater, mitigating water pollution and recuperating valuable resources while minimizing the transport and disposal of the effluent [63,121,122]. Decentralized systems present a practical circular solution, especially appealing in isolated or water-scarce regions or in communities lacking access to centralized WW treatment plants [63,119,123]. In addition, this option opens the way to more robust systems, particularly important in periods of water scarcity. As a result, decentralized treatment systems may be inherently more environmentally sustainable than their centralized counterparts [124].

Rainwater harvesting and GW reuse represent the focal points of global research in decentralized systems [125]. Published works into decentralized GW treatment and reuse systems have reported successful results using a diverse array of technologies. For instance, Lalley et al. [119] showcased the feasibility of a combined train of ultrafiltration and reverse osmosis (RO) for reuse purposes of low strength GW. The potential of decentralized GW treatment in airports was explored using an anaerobic filter followed by UV disinfection [126]. Another study adopted a composite approach involving sand filtration, granular activated carbon filtration and ozone for treating domestic GW blended with rainwater [127]. Atanasova et al. [21] demonstrated the effectiveness of a membrane bioreactor (MBR) in achieving high-effluent quality from light GW sourced from a hotel, satisfying Spanish legislative requirements for water reuse. Other investigations have underscored successful results with constructed wetlands [72], green walls [128] or green roofs [129]. Hence, a spectrum of possibilities exists for integrating decentralized systems for on-site GW treatment and reuse: intensive and extensive ones. Intensive technologies are compact and usually achieve higher removals rates in shorter operation times than extensive technologies, which also require larger spatial footprints. However, extensive technologies are generally simpler and cheaper to maintain than intensive technologies and, at the same time, they provide environmental and social co-benefits [130–132]. With the detection of a great diversity of water contaminants, it is necessary to investigate systems that can retain them to promote safe reuse in different decentralized scenarios. The selection of applied technology, or the combination of various (i.e., hybridization) will depend on diverse factors encompassing costs, logistical considerations, water characteristics, or the intended purpose of reuse.

1.4. Intensive GW treatment: membrane technologies

Membrane technologies act as a physical barrier against a broad spectrum of water contaminants, including OMP [91,133]. The remarkable rejection rates achieved by these systems makes them highly effective solutions for WW treatment and reuse, producing effluents that meet strict regulatory standards [88,123,134]. The high recovery rates (i.e., percentage of WW converted into reclaimed water) achieved by these technologies mitigates waste generation and allows the concentration and subsequent recovery of valuable resources, such as metals, organic compounds, or salts [135,136]. In comparison with other technologies for water treatment, membranes require lower footprint due to their compact design, frequently in a modular setup and offer effective treatment with economic feasibility [123]. The versatility of these systems facilitates their implementation in diverse scenarios, both centralized and decentralized, and their hybridization with other technologies to enhance the contaminant removal capacity [137]. On the evaluation of these technologies for GW treatment and reuse, several studies have reported successful results implementing nanofiltration [138], ultrafiltration [139], membrane distillation [140], RO [141], or forward osmosis [142].

1.4.1. Forward osmosis

The concept of forward osmosis (FO) for water treatment, projected as one of the solutions for the water-energy nexus for coastal cities [143], trace back to the 1970s, with two articles published in *Desalination* in 1976 by Moody and Kessler [144]: *Forward osmosis extractors*, and by Kessler and Moody [145]: *Drinking water from sea water by forward osmosis*, although Cath et al. [146] provided the first comprehensive overview of the process in 2006 [37]. In recent years, FO has emerged as a prominent membrane technology, gaining recognition for its distinct advantages over other membrane-based processes, capable of recovering water from impaired streams and with energy recovery capacity [147–149]. The FO process benefits from the osmotic gradient generated by the difference in salinity between the feed solution (FS) and draw solution (DS), separated by a dense semipermeable membrane (Figure 1). This osmotic gradient serves as the driving force pulling water molecules from the lower salinity FS to the higher salinity DS, consequently diluting the DS and concentrating the FS [150,151]. Unlike pressure-driven membrane processes like RO, FO relies on osmotic pressure, resulting in less energy consumption to transport water across the membrane [37,152]. In comparison to other membrane technologies, FO has gained attention for its lower fouling propensity and higher rejection of pollutants [153,154], including OMP [155,156]. Its operation at a reduced cost, attributable to the absence of hydraulic pressures [157], further enhances the attractiveness of FO across a diverse range of applications. At real scale, improvements in process performance were reported, with FO as pretreatment for RO in a desalination plant in Oman [158], for the treatment of coal-fired power plant in South Korea [159], or for the treatment of WW effluent up to potable reuse quality in the United States [160].

Ideally, FO membranes should exhibit high water fluxes and solute retention, along with low fouling potential and chemical stability [158,161]. First commercial FO membranes were released in 2002 for emergency potable water supply for the United States army [162], and currently there are only ten FO membrane suppliers, most of them from the United States [163]. FO membrane modules are configured in various formats such as flat sheet, hollow fiber, spiral-wound, or tubular [164], with higher water fluxes obtained with hollow fiber membranes in comparison to flat membranes [165]. Developed FO membranes exhibit a distinctive structure comprising a porous layer, of approximately 150 µm in thickness, coated with an ultrathin active layer of less than 1 µm and made of polyamide [166]. Commonly, support layers are made of cellulose triacetate (CTA) or polysulfone-thin film composite (TFC), with TFC demonstrating greater resistance to variations in the pH and temperature [167]. Enhanced water fluxes and salt rejection are attributed to the negative charge characteristic of TFC membranes in comparison to CTA membranes [168,169], with electrostatic interactions reported as primary rejection mechanism for charged species within TFC membranes [170,171]. Biomimetic FO membranes, which integrate TFC layer embedded with aquaporin proteins showcasing 100% selectivity towards water molecules [164], have earned attention for their outstanding performance, surpassing conventional FO membranes in water fluxes and salt selectivity [172,173].

Despite its early introduction, the development of FO progressed at a slower pace than RO, likely hindered by intrinsic process limitations. Main points of concern affecting FO performance are associated with reverse salt transport, internal concentration polarization and DS regeneration [174]. The passage of solutes across the membrane, inherent in all membrane systems, is a complex process involving various mechanisms and influenced by draw and feed solution composition and concentration, membrane properties and operational characteristics. Typically, monovalent cations exhibit the highest solute fluxes [175,176], as they are drawn to the negatively charged TFC membranes, diffusing towards the opposite solution, while anions engage in diffusion to maintain charge balance, process known as solution diffusion mechanism [177–179]. Solute fluxes from FS to DS are known as forward fluxes, while solute fluxes from DS to FS, known as reverse solute fluxes (RSF, Figure 1), emerge as a prominent drawback in FO systems [180]. RSF directly correlate with water flux, DS concentration and temperature, and exhibit an inverse correlation with hydrated radii and DS speciation [181–183]. The economic implications of RSF are significant, causing difficulties for feed concentrate management and inducing a reduction in osmotic pressure, subsequently diminishing the driving force of the process [150,184–186]. Therefore, the control and minimization of RSF are imperative in the design of osmotically driven processes [187,188].

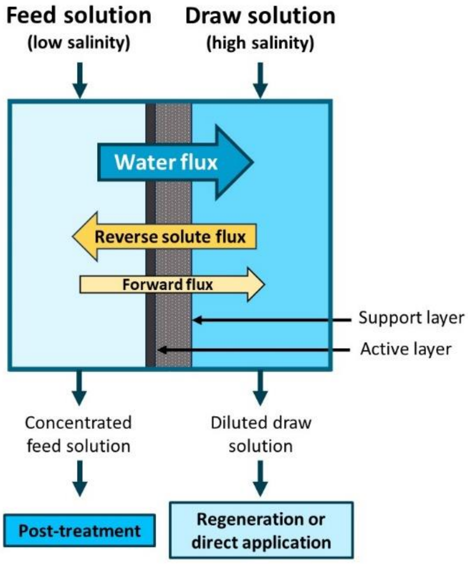

Figure 1. Schematic overview of the forward osmosis process.

Other factors impacting the effectiveness of FO include concentration polarization (CP) and fouling. Both phenomena arise from alterations in solute concentration near the membrane surface, resulting in reduced water fluxes. FO is generally less susceptible to fouling compared to other pressure-driven membrane processes, and unlike in RO, fouling in FO is irreversible[189]. Conversely, CP has been identified as a primary impediment to FO performance [146]. Therefore, initiatives to alleviate these effects are imperative for improving FO performance, although complete elimination of CP effects and fouling is impossible as these phenomena are inherent in all membrane processes [123,190].

The use of impaired sources, such as brackish water, WW, or GW are desired FS to enhance the effectiveness of FO [37]. However, limited research exists on FO for GW treatment (Table 2), with available studies from only 2018, and predominantly stemming from a single research group from Shanghai, China; consistently reporting remarkably high rejection rates for most GW constituents (FS) with NaCl as DS. Initially, their focus was on investigating fouling in TFC membranes, synthesizing membranes in hollow fiber [61] and flat-sheet configurations [191] for synthetic GW treatment. Then, they evaluated the temperature effects of the FO process with CTA membranes, designating 40°C as the optimum operational temperature to achieve the highest water fluxes with the lowest RSF [192].

Subsequent studies evaluated the performance of aquaporin membranes by modelling the rejection of 11 GW constituents [193] and examined the effects of sodium dodecyl sulfate, a common GW constituent, on membrane fouling and cleaning [194]. In their latest publication, they reported that membrane surface morphology and temperature significantly influenced the rejection of constituents from real GW using flat aquaporin membranes [142].

Table 2. Studies in FO employing GW as feed solution.

Membrane type	**Membrane configuration**	**Membrane area, cm²**	**Feed solution**	**Draw solution**	**Year of publication**	**Reference**
Aquaporin	Flat	620	Light GW	NaCl	2023	[142]
Aquaporin	Flat	28	Na-dodecyl-SO_4 plus organic (Na-alginate) and inorganic ($CaCl_2$) foulants	NaCl	2020	[194]
Aquaporin	Flat	200	Individual GW constituents*	NaCl	2018	[193]
CTA	Flat	28	Synthetic GW	NaCl	2018	[192]
TFC-surface modification	Flat	24	Synthetic GW	NaCl	2018	[191]
TFC	Hollow fiber	n.a.	Synthetic GW	NaCl	2018	[61]

*NH_4Cl, KCl, $CaCl_2$, $MgCl_2$, $NaNO_3$, $NaSO_4$, KH_2PO_4, lactic acid ($C_3H_6O_3$), glucose ($C_6H_{12}O_6$), sodium dodecyl sulfate ($NaC_{12}H_{25}SO_4$) and sodium dodecyl benzene sulfonate ($C_{18}H_{30}NaO_3S$)

In contrast to FS, the ideal DS should contain small-sized charged ions, exhibit low viscosity and possess non-toxic attributes [164,195]. Sodium chloride remains the most common DS due to its high osmotic potential and abundant availability, primarily in seawater. Frequently, a secondary step is introduced, to regenerate the DS, impacting the overall energy efficiency of the system [162]. Certainly, existing literature underscores the synergistic potential of FO with other technologies to enhance efficiency, as RO [158,196,197], nanofiltration [198,199] or membrane distillation [200,201], even the integration of FO in MBR (i.e., osmotic membrane bioreactors [202–204]). An interesting approach can be the direct use of draw solutions without necessitating a reconcentration step, remaining as the only way FO can be applied as a standalone process for efficient performance [205]. In this context, fertilizer salts, with their elevated osmotic potential [150], emerged as promising DS candidates as they can be directly used for irrigation purposes [186]. This approach, termed fertilizer-drawn forward osmosis (FDFO) was developed over the last decade, with the initial reference to this term found in a publication from 2011 entitled *A novel low energy fertilizer driven forward osmosis desalination for direct fertigation: Evaluating the performance of fertilizer draw solutions* [186]. FDFO holds significant potential for on-site reuse of the diluted DS. Studies on FDFO have explored the performance of different fertilizer salts [178,186,206–208], and in certain cases, commercially available solutions were employed as DS for subsequent irrigation purposes [176,209–211]. However, most published studies on FDFO indicated the necessity for further dilution of the DS to align nutrient concentrations with crop requirements. Proposed strategies to enhance DS dilution are the application of additional pressure [187,205,209] or the integration within osmotic MBR [212]. Pilot-scale investigations into FDFO have also been predominantly conducted by a specific research group from the University of Technology of Sydney, Australia. These studies integrated FO with nanofiltration to reduce nitrogen concentration in the diluted DS, employing tap water [213] or brackish water [214] as FS to assess various membrane performances. Later on, the pilot system was employed for the desalination of saline groundwater from coal-mining activities, meeting the quality standards for irrigation, but the forward solute fluxes caused salinity buildup in the DS, impacting the final water quality for irrigation [215]. Then, they used spiral-wound TFC membranes to osmotically dilute seawater with a commercial nutrient solution for crop production as DS and applied additional pressure until obtaining the required nutrient concentrations, resulting in successful lettuce growth comparable to the control group [209]. While several studies exist on the concept of FDFO, there is a knowledge gap on assessing the performance of FO and particularly of FDFO with alternative water sources like GW.

1.4.2. Organic micropollutants in forward osmosis

The exploration on the behavior of OMP during forward osmosis consistently reported remarkably high OMP rejection rates, often exceeding 90%, surpassing that of RO, likely due to the impact of reverse solute fluxes, which induced a retarded diffusion of OMP [155,216]. Studies evaluating the rejection mechanisms of OMP in FO showed dependencies on the nature of both feed and draw solutions, operational characteristics and OMP properties [170,179,217,218]. Similar to the previous discussion on ions, the primary rejection mechanisms for OMP involve size exclusion, electrostatic repulsion and hydrophobic affinity [179,219]. Accordingly, small positively charged and hydrophobic compounds exhibit greater affinity for the membrane, while negatively charged compounds are rejected and neutral compounds demonstrate increased permeability due to reduced interactions with the membrane [170,217].

Despite the diverse number of studies on the behavior of OMP in FO, limited research exists considering the rejection of OMP in FO during WW treatment, with most of the publications released over the last five years (Table 3). While no studies were found including GW and OMP, most studies employing feed types with alternative water sources (comparable to GW) were performed at laboratory scale, with small flat membranes and usually testing synthetic feed solutions (Table 3). Previous studies predominantly employed NaCl as DS, only three of them applied fertilizers as DS [220–222] and just one of them tested blended fertilizers [222]. Studies evaluating OMP behavior during the treatment of WW (real or synthetic) with FO reported rejections influenced by different factors, including DS chemistry [179], increased rejections with biofouling [223] and decreased rejections with ethanol exposure, while remaining stable under temperature variations [218]. Other studies focused on concentrating WW with FO as a pre-treatment for anaerobic digestion and they reported elevated concentrations of PhACs and salinity buildup in the reactor [224]. Notably, OMP rejection in FO applied to anaerobic MBR effluent exceeded 90%, and was influenced by concentration polarization effects resulting from different membrane orientations and applied DS [221]. In pilot-scale applications using MBR effluent as FS, reported OMP rejections ranged from 80% to 99.9%, making the effluent suitable for various reuse applications [225,226]. Other studies incorporating FO into MBR (referred to as osmotic MBR) exhibited superior OMP removal performance due to the presence of a double membrane barrier and the high selectivity of FO [172,212,220].

Table 3. Studies evaluating treatment of alternative domestic WW sources with forward osmosis and including OMP.

Membrane type	Membrane configuration	Membrane area, cm^2	FS constituents*	DS constituents	OMP, n	Year of publication	Reference
Aquaporin	Hollow fiber	23,000	MBR effluent	NaCl	35	2019	[226]
Aquaporin	Flat	120	Synthetic WW	NaCl, $MgSO_4$, $C_6H_{12}O_6$	30	2018	[218]
Aquaporin, CTA and TFC	Flat	120	Synthetic WW	NaCl	30	2018	[172]
TFC	Flat	20	Synthetic WW	NaCl	8	2021	[223]
TFC	Flat	3,360	Domestic WW	NaCl	80	2021	[224]
TFC	Flat	806	Synthetic WW	$K_4P_2O_7$	5	2021	[220]
TFC	Flat	45	Primary settled municipal WW	NaCl, LiCl	43	2019	[179]
TFC	Flat	20	Syn. secondary effluent	NaCl	12	2018	[170]
CTA	Flat	14	Synthetic WW	commercial fertilizer (mainly N) + $Zn(NO_3)_2$	5	2022	[222]
CTA	Flat	20	Anaerobic MBR effluent	$(NH_4)_2HPO_4$, $NH_4H_2PO_4$, KCl	3	2017	[221]
CTA	Flat	138	Synthetic WW	NaCl	30	2015	[212]
n.a. (commercial)	Flat	2660	Secondary and tertiary domestic WWTP effluents	synthetic sea salt	4	2010	[147]
CTA	Flat and spiral wound	n.a.	Permeate from sequencing batch MBR	NaCl and seawater	23	2011	[225]

*Only the water of interest (WW from domestic sources, comparable to GW) is indicated, as most studies also evaluated the performance with DI/tap/milliQ water as FS, and some also tested seawater or brackish water as FS.
n.a. stands for “not available”.

To sum up, the performance in terms of energy requirements, contaminant rejection and fouling behavior has positioned FO as a prominent membrane technology. The observed limitations in FO applicability appear to culminate in solute fluxes, ultimately contributing to the reduction of osmotic gradients, thereby reducing water fluxes and introducing contamination risks to feed or draw solutions with the presence of solutes from the opposing solution. The optimization of current hybrid FO systems and the exploration of alternative combinations and applications to unlock the full potential of this process are necessary for the adoption of FO in widespread applications. Addressing the existing research gaps in FO, particularly in the treatment and reuse of GW in FDFO, appears as an attractive option to fill the gap of information on FO applied to GW and OMP removal as well as to push the development of FO and its application on a large scale.

1.5. Extensive greywater treatment: nature-based solutions

Nature-based solutions (NBS) have emerged as central technologies facilitating the transition towards circular economy [227], also in the field of decentralized urban water management [25,228,229], due to their contributions to sustainable water management and the additional benefits they provide. Notable examples of NBS include green roofs, retention ponds, vegetated pavements, or constructed wetlands (CW). Numerous NBS are applied worldwide, with CW as the most popular NBS. For example, CW have been commonly used in small communities (<5,000 people equivalent) in France for the past 30 years [230] and are experiencing a rapid growth in the east of China since 2006 [231]. Another example is the extensive application of stabilization ponds for WW treatment in Australia [232]. In Europe, the widespread adoption of NBS in urban environments is promoted by the European Commission, with the determination of four key domains for NBS implementation, encompassing sustainable urbanization, enrichment of ecosystem services, carbon capture for climate change adaptation and mitigation, and risk management improvement [233].

NBS mimic processes characteristic from natural systems to remove diverse contaminants from water through synergistic physical (sedimentation, filtration), chemical (precipitation, adsorption) and biological (microbiological degradation, plant uptake) processes [63,234,235]. Substrates in these systems possess the capacity to adsorb contaminants, subsequently permitting their biodegradation—whether aerobically or anaerobically—by the microorganisms. The integration of plants, a common feature in NBS, contributes to phytoremediation by absorbing and degrading contaminants through various mechanisms [235]. Additionally, NBS have the potential for thermal regulation in buildings, thereby enhancing energy efficiency and the capacity to store carbon [25,236,237]. Beyond these advantages, NBS yield several co-benefits, such as habitat creation, fostering biodiversity [238], air quality improvement and noise reduction [239] and enhancing aesthetic experiences, thus generating economic benefits through the projection of a green image [240]. Thus, they present an appealing option for addressing challenges related to biodiversity loss, ecological restoration, and degradation of natural resources [241]. In contrast, NBS demand larger footprints than other technologies, necessitate consistent water supplies and their performance may be susceptible to seasonal variations [63,64,242]. Moreover, the effluents from these systems often fall meeting reuse standards concerning pathogens [243] necessitating an additional disinfection step to ensure safe reuse [243,244].

Over the past two decades, considerable attention has been assigned to the exploration of diverse benefits associated with GW treatment with NBS, with most studies carried out at pilot-scale [234]. Some examples are CW treating GW and producing effluent applied for irrigation of school landscapes [245], or with effluents meeting the USEPA reuse standards [246]. Effluents from a pilot green wall treating GW complied with Indian guidelines for toilet flushing and irrigation [247], or with Austrian reuse legislations [248]. Additionally, the economic efficiency and social benefits of applying green roofs in highly urbanized areas was underscored [249].

Despite the multiple studies on NBS for GW treatment, limited attention has been dedicated to the evaluation of NBS performance for GW treatment specifically considering OMP. In general, studies focused on the performance of NBS achieved removal rates higher than 80% for most studied OMP with different CW configurations and substrate types [250–252]. Other studies have focused on the evaluation of the uptake and effects on plants of specific OMP, spiked at much higher concentrations than those found in real water streams. Examples of such works are ibuprofen in *Phragmites australis* [253], iopromide in *Typha latifolia* [254] or atenolol, carbamazepine and diclofenac in *Canna indica* and *Chrysopogon zizanioides* [255]. CW planted with *Phragmites australis* and *Acorus calamus* removed more than 80% of OMP from GW in most cases, and complied with the Chinese legislation for water reuse [256]. Similarly, a vertical flow CW planted with *Canna indica* and *Phragmites australis* achieved 81 to 98% removals of 5 OMP from domestic GW, and reported low risks for the environment related to the presence of OMP [257]. An option to implement in hotels and buildings is the so-called "vertECO" technology, a system with a diverse array of plant species in hydroponic regime (soilless, see next section 1.5.1.) that combines sub-surface horizontal water flow with stage-wise vertical flow in several cascading stages (Figure 2a, [258]). A vertECO unit installed at Hotel Samba (Lloret de Mar, Spain, Figure 2b) has been in operation for a decade to treat pre-settled light GW from hotel showers and washbasins. The system achieved removal rates over 80% for the majority of OMP (14 PhACs and 12 EDCs) [22] and the effluent complied with various reuse scenarios of Spanish and European legislations after a disinfection step [258,259].

Figure 2. a) Schematic overview of the vertECO technology (patent number AT516363), all stages are planted and filled with LECA. b) Picture of the system installed in Hotel Samba. Images retrieved from Alchemia-nova website (https://www.alchemia-nova.net/products/verteco/).

1.5.1. Hydroponic systems for simultaneous GW treatment and crop production

The hydroponic cultivation method involves the growth of plants directly in contact with water (bare-rooted or on a solid substrate) containing balanced concentrations of dissolved nutrients essential for optimal plant development [260]. This approach emerges as a viable alternative, particularly in arid regions and in areas with limited land availability and adds mitigation of risks related to nutrient and pesticide runoff inherent to conventional crop practices [92,261]. The adaptability of these systems facilitates their installation in diverse locations and contributes to the achievement of a most stable production through efficient nutrient management and pest control, with increased resilience against weather events [262]. Comparative studies on lettuce production reveal that hydroponic systems produce 11 times higher yields with 30–50% faster plant growth rate and 13 times less water consumption than in conventional cultivation in soil [263,264]. Furthermore, lower specific greenhouse gas emissions were reported for hydroponics in contrast to traditional cultivation [265]. Therefore, hydroponic food production is widely applied worldwide and there is a growing interest in using alternative water sources to reduce reliance on freshwater [206]. In case hydroponics are used at the same time for GW treatment and crop production, the water provides essential nutrients for the plants, which have the capacity of removing a wide array of pollutants, producing an effluent with further reuse possibilities [264,266]. This dual capacity, linking sanitation and agriculture, positions these systems as promising alternatives for decentralized scenarios, ensuring continuous food production and enhancing environmental protection [260,264]. Despite the promising potential of this dual functionality, the existing body of literature lacks studies exploring simultaneous hydroponic crop production and water treatment (and even more deficient regarding GW), with most published works using lettuce as reference crop and not including OMP (Table 4). The earliest investigation of this approach dates back to 1993, reporting successful results of tomatoes in a hydroponic system fed with synthetic secondary effluent [267]. Subsequent studies evaluated the treatment of primary treated municipal effluent in hydroponic systems with lettuces or peppers, obtaining satisfactory removals, but raising concerns regarding the accumulation of heavy metals and viruses in edible tissues [268–270]. NASA study on chives grown in biologically treated GW (containing also urine) in a closed-loop hydroponic system revealed challenges related to pH fluctuations, nitrite presence and sodium content, hindering plant growth [271]. In contrast, Eregno et al. [86] reported successful lettuce growth in hydroponic systems containing treated GW amended with urine from Norwegian student residences, and also demonstrated minimal risks associated with heavy metals and pathogens. Additionally, the high potential of green roofs for combined GW and rainwater treatment was highlighted, with the successful performance of honeysuckle *(Lonicera japonica)*, a traditional medicinal plant from Asia [128]. A recent study in Ivory Coast proposed hydroponic systems as a successful alternative for growing lettuces on raw dishwasher GW while obtaining high removal rates of standard pollutants with no detectable *E. coli* in the edible tissues[272] but without information on OMP.

Further studies reported successful lettuce growth and pollutant removal in hydroponic systems fed with raw WW [273] or treated WW [274], but requiring nutrient supplementation for optimal plant development. Examples involving other edible crops include a decentralized multistage vertical flow hydroponic system using WW from An-Najah National University in Palestine, which included corn, barley, alfalfa and sunflowers and produced high-quality effluent suitable for reuse [275]. Adrover et al. [276] showed successful results of barley growth in hydroponic systems fed with effluent WW from conventional treatment plants, but did not address effluent's quality or reuse potential.

Table 4. Studies evaluating hydroponic production of edible crops using raw or treated domestic GW/WW.

Water type	**Edible plants**	**OMP, n**	**Year of publication**	**Reference**
Nitrified urine and GW + nutrient supplementation	*Cucumis sativus* (cucumber)		2023	[277]
GW - dishwasher	*Lactuca sativa* (lettuce)		2021	[272]
Synthetic GW	*Lonicera japonica**		2020	[128]
Treated GW + urine	*Lactuca sativa* (3 varieties)		2017	[86]
Biologically treated GW + urine	*Allium schoenoprasum* (chives)		2007	[271]
GW surfactants[1] (separately) + nutrient supplementation	*Triticum aestivum* (dwarf wheat)		2004	[278]
Domestic wastewater or UASB[2] effluent (with and without nutrient supplementation)	*Lactuca sativa* (3 varieties)		2019	[279]
Domestic WW	*Ipomoea aquatica**		2018	[280]
Domestic WW	*Bidens pilosa L** and *Amaranthus hybridus L**		2018	[281]
Domestic WW	*Medicago sativa, Zea mays, Hordeum vulgare, Helianthus annuus* (alfalfa, corn, barley, sunflower)		2012	[275]
Synthetic WW	*Solanum lycopersicum* (midi-tomato)		1993	[267]
Primary treated municipal effluent	*Lactuca sativa*		2009	[270]
Primary treated municipal effluent	*Lactuca sativa*		2000	[269]
Primary settled municipal effluent	*Lactuca sativa*		1996	[268]
Treated municipal WW + nutrient supplementation	*Lactuca sativa*	9	2021	[282]
Treated domestic WW (with and without nutrient supplementation)	*Lactuca sativa*		2018	[274]
Treated municipal WW from a conventional treatment plant	*Hordeum vulgare* (barley)		2013	[276]
Secondary effluent	*Oryza sativa, Solanum lycopersicum, Triticum aestivum* (rice, tomatoes, wheatgrass)		2023	[283]
Secondary effluent, diluted 50% and not diluted; tertiary effluent and UASB effluent	*Lactuca sativa*		2005	[284]
Tertiary effluent from a local WWTP + nutrient supplementation	*Sorghum bicolor*	16	2021	[285]
Tertiary WWTP effluent	*Lactuca sativa* and *Spinacia oleracea* (spinach)	14	2021	[286]

[1] Sodium laureth sulfate (anionic), alcohol polyethoxylate (nonionic), cocamidopropyl betaine (amphoteric)
*Plants employed in traditional medicine.

1.5.2. Organic micropollutants in hydroponic systems with edible crops

The journey of OMP from water to the different parts of plants is a complex process, influenced by environmental and OMP-specific factors. A first step is their rapid adsorption onto the roots [287], depending on plant type and OMP properties. MW determines whether the compound can enter the plant, with compounds with MW > 400 g/mol predominantly accumulating in roots [288]. Additionally, hydrophobic OMP tend to also accumulate in the roots because of their affinity for the lipid content [107,255,289]. The charge of OMP, determined by pKa, affects their interactions with the negatively charged plant roots [290]. Subsequently, OMP gradually move to the shoots, leaves and fruits with the transpiration flow [287,288], with high transpiration rates related to higher OMP accumulation [291]. Highly water soluble, neutral compounds with MW<300 are more prone to translocate to different parts of the plants, with minimal accumulation in roots [255,288]. Finally, the OMP undergo degradation within plant tissue through complex biochemical processes [292] leading to TP formation [293]. In addition, the type of plant influences OMP accumulation, with leafy crops exhibiting the highest propensity for uptake, followed by root vegetables, cereals and fruits [294,295].

Over the last decade, numerous studies have focused on the study of the behavior of OMP in water-plant systems. Several laboratory-scale studies evaluated OMP behavior in hydroponics with edible crops (commonly lettuce) grown in DI (deionized) water with dissolved nutrients, usually including a limited number of OMP at elevated concentrations [296–299]. Publications focused on uptake and effects of single OMP in edible crops reported safety for most cases but emphasized on the need for further research to refine the risks associated with other OMP [108,300]. Importantly, in fact, cumulative exposure to multiple compounds increases the associated risk [90,301] and, thus, expanding the knowledge on the effects and behavior of OMP mixtures is crucial [92]. Most studies evaluating OMP uptake in crops irrigated with reclaimed water were performed in soil but not in hydroponics [113,293,295,302]. A larger plant uptake in hydroponics is foreseen due to the absence of interactions with the soil system [107], thus more studies are required to evaluate the potential of alternative water sources for crop production in hydroponics. Kreuzig et al. [282] evaluated hydroponically cultivated lettuces in reclaimed WW, and reported over 90% removal of most studied OMP, with just carbamazepine reaching the edible parts. Removal rates over 80% were reported for most OMP in a hydroponic system testing sorghum grown in tertiary effluent [285], while the accumulation of different perfluoroalkyl carboxylic and sulfonic acids was observed in lettuces and spinach grown in WWTP effluent [286].

To sum up, the potential of NBS for decentralized GW/WW treatment as well as of hydroponic cultivation have been acknowledged. Even so, notable research gaps exist on the integration of NBS and edible crop production with GW, OMP removal, OMP uptake by the crops and the related risks.

1.6. Bibliometric study

A bibliometric study on the Scopus database [303] was carried out with the aim of analyzing the evolution of the interest of the scientific community about relevant topics to this thesis. The criteria were to find scientific articles including the topics in title-abstract-keywords. Document type was limited to article (excluding reviews) and source type was limited to journal (excluding books or conference papers, for example). The query string was used with the following terms using the *advanced search tool* in Scopus: *TITLE-ABS-KEY ((term A AND term B) AND (LIMIT-TO (SRCTYPE, "j")) AND (LIMIT-TO (DOCTYPE, "ar")).*

The bibliometric analysis revealed notable disparities in number of publications, with the terms "*OMP and water treatment"* exhibiting the highest number of published studies, followed by "*forward osmosis"* and "circular economy *and water"* (Table 5). Conversely, *"circular economy and forward osmosis"* had the lowest number of publications. Notably, while publications on forward osmosis have declined in the past years, there was a marked increase in publications related to *"Circular economy and water"* and *"NBS and water treatment"* (Figure 3 left), indicating the emergence of a relatively emerging fields. Interestingly, a similar trend was observed in the evolution of "*Nature-based solutions"* and either *"circular economy"* or *"greywater"* (Figure 3 left) or *"OMP"* (Figure 3 right), highlighting the growing significance of NBS technologies.

Table 5. Number of scientific articles obtained from the search in Scopus database (reviews are excluded). Results from March 7th, 2024.

Searching terms	Published articles (up to 2023)
Tourism AND water reuse	72
Tourism AND greywater¹	60
Circular economy AND water	3134
Circular economy AND greywater¹	46
Circular economy AND nature based solutions	104
Circular economy AND forward osmosis	7
Greywater AND reuse	907
Decentralized² AND greywater¹ treatment	184
Greywater AND organic micropollutants³	118
Organic micropollutants³ AND water treatment	15230
Organic micropollutants³ AND water reuse	884
Forward osmosis	3146
Forward osmosis AND greywater¹	14
Forward osmosis AND OMP	91
Fertilizer⁴ drawn forward osmosis	126
Nature based solutions AND water treatment	1151
Nature based solutions AND greywater¹	108
Nature based solutions AND organic micropollutants³	389
Hydroponic AND greywater¹	18
Hydroponic AND organic micropollutants³	110

Other keywords included under the same search related to the term:
[1] Greywater OR (grey AND water) OR graywater OR (gray AND water)
[2] Decentralized OR decentralised
[3] (Organic AND micropollutants) OR (emerging AND contaminants) OR pharmaceuticals
[4] fertilizer OR fertiliser

The importance of OMP is underscored by the substantial volume of publications on this subject. Although the progression of studies concerning *"OMP and water treatment"* parallels that of *"OMP and water reuse"* (Figure 3 right), the vast disparity in publication numbers (over 15,000 published articles for treatment versus approximately 900 for reuse, Table 5) delineates the extensive exploration of such compounds in the treatment, yet not that abundantly considered in reuse purposes.

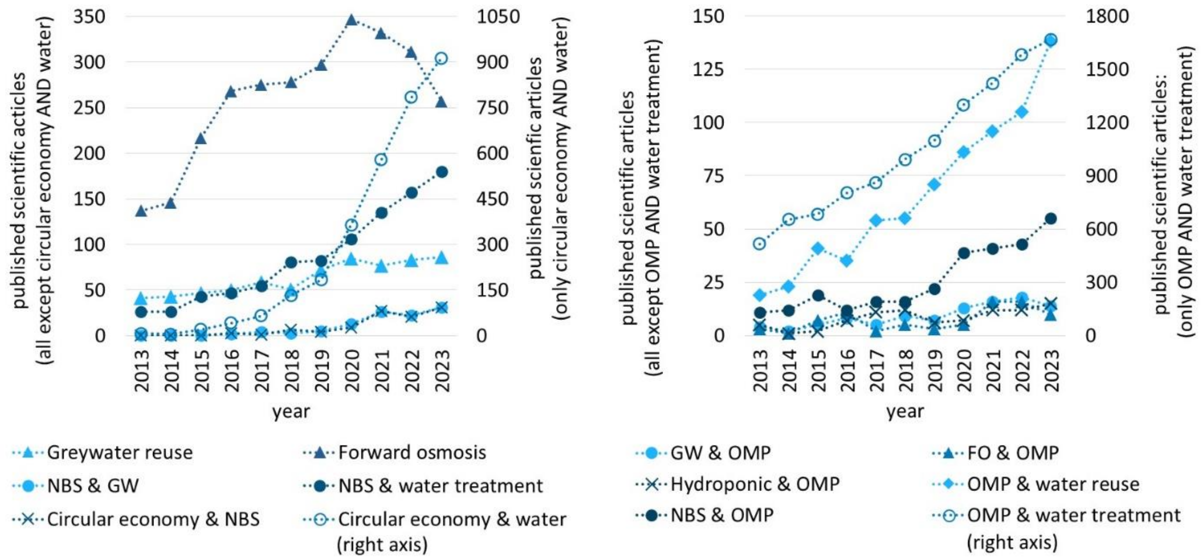

Figure 3. Number of scientific articles (reviews excluded) over the last ten years (2013-2023) for the topics with highest number of publications increase over the last ten years (left) and publications considering OMP (right). Results of the search in the Scopus database carried out on March 7th, 2024.

With regards to FO, limited studies have focused on the FDFO approach or have included OMP, offering avenues for further investigation. Moreover, the bibliometric analysis revealed a substantial gap in knowledge concerning GW, particularly within the tourism sector (Table 5). Implementing FO and hydroponic systems for GW treatment and crop production offers a promising pathway for sustainable development. However, limited literature exists on these matters, including the performance of FO in GW treatment considering OMP and the fate and risks associated to OMP in hydroponic systems using alternative water sources. Addressing the escalating challenges of water scarcity and quality necessitates innovative approaches, especially in the context of water reuse, where substantial untapped potential remains, particularly concerning GW and OMP. Bridging these gaps is essential to develop transformative solutions aligned with circular economy principles in water management, while enhancing water security, mitigating environmental and human health risks, and promoting sustainable tourism practices.

2. Objectives

The general objective of this thesis was to **explore the feasibility of decentralized greywater treatment using forward osmosis and hydroponic systems, with a focus on ensuring safe reuse**.

In order to achieve the general objective, the research sub-objectives involved various aspects, examining:

1. the existing water management practices in hotels, as a relevant scenario for decentralized GW treatment and reuse in water scarce areas, providing recommendations for improvement.
2. the potential of FO for GW treatment and reuse related to:
    - the performance of the fertilizer-drawn forward osmosis approach, in particular close to osmotic equilibrium,
    - the achievement of the proper draw solution dilution for direct application in hydroponics,
    - the use of recovered MgP salts as draw solution in FO and their suitability as fertilizers in hydroponic systems,
    - the fate of OMP in FO and the impact of the characteristics and contact time of feed and draw solutions on OMP rejection,
    - the compliance with the EU water reuse legislation.
3. the potential of hydroponic systems to integrate GW treatment with edible crop production (lettuce as a reference crop) and estimating:
    - the suitability of GW as a growing medium for plants,
    - the pathway of OMP from GW to the edible parts of the crops,
    - the compliance of the effluent respect to the EU and Spanish water reuse legislations,
    - the associated risks to human health concerning OMP exposure through the consumption of crops grown in GW.
4. the exploration of the feasibility of combining FO and hydroponics for the treatment and reuse of GW in hotels, as well as the identification of the main barriers to this implementation.

3. Results

ARTICLE 1. Water management practices in Euro-Mediterranean hotels and resorts.

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Water management practices in Euro-Mediterranean hotels and resorts

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ABSTRACT
The Mediterranean region, which is one of the world's leading tourist destinations, is vulnerable to climate change and impacted by human water demand. Tourism is recognized as a major water-consuming sector, and the growth in tourism establishments has been matched by a growth in water demand. Hotels represent the highest water consumption rates in the tourist sector. In this study, a survey was carried out in the Mediterranean region. Responses from 80 hotels of different categories and countries were gathered, discussed and compared regarding water supply, water consumption and monitoring, water-saving strategies, and environmental awareness and willingness for future improvements.

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Introduction

Tourism is not only the most important socio-economic sector in many countries but also one of the fastest-growing economic sectors internationally (Rico-Amoros et al., 2009). In 2019, global tourist arrivals (overnight visitors) grew by 4%, reaching 1.46 billion (UNWTO, 2020). The Mediterranean region is as one of the world's leading tourist destinations, with more than 20% of worldwide arrivals (Gabarda-Mallorquí et al., 2017), which increased by 5% in 2019 (UNWTO, 2020). However, at the same time tourism has been recognized as a significant water-consuming sector at local, regional and global scales (Gössling, 2015). The estimated 300 million tourists per year in the Mediterranean region are putting substantial pressure on the local water demand (Gössling et al., 2012; Kent et al., 2002), indicating a similar growth in water demand for tourist establishments (Kasim et al., 2014). Tourist facilities in water-scarce areas of the Euro-Mediterranean region are facing the same growth in the numbers of tourists but also a simultaneous decrease in the availability of water resources (Cazcarro et al., 2014). In fact, Parry et al. (2009) estimated that globally approximately 3.2 million people will face water stress by 2100, based on a climate change scenario associated with an increase in temperature of 4°C. Thus, future climate change scenarios are forecasting increasing pressure on water resources globally

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(Nguyen et al., 2016) and in the Mediterranean region, where both water quality and availability have decreased due to the change in rainfall patterns and overexploitation of water resources (Deyà-Tortella & Tirado, 2011; Gabarda-Mallorquí et al., 2018).

Tourism sustainability depends on an adequate water supply in terms of both quantity and quality (Deyà-Tortella & Tirado, 2011). The optimization of the use of water resources is also important to cope with the growing tourist numbers and their seasonality (Kasim et al., 2014). Therefore, water consumption in tourism is receiving increasing attention from organizations such as the United Nations World Tourism Organization (UNWTO), United Nations Environment Programme (UNEP), and Organisation for Economic Co-operation and Development (OECD), which recognize the urgent need to optimize and reduce water consumption (Gössling, 2015).

Becken (2014) reported that the tourism water consumption in 21 countries across the world ranged between 200 and 900 L per guest per night. In the Mediterranean area, the daily consumption is estimated to range between 300 and 880 L (Dworak et al., 2007). Tourists consume water for showering, flushing toilets and water-related activities such as spas, swimming and diving. Indirectly, tourist water consumption also includes water used for washing textiles, preparation of food, and maintenance of water features and green areas (e.g., golf courses and parks), although it varies based on the number of beds and occupancy as well as the facility's star classification (Barberán et al., 2013; Rico-Amoros et al., 2009). Hotels represent the highest water consumption rates in the tourist sector (Hocaoglu, 2017), where guests consume up to three times the volume they would consume at home (Barberán et al., 2013). In general, there is a tendency for higher standard accommodation to consume significantly higher water volumes, with the highest water use rates in hotels with spas and large or multiple swimming pools (Bohdanowicz & Martinac, 2007; Gössling et al., 2012).

Various surveys have been designed to describe general hotel information (e.g., hotel size, stars and number of guests), water use and consumption (Rico et al., 2020; Scanlon, 2007; Torres-Bagur et al., 2019; Wyngaard & De Lange, 2013), and water-saving measures (Barberán et al., 2013; Gatt & Schranz, 2015; Rico et al., 2020). These surveys were usually addressed to hotel managers and technical staff (Chan et al., 2017; Deyà-Tortella & Tirado, 2011; Gabarda-Mallorquí et al., 2017; Wyngaard & De Lange, 2013), although some included hotel guests (Gabarda-Mallorquí et al., 2018; Gössling, 2015) and other stakeholders (Tekken & Kropp, 2015). Previous studies also focused either on water saving/treatment technologies or on water management and consumption within the establishment, but never considered both elements in the same study. Moreover, these studies were usually implemented on individual hotel, city or national scales, but did not cover larger areas that span multiple countries (McLennan et al., 2017). Additionally, most existing surveys included only up to 30 responses (Chan & Hawkins, 2012; Gössling, 2001; Kasim, 2009; Wyngaard & De Lange, 2013).

This study assessed the current water management practices and potential for on-site water treatment and reuse via a survey answered by 80 hotels throughout the Euro-Mediterranean region. We aimed to expand the existing body of literature on water and tourism by understanding patterns in a wider multinational area. A comprehensive approach was applied within the establishments combining both infrastructural characteristics and environmental management approaches, including certifications. The novelty of this research lies in: (1) coping with both the topics of water management and technologies for (waste)water treatment and water-saving devices, which are generally assessed separately; (2) incorporating a large number of countries in the study; (3) applying cluster analysis (CA) to understand patterns among the responses and types of establishments; and (4) including more survey responses than in most other published research on these topics. The goal was to provide overall and specific recommendations for the identified hotel clusters to water practitioners and policymakers on the most appropriate ways to improve water management in tourist facilities.

Methodology

Questionnaire

A questionnaire was delivered to hotels in different countries in the Mediterranean region, within a 1 km range of the Mediterranean Sea, since coastal areas have the highest concentration of tourist-related establishments and the highest number of visitors (Rico-Amoros et al., 2009). A database with hotel contacts from the coastal Euro-Mediterranean basin comprising 13 countries (Albania, Bosnia and Herzegovina, Croatia, Cyprus, France, UK (Gibraltar), Greece, Italy, Malta, Monaco, Montenegro, Slovenia and Spain) plus Turkey was compiled. Questionnaires were addressed to hotel owners or managers, in accordance with other studies (Chan et al., 2017; Deyà-Tortella & Tirado, 2011; Gabarda-Mallorquí et al., 2017; Wyngaard & De Lange, 2013). Collecting information about the water uses was mainly focused on needs other than tap/shower water. In particular, the hotels were asked to provide information about the presence and capacity of indoor/outdoor swimming pools and spas, as well as other infrastructures consuming large(r) amounts of water or for water treatment.

The questionnaire, developed in SurveyMonkey (http://www.surveymonkey.com), was answered either by using the link sent via email or by telephone (randomly selected hotels). It was translated into nine languages: Albanian, Croatian, English, French, Greek, Italian, Slovenian, Spanish and Turkish. For the list of questions in the English version, see Table S1 in the supplemental data online. In total, 5269 hotel facilities included in the obtained database received the survey in the framework of an European Union (EU) project (2014–17). The questionnaire consisted of three sections, as follows:

- *General information*. This section covered general questions about the establishment, such as star category, year of construction, capacity (number of beds), whether the establishment opens continuously or seasonally, occupancy and certification (quality assurance, environmental management or others).
- *Water cycle*. This part was the core of the questionnaire, containing the questions to collect data on the sources of water supply (tap and/or others); the extent of water consumption monitoring; the presence and size of pools/spas; water-related maintenance of pools/spas; the presence and size of golf courses/green areas; the presence of other water-consuming features; the use of water-saving devices; grey-/black-/wastewater management and treatment, where applicable.

- *Conclusion*. General questions about environmental awareness were posed, as well as the willingness of respondents to actively participate in future efforts towards innovative water treatment and reuse solutions.

Where possible, the missing values of some complementary questions (e.g., number of bedrooms or number of guests) were substituted based on the most complete information (i.e., number of beds).

Statistical analysis

Cluster analysis (CA) was used to identify individual hotels with similar characteristics and classify them into groups with high internal homogeneity (large similarities within each group) but high external heterogeneity (large differences across groups) (Hair et al., 1999). It was used in this study to sort hotels so that those allocated to a particular group were in some way similar. This can be summarized in the following steps:

- Measurement of the distance apart of all pairs of hotels (equation 1).
- Development of a routine or algorithm for forming clusters based on these distances.

CA has been used in many types of applications, for example, to investigate groundwater diffuse pollution (Azzellino et al., 2019), patterns of atmospheric pollution (Lu et al., 2006) or to investigate hotel energy performances (Pieri et al., 2015).

A hierarchical clustering algorithm (HCA) (Afifi et al., 2004) was applied to the general information items (i.e., number of bedrooms, beds and guests, certifications, and the presence of pools or spas) to analyse the similarities among different hotels' facilities. At each step of this agglomerative hierarchical approach, the two closest clusters are merged into a single new cluster. In each step of the agglomerative hierarchical approach, an observation or a cluster of observations is merged into another cluster. Thus, the number of clusters shrinks and the clusters themselves grow larger. The Euclidean distance was used as the distance metric:

$$d(x,y) = \sqrt{\sum_{k=1}^{p} (y_k - x_k)^2} \tag{1}$$

where x and y refer to a pair of hotels; and p is the considered parameters; while the Ward linkage method was selected as the agglomeration criterion. The obtained dendrogram (see Figure S1 in the supplemental data online) was used to choose the number of clusters to retain.

CA was also chosen to smooth the potential over- and underrepresentation of some countries in the sample, to dilute such differences in clusters of similar characteristics.

The representativeness of the sample obtained from the survey was tested through both a Kruskal–Wallis test (see Table S2 in the supplemental data online) and a Chi-square test (see Table S3 online), respectively testing for differences in hotel characteristics, and for the homogeneity of distribution of hotel categories among countries.

Results

General data about participation and hotel clustering

In total, 113 responses were obtained, although in 28.3% of these the general information was insufficient for further analysis. Therefore, the sample size of the multivariate dataset used to implement CA was 80 hotels (see Figure S2 and Table S4 in the supplemental data online).

The responses covered the whole range of hotel star category, age and size (Figure 1), and were obtained from Turkey and all the Euro-Mediterranean countries but two. The highest level of participation was recorded in Greece (30%). There were no responses from two of the countries contacted: Bosnia and Herzegovina, and Montenegro.

Even though the sample was not fully representative of the Euro-Mediterranean basin's and Turkey's availability of establishments, with some countries overrepresented (e.g., Greece, Malta, Albania and Turkey) and some others underrepresented (e.g., Italy and Croatia), the information collected is valuable since data were obtained from almost all the Euro-Mediterranean countries, making information also available for countries (e.g., Albania, Monaco and Gibraltar) which are generally missing from Eurostat's global statistics (see Figure S3 in the supplemental data online). Moreover, the sample representativeness was confirmed in a Kruskal–Wallis test applied to the hotel characteristics, assessing the absence of significant differences between countries (see Table S2 online), and, through a Chi-square test, whether the distribution of hotel categories was different between countries (see Table S3 online). Both tests confirmed that it was not possible to obtain unbiased results from the sample.

The responses covered the entire range of hotel star ratings, age and size (Figure 1). Most hotels (87.6%) belonged to three to five-star categories, and four-star hotels were the most represented (Figure 1a). Regarding the year of construction, 38.2% of the hotels were built before 1990 and 59.2% were built from 1990 onwards (Figure 1b). More than half of the hotels (58.0%) had fewer than 250 bedrooms (Figure 1c).

Hierarchical cluster analysis (HCA) was used to group the 80 hotels based on their size and main characteristics (i.e., number of beds/bedrooms, certifications, number of guests and presence of pool/spa facilities) (Table 1). These characteristics were chosen for the multivariate data exploration performed through CA since they were very effective in profiling the different hotels and they also presented the lowest rate of missing information. CA is in fact sensitive to missing values and, to give reliable results, it is necessary to use only complete data, a condition that would cause our sample size to significantly shrink.

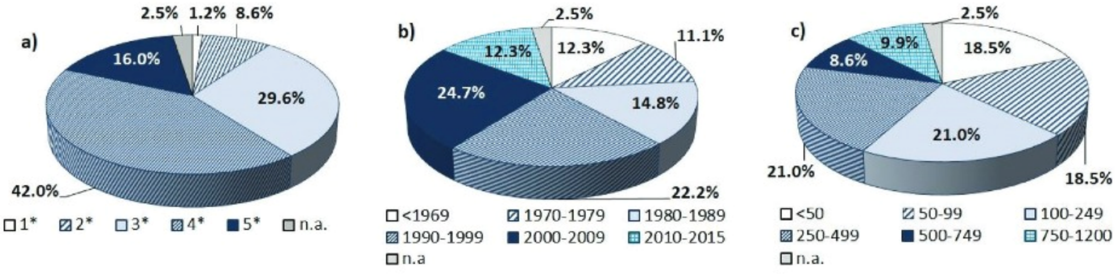

Figure 1. General data for hotels participating in the survey: (a) stars; (b) year of construction; and (c) number of beds.

Table 1. Characteristics of the hotel clusters.

Cluster	Hotels (*n*)	Beds/bedrooms (median)	Certification (yes/no, %)	Number of guests (median)	Median number of guests (above/below sample mean)	Pool (yes/no, %)	Spa (yes/no, %)
1	18	51/25	No (100%)	4750	Below	No (100%)	No (100%)
2	17	400/179	Yes (76.5%)	20,000	Above	Yes (100%)	Yes (100%)
3	11	76/41	Yes (100%)	5000	Below	Yes (72.7%)	No (100%)
4	23	145/75	No (100%)	8606	Slightly below	Yes (100%)	No (100%)
5	11	811/328	Yes (41.7%)	125,750	Above	Yes (100%)	Yes (83.3%)

HCA was used to identify five main clusters of well-defined characteristics that are shown in Table 1 in terms of variable *Z* scores (Figure 2).

Certification seemed to be an important aspect for hotel performance since many respondents in this study reported having one or more certifications (e.g., ISO 14001, ISO 9001, Travelife or European Ecocertification). Cluster 1 had the smallest hotels, no certifications and no pools or spas. Clusters 2 and 5 had the largest hotels, all with certifications, and most of them had pools and spas. Clusters 3 and 4 were small and medium-sized hotels, respectively; most had certifications and pools, but no spas. Most hotels presented a seasonal variation in guest occupancy and the highest number of hotels with no seasonality were concentrated in clusters 4 and 5 (see Figure S4 in the supplemental data online).

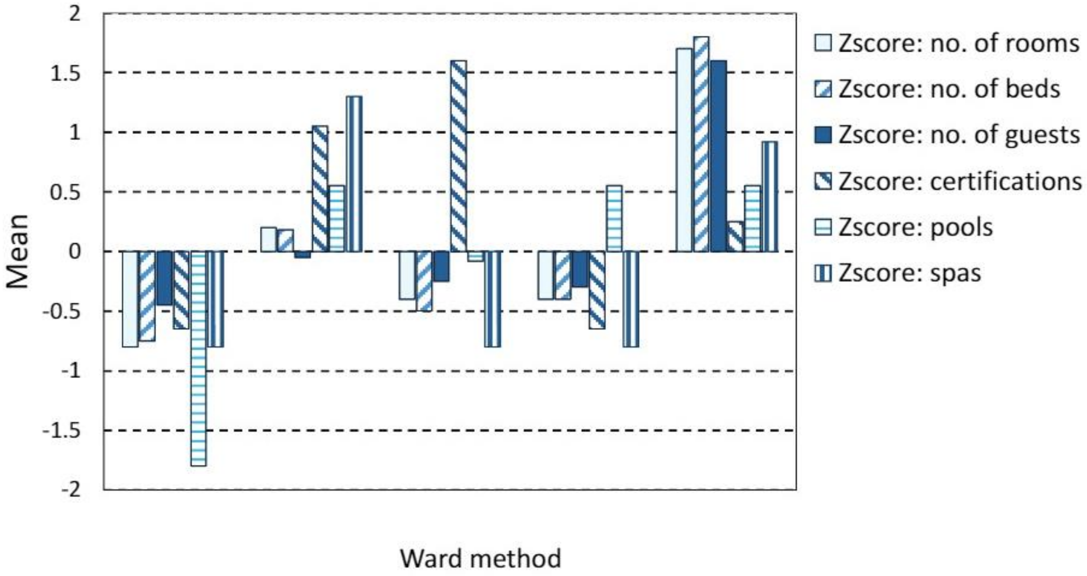

Figure 2. Hierarchical cluster analysis (HCA) in terms of variable *Z*-scores (average = 0, standard deviation = 1): characteristics of the five clusters in terms of rooms, beds, guests, certifications, pools and spas.

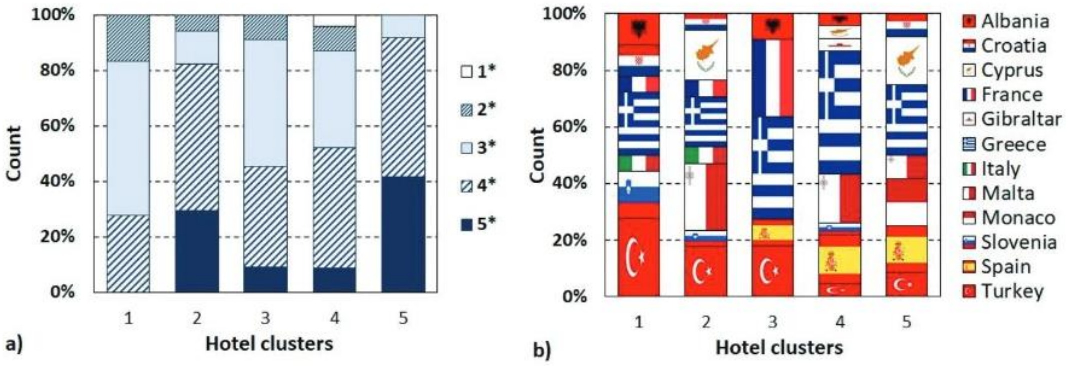

Figure 3. (a) Hotels categorized by cluster; and (b) hotels clusters categorized by country.

Figure 3 shows the star classification and country composition of each cluster. Note that the five-star category was not present in cluster 1, while clusters 2 and 5 were characterized by the largest amount of four- to five-star hotels (Figure 3a). It is noteworthy that the country composition of the clusters is quite variable (Figure 3b). Even though some of the countries were more strongly associated with some of the clusters, no cluster was dominated by a single country, which confirmed the transnational representativeness of the sample. In particular, 83.3% of Turkish hotels (*n* = 12) were mostly associated with the first three clusters, while 54.2% and 85.7% of Greek (*n* = 25) and Spanish (*n* = 6) hotels were associated with clusters 4 and 5. French hotels (*n* = 5) were mostly associated with cluster 3 (60.0% of hotels), while all the hotels from Malta (*n* = 9) belonged to clusters 2, 4 and 5.

Hotel water supply

The water sources for most applications (i.e., tap water, toilet flushing, heating, swimming pools and spas, water features, laundry, irrigation, and cleaning the exterior) were the municipal network water supply and own well (see Figure S5 in the supplemental data online). In fact, most hotels that provided this information relied on the municipal water supply network as their main or only water source (69.9%), followed by their own well (16.0%), treated wastewater (4.3%), surface water (2.9%), seawater (2.1%) and collected rainwater (1.1%). It should also be noted that alternative water sources were only for specific uses within the hotels, and always in addition to municipal network water for most of the other uses. Among alternative water sources, seawater was mainly used for indoor/outdoor swimming pools and spas (seven hotels); treated wastewater was used for flushing toilets, irrigation and cleaning purposes (eight hotels); and collected rainwater was used for irrigation, golf courses and cleaning purposes (four hotels) (see Table S5 online).

When the results were disaggregated by cluster, clusters 1 and 3 had the least use of alternative sources (only one hotel) (see Figure S6 in the supplemental data online). These two clusters had the smallest hotels, with a lower incidence of water features such as green areas or pools. Nonetheless, all the hotels in cluster 3 had certifications, in contrast to cluster 1 where none of the hotels had certifications. Hotels in cluster 2 (large, with pools and certifications) were the ones using more alternative water sources. Within cluster 5 (which includes the largest hotels and 42% of hotels with certifications), only 8% of the hotels that answered this question used alternative water sources for some of the uses within the establishments (see Figure S6 online). These results indicate that having certifications was not related to the implementation of alternative water sources or with hotel size. Seawater was mainly used for swimming pools in clusters 2 and 4, and rainwater for irrigation, golf courses and cleaning purposes in clusters 2, 4 and 5 (see Table S5 online).

Hotel water consumption

In this study, 74.1% of all hotels had swimming pools and 33.3% of all hotels also had a spa. Conversely, 25.9% of the hotels participating in the survey had neither pool nor spa. None of the hotels had a spa without a pool. The average number of indoor pools was only 0.9, while the average number of outdoor pools was 1.6; two out of three hotels had more than one outdoor swimming pool. The presence of a pool was related to star category, with 100% of five-star hotels having pools, followed by 79.4% of four-star and 66.7% of three-star hotels. Regarding pool capacities, most of the respondents with a total swimming pool volume over 750 m^3 belonged to four- to five-star hotels. In contrast, small-capacity swimming pools were distributed throughout the different star categories.

The distribution of swimming pool sizes in the sample population depended greatly on the location of the pool (indoor or outdoor). Indoor and outdoor pool size ranged from < 50 m^3 to > 2500 m^3 (see Figure S7 in the supplemental data online). Almost half of the indoor pools had a capacity of 50–100 m^3, while the size of outdoor pools was distributed more equally. For hotels with more than one pool, the capacity corresponds to the sum of all the outdoor pools. Hence, in some cases high outdoor pool capacity could be associated with multiple pools of smaller size.

The most frequent type of pool/spa water treatment was rapid sand filtration (24.8% of respondents), followed by cartridge filter (17.6%) and coagulation (13.6%). Disinfection was mainly carried out by chlorination (32.0%), followed by sodium hypochlorite (10.4%). Only 1.6% of the hotels used alternative disinfection methods (ozone or ultraviolet (UV) irradiation).

To determine water consumption other than for pools/spas, specific questions targeted the laundry and maintenance of green areas. The survey revealed that 39.5% of hotels outsourced their laundering (bed linen, towels, kitchen textiles, etc.). A further 33.3% carried out laundry on their own premises, while 2.5% of the hotels relied on both internal and external laundry services (24.7% of the respondents did not provide this information) (Table 2).

Table 2. Percentages of laundry carried out on-site, monitoring water consumption and willingness for future improvements, by cluster.

	Laundry on-site (%)				Monitoring of water consumption (%)					Willingness for future improvements (%)			
Cluster	Yes	No	Partly	n.a.	Complete	Indoor/outdoor	None	Other[a]	n.a.	Yes	No	Other[b]	n.a.
1	50.0	44.4	5.6	0.0	55.6	16.7	0.0	0.0	27.8	44.4	11.1	22.2	22.2
2	29.4	29.4	0.0	41.2	35.3	11.8	0.0	11.8	41.2	11.8	29.4	5.9	52.9
3	18.2	45.5	9.1	27.3	54.5	0.0	0.0	9.1	36.4	18.2	0.0	36.4	45.5
4	30.4	43.5	0.0	26.1	39.1	8.7	4.3	8.7	39.1	47.8	0.0	13.0	39.1
5	33.3	33.3	0.0	33.3	25.0	25.0	0.0	0.0	50.0	41.7	8.3	8.3	41.7
Total	33.3	39.5	2.5	24.7	42.0	12.3	1.2	6.2	38.3	34.6	9.9	16.0	39.5

Note: n.a., Not answered.

[a] Consumption is monitored independently.

[b] Answers such as 'not yet', 'planning for the future', etc.

Outsourcing or doing their own laundry did not show a correlation with hotel size (Figure 4). Additionally, average bed capacity was not associated with either outsourcing or washing laundry on-site. Although outsourcing was not related to hotel size, when disaggregating the hotel clusters, laundry outsourcing took place in both smaller hotels in cluster 1 and in larger hotels in clusters 2 and 5 (Table 2).

Regarding water metering, many hotels (42.0%) monitored only the overall water consumption, while 12.3% of hotels monitored indoor and outdoor consumption separately (Table 2). Only two hotels reported that they did not monitor their water consumption. Three-star hotels monitored only total water consumption, while some of the larger four- to five-star hotels also implemented separate monitoring. A few hotels (6.2%) monitored the consumption in the various hotel facilities (e.g., separately for bedrooms, kitchen, pool, spa, green areas and air-conditioning) independently. Disaggregating the analysis by hotel cluster (Table 2), we can observe how larger hotels (clusters 2 and 5) had the lowest percentage of full monitoring of water consumption. Hotels with certifications were more active in water monitoring by collecting information about water consumption and reported their willingness to provide more information. Conversely, hotels with more certifications were not necessarily the most active in using innovative systems to reduce their water consumption or directly related to their willingness for future improvements.

Maintenance of green areas was another cause of high-water consumption, and directly related to the hotel's surface area: the larger the area, the higher the need for irrigation, also due to the higher rate of evaporation (especially in dry regions). Results showed that most hotels (65.5%) had small green areas (< 1000 m^2), and just 5.2% had a large area to be irrigated, between 10,000 and 15,000 m^2 (see Figure S8 in the supplemental data online).

Just four establishments had golf courses (all these hotels also had pools), but they did not provide further information about star category, guests or any other data.

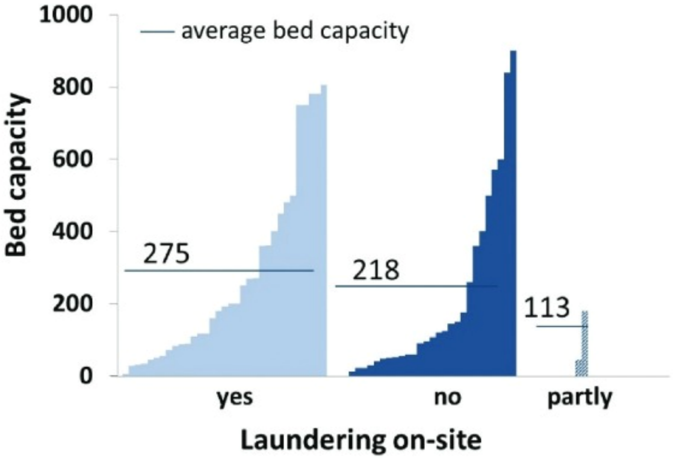

Figure 4. Proportion of hotels laundering on-site as a function of bed capacity. Note: Each bar corresponds to one response (*n* = 79).

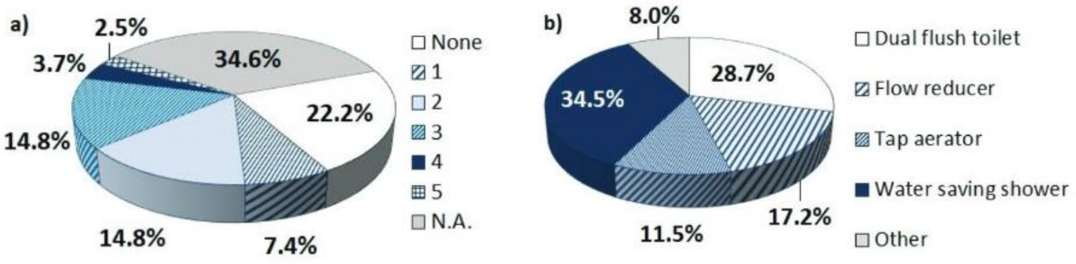

Figure 5. Water-saving devices installed in the hotels by (a) number and (b) type. Note: n.a., Not answered.

Table 3. Separation, treatment and reuse of different types of water.

Water management activity	Yes (%)	No (%)	n.a. (%)
Separation of grey/blackwater	18.5	50.6	30.9
Treatment of wastewater	8.6	39.5	51.9
Treatment of greywater	4.9	12.3	82.7
Treatment of blackwater	3.7	13.6	82.7
Reuse treated wastewater, including grey, black and wastewater	9.9	0.0	90.1

Note: n.a., Not answered.

Hotel water-saving strategies

Basic water management strategies included water-saving devices and reuse of (waste)water. A total of 22.2% of the total sample size had not installed any water-saving device, 43.2% had implemented at least one water-saving measure and 37.0% had implemented from one to three measures (Figure 5a). Among these, the most frequent devices were water-saving showers and dual-flush toilets (Figure 5b).

Wastewater collection, treatment and reuse

Most hotels (50.6%) did not separate grey-/blackwater, nor did they treat any of the liquid waste (Table 3). A total of 18.5% of the responding hotels separated grey-/blackwater, and some of them (9.9% of the total) reused it (Table 3), mainly for flushing toilets.

Most of the non-reused treated and non-treated liquid waste was discharged into the municipal sewage system, either directly (27.2%) or after collecting it in a septic tank (8.6%). Only 3.7% of the respondents (n = 3) had other options for discharge, and 60.5% did not answer this question.

Infrastructure improvements

The questionnaire addressed past infrastructure improvements at any step in the water cycle and/or the willingness of hotel managements to initiate or continue such improvements in the future.

Of the 80 hotels that participated in the survey, 27.2% had improved part of their water infrastructure, and 48.1% had not upgraded, not even partially, their water infrastructure in the last 16 years (40.9% and 81.8% of these were built before 1980 and 2000, respectively). The most frequent answer was the upgrade of the water distribution system (22.2% of hotels). Just one hotel had improved its wastewater collection system (1.2%), and 3.7% of hotels had implemented other types of improvements (72.8% of the respondents did not answer this question).

Environmental awareness, willingness for future improvements and recommendations

Almost half of the hotels (48.1%) considered environmental awareness, preservation of natural resources and eco-tourism as part of their business strategy. A total of 7.4% of the hotels considered this issue to be of secondary importance, while 6.2% were not environmentally aware, and 38.3% did not answer this question. Many hotels replied that they were considering improving their water-related infrastructure (34.6%). Conversely, 25.9% were not willing to implement any measure due to the lack of financial means (39.5% did not answer this question).

Disaggregating the analysis by hotel cluster, the willingness to optimize the water cycle was not homogeneous among the different hotel clusters (Table 2). The highest propensity to invest in technological improvements seems to be concentrated in larger hotels with environmental certification and pools (cluster 5) and in the medium-sized category in cluster 4, but also in small hotels in cluster 1 (with a range between 41.7% and 47.8% of respondents willing to undertake improvements) (Table 2). Cluster 2, with the largest variety of alternative water sources, showed the lowest propensity for further improvements.

Discussion

General information about participation and hotel certification

The response rate in this study was low (1.5%) with 113 responses (80 of them complete) out of 5269 invitations sent. The responses covered the whole range of hotel star category, age and size (Figure 1), and were obtained from Turkey and all but two Euro-Mediterranean countries (see Figure S2 in the supplemental data online). However, the number of respondents appears to exceed that of other studies on water management strategies in hotels (Deyà-Tortella & Tirado, 2011; Gabarda-Mallorquí et al., 2017) and there are very few studies covering larger areas or different countries (McLennan et al., 2017). CA was used to smooth the over- and underrepresentation of some countries in the sample, diluting these differences in clusters with similar characteristics. Most of the respondent hotels belong to the three- to five-star category, while only 9.8% of the responses concerned one- and two-star hotels.

The fact that clusters of hotels with similar characteristics were found to be transnational suggests that country-specific legislation might be of secondary importance. Acquiring information on country-specific regulations was out of the scope of our study, but this should certainly be considered in future investigations.

In accordance with other studies in the Mediterranean area (Deyà-Tortella & Tirado, 2011; Essex et al., 2004; Rico-Amoros et al., 2009), 19.8% of the hotels in this study were only open for the summer tourist season (i.e., approximately from May to October). From a water management standpoint, seasonality is very important since the number of months the establishment stays open for has more weight on water consumption than hotel occupancy (Deyà-Tortella & Tirado, 2011). Therefore, it is expected that hotels with a similar number of guests or even seasonal hotels with more guests that are open the whole year (54.3%) will have higher water consumption than those open seasonally.

This study also shows that hotels with certifications were more active in sharing their information, showing a positive relation between certifications and communication. Certification helps hotels to improve their relationships with stakeholders by creating a better corporate image and reputation (Bernardo et al., 2009; Domingues et al., 2016; Zeng et al., 2007), which in return helps in increasing the willingness of guests to stay at environmentally certified hotels (Martínez García de Leaniz et al., 2018). Studies have shown how implementing ISO 14001 certification in hotels has a significantly positive economic impact and leads to image improvement (Agan et al., 2013; Segarra-Oña et al., 2012). In contrast, He et al. (2015) did not see any relationship between certification implementation and a more sustainable water management, concluding that obtaining certification was more a market-oriented strategy or focused on improving the reputation of the hotel or business. Consequently, there is still a lack of understanding of what part of the improved performance is due to self-motivated improvement, the size of the hotel or the organizational maturity of the management. Adopting these kinds of certifications could be more related to external pressure and gains in terms of image rather than in the pursuit of cost reduction.

Water supply, consumption and reuse

The primary water supply for most of the surveyed hotels was municipal water, and alternative sources were only adopted for specific uses. Hotels are usually larger water consumers than households (Gössling et al., 2012), and with a greater variety of water uses (e.g., green areas watering, swimming pools and showers). Thus, the use of alternative water sources and/or water reuse practices could lead to important water and cost savings, albeit requiring investment for construction and maintenance. However, grey- or wastewater treatment and water reuse are not yet common practice, and almost half of the hotels applying wastewater treatment on their premises discharged it into the sewer system after treatment. Decentralized waste- and greywater treatment systems and water reuse could be increased in future in hotels and tourist facilities to help cope with water scarcity, and to reduce the burden on both municipal wastewater treatment facilities and the environment. Greywater has the potential to be treated and reused for several hotel-related activities, such as the watering of green areas or flushing toilets (Kasim et al., 2014), while harvested rainwater can be used for irrigation. In this way the water cycle could be optimized and the need for the municipal water supply greatly reduced. A good example of this practice is Hotel Samba (Lloret de Mar, Spain), which separates the greywater and reuses up to 15,000 m^3/year for toilet flushing and to feed a hydroponic system (Zraunig et al., 2019). Moreover, this hotel's wastewater treatment and/or pool water disinfection

(Atanasova et al., 2017; Ekowati et al., 2019; Estelrich et al., 2021; Zraunig et al., 2019) could be the way forward for many hotels in the Mediterranean and beyond. Another good example is the Frangipani Langkawi Hotel Resort and Spa in Malaysia, which has a wetland as a recycling and purification system (Kasim et al., 2014). Nevertheless, several studies point out the limited number of hotels with water recycling systems. For example, none of the 19 hotels surveyed in the Muga River basin (Girona, Spain) had greywater reuse or rainwater harvesting in place (Torres-Bagur et al., 2019). A similar scenario was observed outside the Euro-Mediterranean region (Chan et al., 2017), although, overall, rainwater harvesting has been reported as a more common practice in tourist facilities (Charara et al., 2011; Deyà-Tortella & Tirado, 2011), with a potential saving of up to 55% of potable water (Kasim et al., 2014), especially for non-potable purposes (Wyngaard & De Lange, 2013). The EU water-saving potential report (Dworak et al., 2007) recognized the capability of desalination and rainwater harvesting in the Euro-Mediterranean tourism sector. The use of seawater could be a solution to alleviate water stress, as in the case of Hong Kong, where hotels commonly use seawater for toilet flushing (Deng & Burnett, 2002). In our study only seven respondents recorded seawater desalination on their premises as their primary water source (although they might actually have been referring to their municipal desalination plant), which confirms that seawater is a marginal source in Mediterranean hotel facilities.

Alternative water sources for larger hotels may lead to larger water saving than for small hotels, and larger hotels might be more capable of implementing these options due to their greater economic capacity. However, it should be noted that currently there is no evaluation tool specifically addressing the role and effectiveness of water-saving programmes (Dworak et al., 2007) or on non-conventional water sources.

Swimming pools and green areas

Swimming pools and green areas have a large influence on water consumption (Gössling, 2015) and are commonly found in hotels (Rico et al., 2020). Pools account for approximately 15% (Gössling, 2001) to 20–25% (Antakyah et al., 2008) of hotel water demand and, therefore, they need to be considered in hotels' water management strategies. Larger swimming pools require more water, but as indicated by Gabarda-Mallorquí et al. (2017), they can be used by more tourists, which translates into greater water efficiency.

The indoor pools reported in this survey were generally smaller and less common than outdoor ones. Limited space dedicated to indoor pools is probably related to the Mediterranean climate that is conducive to more outside water-related activities, as well as the fact that some hotels open only during the high tourist season. The most common swimming pool water treatment technologies identified in our study (i.e., rapid sand filtration, cartridge filter and coagulation) are conventional pool treatment methods (Barbot & Moulin, 2008). The most typical disinfection method identified in our study and in other studies (Ekowati et al., 2019; Lee et al., 2010) was chlorination, due to the ease of use, low cost and high availability.

Most of the responding hotels did not have large green areas, perhaps because half of the hotels were in municipalities with over 15,000 inhabitants, or in densely urbanized tourist areas (e.g., the Greek Islands or Malta), which have limited space for green areas. Most facilities with green areas had their own well.

Laundry management

Laundry can account for 30% (Antakyah et al., 2008) to 47% of water consumption in hotels (Barberán et al., 2013). Hotels doing their laundry themselves on their own premises can treat greywater so that it can be reused within the hotel's premises, for example, for irrigation, outdoor cleaning or toilet flushing. These water reuse practices within the hotel decrease the water demand on the municipal network, thus reducing the impact on local water resources (Kasim et al., 2014), and also decrease the amounts of contaminants entering the sewer network from hotels. Additionally, detergents contain surfactants and other chemicals which are not only difficult to remove but also can interfere with conventional municipal sewage treatment plants (Jardak et al., 2016).

Since laundry can consume up to half of the water used by a hotel (Deng & Burnett, 2002; Essex et al., 2004; Rico-Amoros et al., 2009), it was assumed that larger hotels in this study would be outsourcing laundry more than smaller ones. However, except for cluster 3, for the rest of the clusters outsourcing laundry or washing on-site was evenly distributed, which indicates that hotel size, bed capacity or category were not related to outsourcing the laundry. Although only 18.2% of hotels in cluster 3 reported that they wash their laundry themselves on their own premises, another 9.1% said that they partially outsourced it, with a small difference compared with the other fraction.

It was previously observed that seasonal hotels benefit more from outsourcing laundry than hotels opened all year round (Yildiz & Demirel, 2014). However, in this study, although most hotels recorded seasonal occupancy, it was observed that outsourcing was not related to seasonality. This could be related to the fact that although outsourcing has been shown to have benefits, it also implies a risk of laundry not being done properly (Yildiz & Demirel, 2014).

Water consumption monitoring

The results of this survey show that the most common typology of separate water monitoring was outdoors versus indoors, and monitoring pools separately. Separate monitoring appears to be more likely related to hotel size than to its certifications, because larger hotels may have more financial means to implement separate monitoring and may be more interested than smaller hotels in knowing the breakdown of their (higher) water consumption and the associated expense. A more detailed knowledge of water consumption in different sections of the hotel facility can lead to a better design and installation of more specific water-saving measures, as well as a greater awareness of the possible cumulative impacts of their water management practices (Kasim et al., 2014).

Hotels from clusters 1 and 3 had the largest proportion of monitoring their own total water consumption only (Table 2), most likely due to the absence of pools and related to their size. Larger hotels in clusters 2 and 5 (Table 2) had the lowest percentage of monitoring overall water consumption, suggesting they lack the relevant information. The 10 hotels that separately monitor their water consumption were large four- and five-star hotels, fairly distributed along the clusters. Thus, the overall monitoring seems to be related to hotel size, but separate monitoring of different uses is not.

Water-saving strategies and water infrastructure upgrade

The installation of water-saving devices is one of the principal ways to reduce water consumption and associated expenses in the tourism sector (Dworak et al., 2007) and it is recognized as a top priority (Deng & Burnett, 2002). They are 'low-cost, low-tech, and legally enforceable measures' (Torres-Bagur et al., 2019, p. 6), affordable for all kinds of hotels, and a small investment can result in a significant water demand reduction (Barberán et al., 2013; Gabarda-Mallorquí & Ribas Palom, 2016). Therefore, it is not surprising that 66.0% of the respondents answering this question were using water-saving devices and only 22.2% were not (Figure 5). Popular measures to decrease water consumption in hotels (Bruns Smith et al., 2015) are tap aerators, low-flow devices and dual-flush toilet systems; Chan et al. (2017) found low-flow tap fittings and sensors to be the most common water-saving measures.

The most common were water-saving showers and dual-flush toilets, in line with other studies (Barberán et al., 2013; Chan et al., 2017; Charara et al., 2011; Torres-Bagur et al., 2019). Water-saving showers showed a reduction from 13 to 7 L/min (Gössling et al., 2012). The implementation of water-saving devices in taps and dual-flush toilets in a hotel in La Gomera (Spain) led to a decrease in water consumption of 33% (Hamele & Eckardt, 2006), and of 48% in a three-star hotel in Malta (Gatt & Schranz, 2015) in the first year after their installation. Similarly, dual-flush toilets were found to significantly reduce the water use in hotels in the Asia-Pacific region (McLennan et al., 2017). Water-saving devices reduced water consumption by 21% in a three-star hotel in Zaragoza, Spain (Barberán et al., 2013), and a 6% decrease was estimated with the implementation of multiple water-reducing measures (e.g., dual flushing, flow reduction and rainwater harvesting) in hotels in Benidorm, Spain (Rico et al., 2020). Dual-flush toilets have previously been associated with star category and were found less frequently in lower star categories (Torres-Bagur et al., 2019), but in our study this saving measure was commonly present in all the star categories.

Other popular saving measures not included in this study are towel reuse (Torres-Bagur et al., 2019) and water auto-sensing devices (flow control by means of sensors; Chan et al., 2017). Thus, it is possible that the surveyed hotels were implementing additional water-saving measures other than the ones listed above.

Infrastructure improvements

The percentage of hotels that upgraded their infrastructure (27.2%) was similar to that reported by Rico et al. (2020). The most frequently reported upgrade was to the water distribution system with two objectives: first, to contribute to water saving, minimizing leakages; and second, to improve water quality. Other improvements included rainwater harvesting, wastewater collection, tanks for saving condensed water from air-conditioners, and the update of pools and laundry systems.

These results highlight that many Mediterranean hotels are continuously upgrading their facilities, representing a tremendous opportunity for sustainable water management. Special attention must be paid to those measures that include water reuse, since they alleviate water stress while contributing to sustainable tourism (Hocaoglu, 2017).

Environmental awareness, willingness for future improvements and recommendations

Awareness-raising strategies can play an important role in hotel performance, increasing the number of guests willing to stay at a particular hotel (Gabarda-Mallorquí et al., 2018). Although many hotels in this study considered themselves environmentally aware (48.1% of the total; 78.0% of the hotels that replied to this question), Gabarda-Mallorquí et al. (2018) showed that environmental proactivity is not necessarily associated with environmental awareness. This means that positive responses do not always correspond to actual business practices (Kasim, 2009). Responses may have been influenced by the will to project a positive and environmentally aware image, rather than by facts. This is confirmed by a lower proportion of hotels that implemented infrastructural improvements (27.2%) compared with those claiming to be environmentally aware or partially aware (55.6%). However, the general positive reaction for the implementation of eco initiatives in hotels has been previously reported (e.g., Wyngaard & De Lange, 2013). One option to promote and foster the environmental concern in hotels, and in the tourist sector in general, is for the hotel staff to follow an environmental training programme (Charara et al., 2011). Studies have shown that small investments can lead to hotels' reduction in water consumption (Barberán et al., 2013) with short amortization times (Gössling, 2015). However, even if all tourist facilities have the potential to reduce their water consumption (Gössling et al., 2012), not many studies have focused on the benefits of introducing water-saving measures. It is thus possible that the lack of knowledge (transfer) about the benefits of introducing water-saving measures for hotels may be preventing them from being more willing to implement these measures.

Disaggregating the analysis by cluster, although hotels in clusters 1 and 4 were small and hotels in cluster 5 were the largest, these three clusters had the lowest number of certifications. Additionally, the willingness of the respondents in cluster 5 to implement new measures might be related to their higher economic capacity that would enable the improvements (Kasim et al., 2014), and they might see a higher impact in total water consumption reductions than other hotels. Conversely, clusters 2 and 3, which were shown to already use the largest variety of alternative water sources, showed instead a low propensity for further improvements (11.8% and 18.2%, respectively). This might be related to the fact that most of these hotels had already received a certification. In fact, it was observed that certified hotels usually experience annual improvements with the largest reductions, especially in the first years after obtaining the certification (Becken & McLennan, 2017). Therefore, it is possible that the certified hotels in this study had already invested in the implementation of measures related to reducing, reusing or recycling water, aimed at improving their efficiency (Martínez García de Leaniz et al., 2018).

There is vast room for improvement in the use of alternative water sources, even if differences exist among the different hotel categories. Possibilities include grey-/wastewater treatment and reuse and rainwater collection for secondary uses (such as flushing toilets, heating, maintenance of green areas and water features, and/or cleaning). When technically possible, and legally allowed, potable water reuse could even be applied. It is encouraging to note that treated wastewater seems to be an accepted water source, albeit to a small extent. In parallel, advanced and separate water monitoring as well as water-saving strategies, including laundry and pool management, would greatly reduce water needs in tourist facilities.

Conclusions

This study shows the status of water management practices in hotels across the Euro-Mediterranean basin and Turkey, as well as their environmental awareness and willingness for future improvements in their water cycle. HCA helpfully grouped hotels in similar categories regarding their characteristics and trends on water management practices. This enabled the observed over- and underrepresentation of some countries in the sample to be smoothed. Cluster 1 included the smallest hotels, no certifications and no pools or spas; clusters 2 and 5 had the largest hotels, all with certifications, and most had pools and spas; and clusters 3 and 4 were small and medium-sized hotels, respectively, most of which had certifications and pools, but no spas.

Although differences existed among the hotel categories, only a small number of hotels were using alternative water sources, and just for specific uses. Grey- or wastewater treatment and water reuse seems to be an acceptable water source for the survey respondents, albeit to a fairly small extent. Decentralized waste- and greywater treatment systems and water reuse should be increased in future in hotels and tourist facilities to help cope with water scarcity and reduce the burden on municipal wastewater treatment facilities and the environment. Clusters 1, 3 and 5 are recommended to increase the use of alternative resources, since they made the least use of them.

Establishment-wide and zoned water consumption monitoring as well as water-saving strategies, including more water-efficient laundry machines and pool management, would in parallel greatly reduce water needs in tourist facilities. Regarding water metering, many hotels only monitored the overall water consumption but had implemented water-saving measures. Larger hotels (clusters 2 and 5) had the lowest percentage of full monitoring of water consumption, suggesting they may lack the relevant data to inform decision-making. These hotel clusters are recommended to monitor more than just the overall water consumption. Zoned monitoring appears to be more likely related to hotel size than to their certifications, because larger hotels may have more financial means to implement the monitoring of separate areas. Pools account for approximately 15–25% of hotel water demand and, therefore, need to be carefully included in hotels' water management strategies. In terms of pool disinfection methods, only a minor percentage of hotels used alternative disinfection methods (ozone or UV irradiation), irrespective of their cluster. All hotels should be considering innovative treatment methods that better withstand known (e.g., bacteria and protozoa) and emerging (e.g., organic micropollutants) threats. As regards washing, HCA revealed that hotel size, bed capacity or category were not related to outsourcing the laundry.

Several respondents were willing to reshape their business strategy by introducing water- and wastewater-related improvements, as well as paying more attention to the preservation of natural resources. However, these answers may have been influenced by the willingness to project a positive image rather than being environmentally aware. Likewise, the possession of certification was found to be statistically unrelated to hotel size, the presence of water-saving devices or the use of alternative water sources. Hotels with certifications were more active in collecting data about water consumption and strived to convey a message of environmental awareness to potential guests. However, hotels with numerous certifications were not necessarily the most active in using innovative systems to reduce their water consumption or more willing to adopt future improvements. Clusters 4 and 5, but also small hotels in cluster 1, are particularly suggested to invest in technological improvements.

In order to face future water scarcity scenarios and to fulfil water demand, water management needs to be a continuous process that evolves with newly available technologies and/or legal requirements. Environmental awareness and willingness to improve are prerequisites for tourist facility management to keep up with the water-related solutions that would prevent, or at least reduce, water stress on the local population, especially in water-scarce areas such as the Euro-Mediterranean basin and Turkey. Targeted capacity-building of environmental awareness and sustainability, as well as incentives in this direction, should be fostered.

Finally, there is a need for specific legislation, more robust guidelines and incentives for environmental innovation in the tourism industry. These should be associated with the development of decision support tools that can help practitioners to navigate sustainable water management practices in the tourism sector.

CrediT authorship contribution statement

E.M.: Conceptualization, methodology, investigation, writing – original draft, writing – review and editing, supervision. G.F.: Conceptualization, methodology, investigation, writing – original draft, writing – review and editing, supervision, project administration, funding acquisition. Y.M. S.: Conceptualization, investigation, methodology, writing – original draft, writing – review and editing. X.A.: Writing – original draft, writing – review and editing. A.A.: Methodology, writing – original draft, writing – review and editing. G.B.: Conceptualization, methodology, investigation, writing – original draft, writing – review and editing, supervision, project administration, funding acquisition.

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ARTICLE 2. Exploring the limitations of forward osmosis for direct hydroponic fertigation: impact of ion transfer and fertilizer composition on effective dilution.

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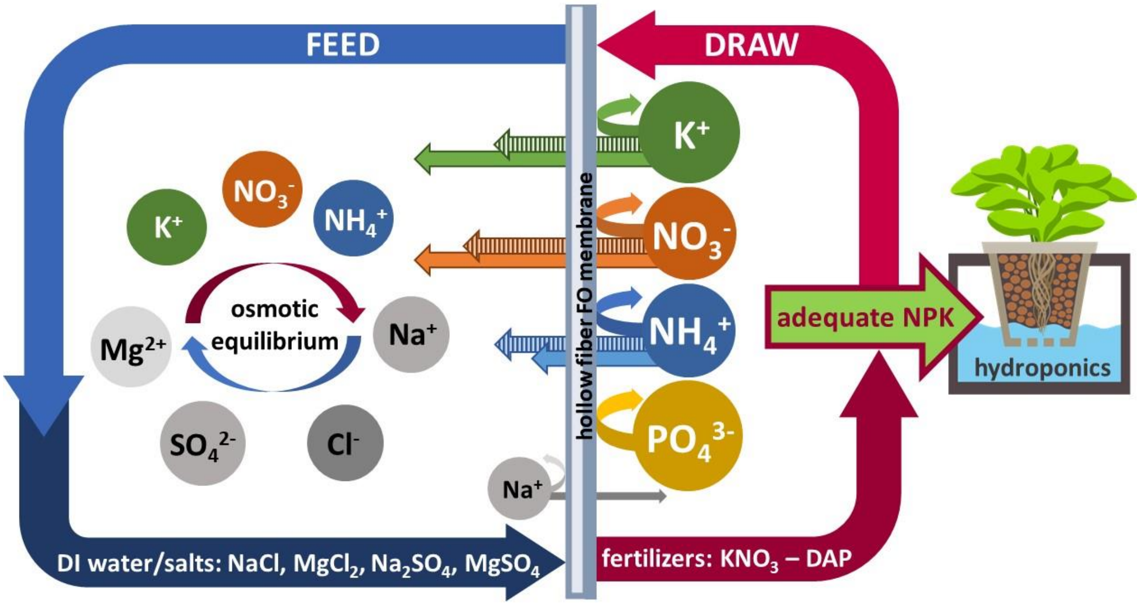

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Exploring the limitations of forward osmosis for direct hydroponic fertigation: Impact of ion transfer and fertilizer composition on effective dilution

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ABSTRACT

There is a need for water reuse technologies and applications to minimize the imminent water crisis, caused by the world population growth, the reduction of freshwater resources and the increasing water pollution. Fertilizer-drawn forward osmosis (FDFO) is a promising process capable of simultaneously extracting fresh water from low-quality sources as feed water (e.g., wastewater or greywater), while diluting fertilizer solutions for direct fertigation, avoiding the demand for freshwater for irrigation. Achieving an adequate level of dilution for direct fertigation is a key element to be evaluated for the implementation of FDFO. This study assessed the performance of the forward osmosis process to dilute fertilizer solutions to be applied directly in hydroponic systems. Experiments were carried out under conditions close to osmotic equilibrium to evaluate the process performance up to the maximum dilution point. Tests were carried out with individual and blended fertilizers (*i.e.*, $(NH_4)_2HPO_4$ or DAP, and KNO_3) used as draw solution (DS) and with deionized water or individual salts (NaCl, $MgCl_2$, Na_2SO_4, $MgSO_4$) in the feed solution (FS). Water fluxes and reverse salt fluxes indicated that both fertilizer DS composition and concentrations play a fundamental role in the process. Suitable nutrient concentrations to be directly applied without further dilution for N, P and K (119, 40, 264 mg.L^{-1} respectively) were obtained with deionized water as FS and blended DAP (0.025 M) and KNO_3 (0.15 M) as DS. However, important fertilizer losses from DS to FS were observed, being the highest for NO_3^- (33–70% losses from DS to FS). The presence of salts in FS decreased the water fluxes and the DS dilution due to the osmotic equilibrium caused by a greater loss of nutrients from DS to FS (up to 100%), compared with tests using just deionized water as FS. This study points out the potential limitations of the FDFO process, due to the high solute fluxes and low water fluxes in conditions close to osmotic equilibrium.

1. Introduction

United Nations has estimated that by 2050 nearly 6 billion people will suffer from clean water scarcity (Boretti and Rosa, 2019). Thus, future scenarios drive the need to improve water management practices and strategies to ensure water supply. Within this context, water reuse is a promising option to alleviate water stress, while moving towards the Circular Economy principles. Nonetheless, water reuse remains a limited practice due to barriers ranging from technical and economic feasibility to legislative restrictions and social acceptance. Therefore, to solve the imminent water crisis, it is necessary to develop efficient technologies that will make water reuse a sustainable and affordable practice to be widely implemented. With irrigation being the world largest water consumer, the application of reused water for irrigation purposes is a crucial strategy capable of significantly decreasing the demand for freshwater and therefore reducing water stress. Among agricultural techniques, hydroponics is a promising approach that can be implemented worldwide. In this soilless cultivation technique, plants grow in direct contact with water that contains the required nutrients for their development. The typical concentrations of nitrogen, phosphorous and potassium (NPK, main nutrients for plants) of common hydroponic solutions are diverse (Table 1), as the nutritional requirements for the plants depend on many factors, such as plant type, stage of plant growth, seasonal differences or weather conditions (Resh, 2013).

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Table 1
NPK concentrations of standard nutrient solutions for hydroponics according to previous studies. Adapted from Trejo-Téllez and Gómez-Merino (2012).

Reference	Nutrient concentration, mg.L^{-1}			Nutrient concentration, mmol.L^{-1}		
	N	P	K	N	P	K
Hoagland and Arnon (1938)	210	31	234	15.0	1.0	6.0
Hewitt (1966)	168	41	156	12.0	1.3	4.0
Cooper (1979)	200–260	60	300	14.3–18.6	1.9	7.7
Steiner (1984)	168	31	273	12.0	1.0	7.0

Given that the hydroponic technique requires large amounts of freshwater (Chekli et al., 2017a), it is of great interest to study the potential of technologies capable of treating alternative water sources for subsequent reuse in hydroponics. Among the variety of available technologies, forward osmosis (FO) emerged as a promising solution for water treatment and reuse, as it can recover fresh water from low quality water sources such as seawater or wastewater (Coday et al., 2014; Zhou et al., 2014). In FO, a highly concentrated solution (draw solution: DS) extracts water from a low concentration solution (feed solution: FS), and the water is transported through a dense membrane (Phuntsho et al., 2013). FO membranes exhibit high pollutant rejection and have low fouling propensity, and the process does not require hydraulic pressure as it is driven by the difference in osmotic pressures between FS and DS (Van Der Bruggen and Luis, 2015). One of the main drawbacks of FO is the reverse salt flux (J_s) (Holloway et al., 2015); *i.e.*, solute losses from draw to feed per membrane area and time (Jamil et al., 2016). J_s plays a fundamental role in the design of osmotically driven processes (Phillip et al., 2010), since it decreases the osmotic driving force (Phuntsho et al., 2011), represents economic losses (fertilizer losses in FDFO) and causes difficulties with feed concentrate management (Phuntsho et al., 2013), hence jeopardizing the benefits of the FO process (Chekli et al., 2012). As pointed out by Zou et al. (2019) in a review of approaches to reduce reverse solute fluxes in FO, it is crucial for FO operations to control and reduce J_s, and they also highlighted the lack of J_s data in FO studies. Therefore, detailed studies of solute fluxes in FO are of great interest to assess their impact on FO performance.

One of the practical applications of FO is the osmotic dilution of soluble fertilizers for irrigation purposes (Sahebi et al., 2015), as most of them are capable of generating a high osmotic potential (Phuntsho et al., 2013). In fertilizer-drawn forward osmosis (FDFO), the osmotic dilution of the fertilizer DS occurs, with the aim of later being used for direct fertigation (application of fertilizer nutrients for irrigation purposes) since it contains the essential nutrients for plant growth. FDFO concept was mainly developed in the last decade and has shown promising results. FDFO is particularly interesting when applied to low quality sources as feed water, such as brackish water or greywater, avoiding the demand for freshwater for irrigation.

Most FDFO studies have focused on the performance of different fertilizer salts as DS (Chekli et al., 2017b; Lotfi et al., 2015; Majeed et al., 2015; Phuntsho et al., 2011, 2012) and their interactions with different membranes (Corzo et al., 2017; Phuntsho et al., 2013). Some recent works have even used commercial fertilizers as DS (Chekli et al., 2017a; J.E. Kim et al., 2019; Xie et al., 2015; Zou and He, 2016). Besides, it should be noted that in most of the previous FDFO studies, authors highlight the need for further dilution because final concentration of nutrients in DS were above the threshold tolerated by the plants. In previous cases, proper DS dilution for direct fertigation was only achieved after coupling FO with other technologies (Jamil et al., 2015; Luo et al., 2015) or by applying additional pressure (Chekli et al., 2017a; Kim et al., 2017; Sahebi et al., 2015). Overall, most of FDFO studies were devoted to demonstrating proof of concept for the use of fertilizers as draw solutions and did not focus on the impact of FS salinity, nor on achieving an optimal dilution to the required level of nutrients for plants, especially when approaching osmotic equilibrium. Final DS concentrations suitable for direct fertigation - without further dilution of the final draw solution - are therefore essential for the success of FDFO and more studies are required on the practical application of the process (Phuntsho et al., 2012). Finally, even if some studies have focused on bidirectional diffusion of the various ions present in both FS and DS (Hancock et al., 2011; Hancock and Cath, 2009), all were carried out on a very small experimental scale and under conditions far from osmotic equilibrium.

For FDFO to be applicable on a full scale, relatively low DS concentrations are required, and it is of interest to achieve the desired concentrations in a single step. Given the current limitations of FDFO concerning the dilution factor of the fertilizer for direct fertigation, it is crucial to conduct more experiments close to osmotic equilibrium, as it will have a great impact on the achievable dilution rate, filtration kinetics and is expected to depend on FS initial salinity and reverse salt diffusion. Within this framework, this study aimed to evaluate the suitability of the FDFO process to achieve an effective DS dilution to generate a suitable nutrient solution for direct application in hydroponic systems (as means of nutrients: N, P and K content in solution). The performance of the FO process at conditions close to osmotic equilibrium, as well as ion fluxes through the membrane were also experimentally evaluated.

2. Materials and methods

2.1. Materials

The tests at lab scale were performed with commercial FO hollow fiber modules (Aquaporin Inside HFFO2, Aquaporin A/S, Denmark). The HFFO2 module, made with inner-selective biomimetic active layers, contains 13,800 membrane fibers 270 mm long, an inner diameter of 195 μm and total effective area of 2.3 m^2 (Nikbakht Fini et al., 2020; Sanahuja-Embuena et al., 2019).

Deionized (DI) water was used as feed solution in most of the experiments; and some tests were then conducted using single salt solutions ($MgCl_2$, $MgSO_4$, Na_2SO_4 or NaCl) as FS (Table 2). Feed salts $MgCl_2.6H_2O$ and $MgSO_4.7H_2O$ (99%) were purchased from Scharlab and Na_2SO_4 was purchased from Merck. NaCl (Sea salt, >99.4% NaCl) was purchased from Vicens i Batllori S.L. (Banyoles, Spain). The FS salts were chosen because they are commonly found in waste-, brackish-, and

Table 2
List of tests (6.5 mM for the salts in FS, when applicable).

	FEED	DRAW		
	Content	Content	DAP (M)	KNO_3 (M)
Baseline tests	DI water	DAP	0.05	
		KNO_3		0.05
		MIX 1	0.05	0.05
Effect of draw solute concentration	DI water	DAP	0.50	
		KNO_3		0.50
		MIX 0.5	0.50	0.50
Optimal nutrient solution	DI water	MIX 2	0.050	0.10
		MIX 3	0.030	0.08
		MIX 4	0.050	0.20
		MIX 5	0.025	0.15
Effect of salts in the feed solution	NaCl	DAP	0.05	
		KNO_3		0.05
		MIX 1	0.05	0.05
	$MgCl_2$	DAP	0.05	
		KNO_3		0.05
		MIX 1	0.05	0.05
	Na_2SO_4	DAP	0.05	
		KNO_3		0.05
		MIX 1	0.05	0.05
	$MgSO_4$	DAP	0.05	
		KNO_3		0.05
		MIX 1	0.05	0.05

seawater, which are good candidates for FS.

The draw solution contained individual salts or blended mixes of KNO_3 and $(NH_4)_2HPO_4$ (DAP), purchased from Scharlab. These salts were chosen as they are commonly used as fertilizers worldwide (Phuntsho et al., 2012), and already tested in previous FDFO studies, showing their potential for FDFO applications.

2.2. Forward osmosis experimental setup

Experiments were performed with constant feed and draw recirculation, leading to continuous DS dilution and FS concentration. All tests were carried out with DS facing the active layer (within the fibers) because this configuration results in higher water fluxes (Phuntsho et al., 2013; Su et al., 2010). Although this configuration of having the active layer facing the DS may lead to fouling, this negative impact was not expected due to FS nature (without any foulant agent). Additionally, although external concentration polarization may increase with DS facing the active layer, internal concentration polarization would decrease in the proposed experimental setup, since it generally used DI water as FS. The module was positioned vertically with the DS and FS circulating in counter-current (Fig. 1), since operation in counter-current leads to better use of osmotic pressure, achieving a higher dilution rate than in co-current mode (Blandin et al., 2020). The initial volumes were 2 L of DS and 60 L of FS. FS and DS were circulated with a peristaltic pump (Watson-Marlow RS232), with an average flow rate of 34.6 L h^{-1} and 60.7 L h^{-1} respectively, according to the manufacturer's recommendations. The water flux crossing the membrane (J_w, from FS to DS) was determined by measuring the volume extracted from FS to DS thanks to the increase in the mass of the DS with a balance (Kern PCB) and considering 1 kg/L as density of DS.

2.2.1. Module evaluation tests

Prior and throughout the experiments, module integrity and performance were evaluated with 1 M NaCl as DS, DI water as FS, and with the active layer of the membrane facing FS, which were the conditions established by the manufacturer.

2.3. FDFO experimental procedure

To evaluate the FDFO process, different tests were performed (Table 2). Water flux (J_w) in L.m^{-2}.h^{-1} was determined by equation (1):

$$J_w = \frac{\Delta V_{FS}}{A^*\Delta t} \tag{1}$$

where ΔV_{FS} represents the decrease in the volume of FS over time in L, A the membrane area (2.3 m^2), and Δt the time variation, in h. Average J_w was calculated considering the total duration of the tests, while initial J_w was calculated as the average of the three values of J_w from the highest J_w value (approximately at 2–3 min). Since operation in batch led to continuous DS dilution and FS concentration, with J_w decreasing along time, initial water flux values served to analyze J_w with the maximum osmotic pressure gradient between DS and FS.

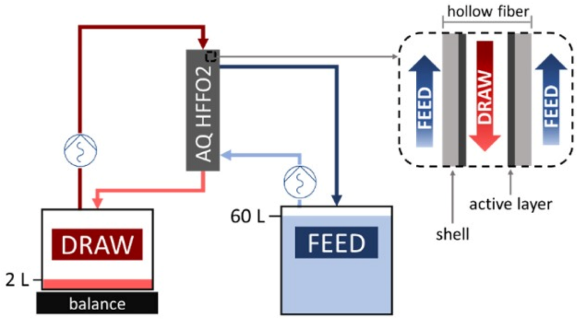

Fig. 1. Experimental setup.

Reverse salt fluxes (J_s) of each ion (from DS to FS), in mmol.m^{-2}.h^{-1} were calculated by equation (2):

$$J_s = \frac{C_{FSf}{}^*V_{FSf} - C_{FSi}{}^*V_{FSi}}{A^*\Delta t} \tag{2}$$

where C_{FSf} and C_{FSi} represent final and initial ion concentrations in FS (mmol.L^{-1}), respectively; and V_{FSf} and V_{FSi} represent final and initial FS volume (L), respectively. Forward solute fluxes (J_{sf}) of each ion (from FS to DS), in mmol.m^{-2}.h^{-1} were calculated by equation (3):

$$J_{sf} = \frac{C_{DSf}{}^*V_{DSf} - C_{DSi}{}^*V_{DSi}}{A^*\Delta t} \tag{3}$$

where C_{DSf} and C_{DSi} represent final and initial ion concentrations in DS (mmol.L^{-1}), respectively; and V_{DSf} and V_{DSi} represent final and initial DS volume (L), respectively.

Nutrient losses from DS to FS were evaluated by analyzing final concentrations in FS (being zero the initial concentration of each nutrient in FS). Since EC increases proportionally to concentration and osmotic pressure (Corzo et al., 2017), it is assumed as a good indicator of osmotic equilibrium. Therefore, osmotic equilibrium was assumed as achieved when the ratio between final EC in FS and DS was between 0.8 and 1.2.

2.3.1. Baseline tests

Baseline tests were performed in duplicates at initial DS of 0.05 M of DAP and KNO_3, alone or blended (Table 2). The aim of these preliminary tests was twofold: to evaluate the differences in terms of flux and ion behavior (when using fertilizers individually or blended) and to serve as a reference for the rest of the tested conditions. Due to setup limitations, it was not possible for DS to extract more than 30 L from FS (*i.e.*, 15 times DS dilution rate). Therefore, initial DS concentrations were designed to achieve adequate nutrient concentrations in the final DS with a 15-fold DS mass dilution. In addition, this configuration was used to evaluate ions behavior under conditions identical or close to osmotic equilibrium between FS and DS.

2.3.2. Effect of draw solute concentration

A set of tests conducted in duplicates, with a concentration 10 times higher than the baseline concentration (*i.e.*, 0.5 M) were carried out to evaluate the effect of DS concentration (Table 2). This concentration was chosen as it was commonly used in previous studies (Irvine et al., 2013; Wang et al., 2020).

2.3.3. Optimal nutrient solution

Four mixes of DAP and KNO_3 as DS were tested in duplicates, with initial concentrations ranging from 0.025 to 0.05 M for DAP and from 0.05 to 0.20 M for KNO_3 (Table 2). The salts were also tested individually and evaluated for their effectiveness to achieve proper DS dilution. It is worth mentioning that this study was designed as a proof of concept, so the objective was to analyze the feasibility of the system to reach certain levels of DS dilution that would lead to nutrient concentration ranges suitable for hydroponics, without focusing on a specific crop or a certain growing stage. Accordingly, the target final nutrient concentrations in the DS were set to range between 100 and 200, 30–60 and 150–300 mg.L^{-1} for N, P and K, respectively.

2.3.4. Effect of salts in the feed solution

To evaluate the influence of feed solutes on reverse fluxes (from DS to FS) and forward fluxes (from FS to DS) close to osmotic equilibrium, four different salts with initial concentration of 6.5 mM in the FS were tested individually. Draw fertilizers were used blended and alone at the previously stated baseline concentration (*i.e.*, 0.05 M, Table 2). The four FS salts were monovalent ions (NaCl), divalent ions ($MgSO_4$), monovalent cation with divalent anion (Na_2SO_4) and divalent cation with monovalent anion ($MgCl_2$). Salts were tested separately to analyze the influence of the different pairs of ions in the process.

2.4. *Sample collection and analytical methods*

Samples from feed and draw solutions were collected at the beginning, after 30 and 60 min, and at the end of each test (generally 24 h). Ion concentrations were analyzed by ion chromatography (ICS 5000 from DIONEX). Electrical conductivity was measured with an EC meter (GLP31+ from Crison).

3. Results and discussion

All tests were characterized by a sharp decrease in ion concentration in the DS during the first 30 min, as already observed in previous studies (Sahebi et al., 2020) and by an increase in the mass dilution of the DS throughout the entire duration of each experiment.

3.1. *Module evaluation tests*

Water fluxes with 1 M NaCl in DS, DI water as FS and with the FS facing the membrane active layer, were above 15 L $m^{-2}.h^{-1}$ throughout all evaluation tests (avg. 16.2 L $m^{-2}.h^{-1}$), while specific reverse salt fluxes (J_s/J_w) were below 0.3 $g.L^{-1}$ in all evaluation tests (avg. 0.21 $g.L^{-1}$). These results are in accordance with manufacturers' guidelines, (*i. e.*, water flux greater than 12 L $m^{-2}.h^{-1}$, specific reverse salt fluxes below 0.3 $g.L^{-1}$ under similar operating conditions), hence confirming that the module was working properly. The obtained results remained similar throughout all tests, confirming that no fouling, nor scaling or other issue was compromising the membrane performance. Further module evaluation parameters can be found in Sanahuja-Embuena et al. (2019).

3.2. *Effect of draw solute type and concentration*

A set of tests using individual or blended draw solutes at 0.50 vs 0.05 M of initial concentrations served to evaluate the effects of DS concentration and composition on the process performance (Table 3). Initial water fluxes were in the same range for all tests using the same DS concentrations and decreased significantly throughout the process due to the dilution of the DS and the consequent loss of osmotic pressure driving force. As expected, water fluxes for 0.05 M DS were low compared to those of the tests with DS at 0.50 M (Table 3) due to the resulting lower difference in osmotic pressure between FS and DS. Working with low DS salinity (0.05 M) not only reduces J_w because of the lower initial flux, but also because of operating near osmotic equilibrium due to dilution over time.

All tests at 0.50 and 0.05 M achieved the targeted dilution rate (around 15 times) except for KNO_3 at 0.05 M (Table 3). Osmotic equilibrium was not achieved in any of the tests (except for KNO_3 at 0.05 M) indicating that the water extraction capacity of the tested DS was higher than the 15 times dilution rate, which was the limit of the setup. Only when operating with KNO_3 as DS at 0.05 M, a higher EC was observed in the final FS than in the DS, indicating that osmotic equilibrium was reached, at a lower DS dilution rate (6-fold) than the target. This behavior results from the reverse salt flux from DS to FS, which not only leads to fertilizers losses but also limits the dilution capacity of the system.

In tests with 0.05 M of fertilizer salts in initial DS, reverse salt fluxes (J_s) did not exceed 1.5 mmol $m^{-2}.h^{-1}$ in any case but were affected by the nature of the ions present in the DS (Table 4). As noted above, the highest J_s were observed when using KNO_3, leading to the highest diffusion of both of its ions. NO_3^- has been widely reported as an ion with high reverse fluxes (Gulied et al., 2019), due to its small hydrated radius. K^+ passed through the membrane in equal equivalent concentration to balance the charges and keep the ionic equilibrium in both solutions (see supplementary S1).

Reverse fluxes of DAP ions were much lower, confirming results from other studies (Y. Y. Kim et al., 2019; Mirshekar et al., 2021). Phosphate J_s was up to two orders of magnitude lower than the counter ions present in the DS (*i.e.*, K^+ and NH_4^+). Higher FO membrane rejection of phosphate compared to ammonium and potassium has already been reported due to its bigger hydrated radius, and the stronger electrostatic repulsion with the negatively charged membranes caused by its negative multivalent charge (Achilli et al., 2009; Xie et al., 2015). Consequently, phosphate reverse fluxes through the membrane are generally reported to be minimal regardless of the DS composition and concentration (Majeed et al., 2015; Minier-Matar et al., 2016).

The observed ions J_s were different when using individual fertilizers or blended (MIX 1). In MIX 1, reverse fluxes followed the trend $NO_3 > NH_4 > K > P$ (Table 4), which is inversely correlated to their hydrated radii at the same charge type (0.34, 0.25, 0.33, and 0.49 nm for NO_3^-, NH_4^+, K^+, and PO_4^{3-} respectively) (Xie et al., 2015), and in accordance to other studies (Gulied et al., 2019; Zou and He, 2016).

When using blended fertilizers (MIX 1), J_s were found to be lower for K^+ and NO_3^-, but higher for NH_4^+ (Table 4). That could be explained by a lower overall diffusivity due to the presence of two or more ions species in the DS, which also leads to lower reverse diffusion (McCutcheon and Elimelech, 2006). It was also shown that the migration of NH_4^+ was favored compared to K^+ as counter ion of NO_3^-. The smaller hydrated radius of NH_4^+ compared with K^+ (0.25 vs 0.33 nm) explains the higher diffusion of NH_4^+ when salts were tested together in DS (Table 4). In addition, the reverse fluxes of the cations were facilitated by the negatively charged membrane surface, which enhances the cation diffusion to FS (Lotfi et al., 2015; Minier-Matar et al., 2016).

Lower percent solute losses occurred with a higher initial DS concentration (Table 4). This is because the DS concentration gradient drives the passage of both water and salts in opposite directions across the membrane, and higher fertilizer losses could be expected with higher water fluxes (Sahebi et al., 2020). However, it is hypothesized that if tests at 0.50 M would have been closer to osmotic equilibrium, as it happened with tests with 0.05 M, the corresponding losses would have been higher. This increase in losses is due to the longer time of contact between the solutions, which is required to achieve the targeted dilution rate but also enables more solute transport across the membrane. This issue is illustrated by the higher reverse salt fluxes in tests at 0.50 M than in the baseline tests at 0.05 M (Table 4). These results highlight the importance of the setup conditions, as FO performance cannot only be

Table 3
Results of tests with 0.50 and 0.05 M of salts in initial DS and DI in FS. Osmotic equilibrium was considered achieved for $(EC_{FS})/(EC_{DS})$ between 0.8 and 1.2.

DS content	initial DS (M)	initial J_w ($L.m^{-2}.h^{-1}$)	avg. J_w ($L.m^{-2}.h^{-1}$)	Mass dilution	EC in final FS ($\mu S.cm^{-1}$)	EC in final DS ($\mu S.cm^{-1}$)	Relation EC final FS/DS
DAP	0.50	14.7	5.7	14	58	5765	0.0
KNO_3	0.50	12.1	3.1	15	1683	2725	0.6
MIX 0.5	0.50	17.5	7.1	14	941	8375	0.1
DAP	0.05	3.8	0.5	15	49	638	0.1
KNO_3	0.05	2.7	0.2	6	228	242	0.9
MIX 1	0.05	5.5	0.7	15	231	894	0.3

Table 4
Solute losses, reverse fluxes (J_s) and specific reverse salt fluxes (SRSF) for tests with 0.50 and 0.05 M of salts in initial DS and DI water in FS.

Initial DS			% solute losses from DS to FS				J_s (mmol.m^{-2}.h^{-1})				SRSF (J_s/J_w)			
Content	DAP (M)	KNO_3 (M)	N–NH_4^+	K^+	N–NO_3^-	P-PO_4^{3-}	N–NH_4^+	K^+	N–NO_3^-	P-PO_4^{3-}	N–NH_4^+	K^+	N–NO_3^-	P-PO_4^{3-}
DAP	0.50		3.1			0.3	12.4			0.6	2.2			0.1
KNO_3		0.50		37.5	37.1			42.2	44.4			13.8	14.6	
MIX 0.5	0.50	0.50	8.3	6.9	19.6	0.2	38.1	19.5	53.0	0.5	5.4	2.7	7.5	0.1
DAP	0.05		8.3			2.6	0.3			0.0	0.5			0.1
KNO_3		0.05		65.9	70.3			1.5	1.5			7.2	7.5	
MIX 1	0.05	0.05	19.4	17.2	46.9	1.7	0.8	0.5	1.1	0.0	1.2	0.7	1.6	0.1

evaluated in terms of water and solute fluxes, but also in solute losses. Hence, it seems reasonable to look for conditions generating lower ion dilution instead of just considering the J_s values. Since J_s increases with DS concentrations (Majeed et al., 2015), solute losses are expected to also be higher at higher mass dilution. For example, in tests with KNO_3 alone, the initial DS concentration of 0.50 M lead to losses of around 37%, while 0.05 M KNO_3 lead to losses of up to 70% for both potassium and nitrate to FS. However, looking at reverse fluxes, the J_s was 1.5 mmol m^{-2}h^{-1} for both K^+ and NO_3^+ at 0.05 M, but 42.2 and 44.2 mmol m^{-2}h^{-1} for K^+ and NO_3^- respectively, for tests at 0.50 M of KNO_3 in the initial DS (Table 4). This fact is also clear when looking at the specific reverse salt fluxes (SRSF: J_w/J_s), since they indicate the mass of each ion passing through the membrane to the FS per each liter of water recovered. The SRSF of all ions except for phosphate were much higher in tests with high DS concentration than in those with low DS concentration (Table 4). Therefore, since reverse fluxes and consequent nutrient losses increased with increasing DS concentration, tests with higher initial concentration can be expected to result in higher losses if the process had continued to run until osmotic equilibrium was reached.

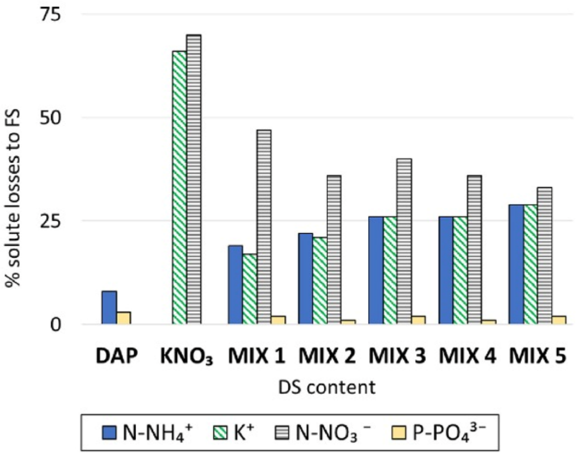

Fig. 2. Nutrient losses (% from mass balance) for tests with DI water as FS and different concentrations of DAP and KNO_3 as DS.

3.3. Draw dilution aiming at nutrient content adequate for hydroponics

To reach adequate NPK concentrations to nourish hydroponic systems, five KNO_3/DAP mixes were tested (Table 2) and compared to the individual fertilizers. All the mixes achieved the target draw dilution (15 times) with initial J_w between 5.5 and 8.7 L m^{-2}.h^{-1} and without reaching osmotic equilibrium (Table 5), which attests the possibility of achieving a higher dilution rate and the benefits of using blended fertilizers instead of individual ones. However, the low average J_w (between 0.6 and 1.0 L m^{-2}.h^{-1}) might limit the feasibility of further diluting the DS, resulting in very large filtration units when the system is operated near osmotic equilibrium, as already mentioned in the previous section.

Similar nutrient losses were experienced for ammonium and potassium (Fig. 2), and they varied analogously along the mixes, (ranging from 19 to 27% for N–NH_4^+ and 17–29% for K^+), due to the similar nature of both cations. In line with previous tests, phosphate losses were almost negligible (lower than 1.8% in all cases), while nitrate losses were the highest with up to 47%. Such high losses have not been reported before in the literature. However, the other studies addressing this topic (Chekli et al., 2017b; Phuntsho et al., 2012) were carried out using higher DS concentrations with much faster filtration kinetics. This may indicate that the migration of draw solutes through the FO membrane in the current study was promoted by the long filtration time due to the operation at low water flux. Former studies probably underestimated potential losses of the FDFO. Nutrient losses observed in this study might be too large in some cases, depending on the composition of salts and their concentrations in the DS. Additionally, the presence of nitrate or phosphate in the FS could make its management and discharge more complex, as these elements can cause eutrophication (Phuntsho et al., 2012). This issue could be mitigated by treating the FS prior to discharge, as proposed by Wang et al. (2020), who added microalgae in their FS that could benefit from the nutrient fluxes from DS to FS. However, we consider that this approach would increase the costs and make the process more complex. Zou et al. (2019) pointed out the need of system optimization, membrane development, long term evaluation, as well as other cost-effective strategies to reduce the reverse salt fluxes in FO, which is crucial for a proper FO operation. In the same line, our results point out the need to evaluate nutrient losses when regard to DS

Table 5
Tests aiming at achieving a suitable NPK content for hydroponics. Osmotic equilibrium was evaluated with electrical conductivity (EC) and considered as achieved when the ratio between final EC in FS and DS was between 0.8 and 1.2

Solution name	DAP (M)	KNO_3 (M)	initial J_w (L. m^{-2}.h^{-1})	avg. J_w (L. m^{-2}.h^{-1})	EC final FS (µS/cm)	EC final DS (µS/cm)	relation EC final FS/DS*	mass dilution	L extracted	L extracted/kg fertilizer
DAP	0.050		3.8	0.5	49	638	0.08	15	28	2092
KNO_3		0.05	2.7	0.2	228	242	0.94	6	10	1029
MIX 1	0.050	0.05	5.5	0.7	231	894	0.26	15	28	1178
MIX 2	0.050	0.10	6.7	0.8	401	1105	0.36	16	30	902
MIX 3	0.030	0.08	5.6	0.6	290	798	0.36	15	28	1147
MIX 4	0.050	0.20	8.7	1.0	732	1473	0.50	16	30	564
MIX 5	0.025	0.15	6.7	0.8	500	1165	0.43	15	28	757

dilution close to real conditions of the FDFO application. Designing the system to limit the filtration time like operating in counter-current mode, applying hydraulic pressure, or increasing membrane surface area may help to avoid such important losses of DS ions. In any case, it is essential to develop membranes with higher reverse flux selectivity, as well as finding suitable FS-DS combinations for a more efficient FDFO process.

The tests also showed that using DAP individually as DS led to lower ammonium losses compared to using blended DAP and KNO_3. On the contrary, KNO_3 alone caused greater nitrate and potassium losses (Fig. 2). Therefore, for practical applications, phosphate fertilizers are a promising DS to be used individually, due to their low J_s, while nitrate fertilizers should be used in combination with other salts to reduce their nutrient losses. These results point out the importance of choosing not only the right salts for the FDFO process but also the right combination.

Nitrogen, phosphorous and potassium (NPK) concentrations at the end of the tests are presented in Fig. 3. Values within the target NPK concentration ranges (yellow bands in Fig. 3) were achieved with MIX 5 (119, 40 and 264 $mg.L^{-1}$ for N, P and K, respectively) without the need for further dilution of DS or changes in nutrient concentrations. Other mixes achieved the targeted concentrations for some of the nutrients. MIX 2 and MIX 4 achieved 117 and 158 $mg.L^{-1}$ of N and 179 and 315 $mg.L^{-1}$ for K, respectively, while MIX 3 achieved 60 $mg.L^{-1}$ of P. However, special attention must be paid to P concentration since values higher than 62 $mg.L^{-1}$ could be toxic for the plants (Termaat and Munns, 1986). Thus MIX 2 and 4, although with acceptable concentrations of N and K, are not considered suitable nutrient solutions due to the concentrations of P well above the reported toxicity level.

It should be noted that some of the tested mixes could still serve as nutrient solutions for some growing stages, despite having a N and K content below the previously mentioned target (*i.e.*, MIX 3). For example, the standard Hoagland solution (Hoagland and Arnon, 1950), which is commonly used in hydroponic experiments, has been applied at half strength in some studies (Adrover et al., 2013; Garland et al., 2004; Wiser and Blom, 2016). In contrast to our results, the final DS concentrations obtained in previous studies (Chekli et al., 2017b; Majeed et al., 2015; Xie et al., 2015; Zou and He, 2016) ware way higher than those required for plant growth, so they pointed out the need for substantial dilution prior to application. Other studies showed the potential of FDFO systems to achieve an adequate DS dilution for direct application for plants, but assuming an unlimited FS volume (Phuntsho et al., 2011), which implies not considering the salinity buildup in the FS; or by applying extra pressure in order to increase the nutrient dilution in DS (Chekli et al., 2017a; Jamil et al., 2016; Sahebi et al., 2015). Results of our study indicate that solutions with an appropriate nutrient content for hydroponics can be achieved with FO (deionized water as FS), showing promising applications of FDFO.

MIX 5 setup could be used in small-scale applications, such as homes or small buildings, considering that only 2 L of concentrated fertilizer solution in DS could extract up to 30 L of FS, to be applied directly in small hydroponic systems within the same building. Extrapolating from the volume of water extracted in the experimental setup (28 L extracted with 37 g of fertilizer salts), 757 L could be extracted for kg of fertilizer using MIX 5 (Table 5). This is a much higher volume than indicated by Phuntsho et al. (2011), who tested the performance of FDFO with 9 fertilizer salts and estimated that 1 kg of fertilizer (DS) could extract up to 29 L water from seawater (FS). However, nutrient losses should be considered in the balances, and low water fluxes could compromise the process. As pointed out by Suwaileh et al. (2020) in a recent review about FO, further work is required regarding membrane development in order to increase the efficiency of the FO process. This study confirms that more selective membranes are required to increase the efficiency of FDFO process, by lowering nutrient losses, especially for monovalent ions.

3.4. *Effect of salts in feed solution*

To evaluate the impact of feed salinity, tests with 6.5 mM of saline solutions in the FS and with 0.05 M of blended or individual fertilizer salts in DS were carried out and compared with baseline tests (DI water in FS) (Fig. 4).

The initial EC for FS ranged between 730 and 1448 μS cm^{-1} and osmotic equilibrium was achieved in all tests (supplementary S2). A good fit of the molar balance for anions and cations in both FS and DS was observed (supplementary S1), showing that even with more ions present in the FS, ions were passing through the membrane to equilibrate the charges (solution diffusion mechanism). Results show that all tests with salts in FS presented lower initial water fluxes compared with the tests with DI water in FS (Fig. 4a), which is in accordance with other studies (Raval and Koradiya, 2016). This is explained by the osmotic pressure present in FS at initial time, related to salt presence (Su et al., 2010), which decreases the net osmotic pressure and thus J_w (Phuntsho et al., 2013). Although J_w were similar along the tests with salts in FS, tests with NaCl in FS showed the best performance in terms of water fluxes and draw dilution (Fig. 4b). A higher difference in osmotic pressures between FS and DS was observed when having NaCl in FS, as its osmotic pressure is lower than those of the other FS salts at the same molar concentration. The results from all tests with salts in FS were far from the target mass dilution and extracted liters and followed the trend of MIX 1>DAP > KNO_3 (Fig. 4c), as it was observed in tests with only DI in FS. All tests performed with KNO_3 alone (except in the case of NaCl) ended up with less DS volume than at the beginning (see negative extracted liters in Fig. 4c), and with the FS having an even higher EC than the DS (supplementary S2). These results show that the presence of salts in FS limits the FDFO performance and application, as the target draw dilution was not achieved in any case. Fig. 5 shows the forward solute fluxes (from FS to DS) as well as the reverse solute fluxes (from DS to FS) for tests with fertilizers alone and blended.

For DAP ions, phosphorous reverse fluxes were not influenced by FS salinity and remained minimal in all tests, including tests with just DI

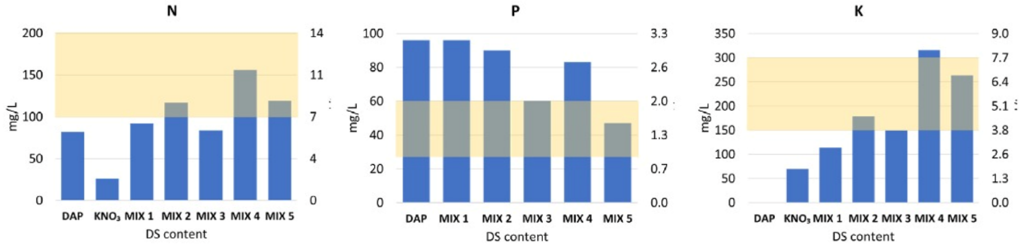

Fig. 3. Final NPK concentrations (blue bars) and desirable NPK ranges (yellow bands) for tests with DI water in FS and individual fertilizers (at 0.05 M initial DS) or blended DAP and KNO_3 in DS (initial DAP concentrations: 0.05 M of for mixes 1, 2, and 4; 0.03 and 0.025 M for mix 3 and 5, respectively; initial KNO_3 concentrations: 0.05, 0.1, 0.08, 0.2, and 0.15 M for mixes 1, 2, 3, 4, and 5 respectively). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

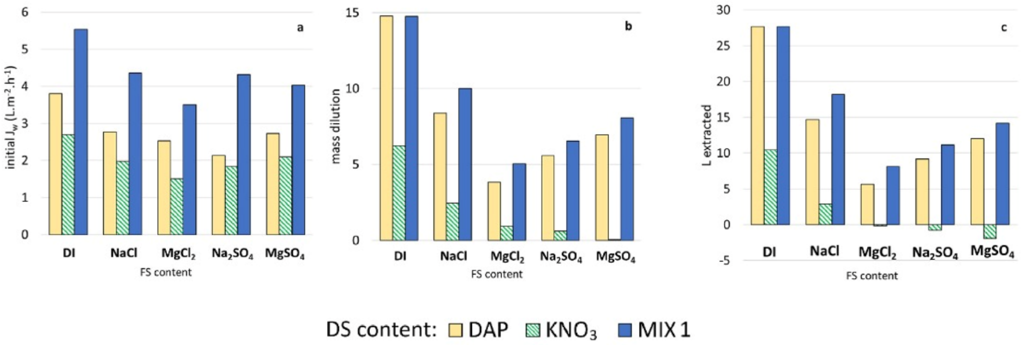

Fig. 4. Initial water fluxes (a), mass dilution of DS (b) and L extracted from FS (c) in tests at 0.05 M initial DS concentration of DAP and KNO_3 individually or blended. FS content refers to DI water or 6.5 mM initial FS concentration of individual salts when applicable.

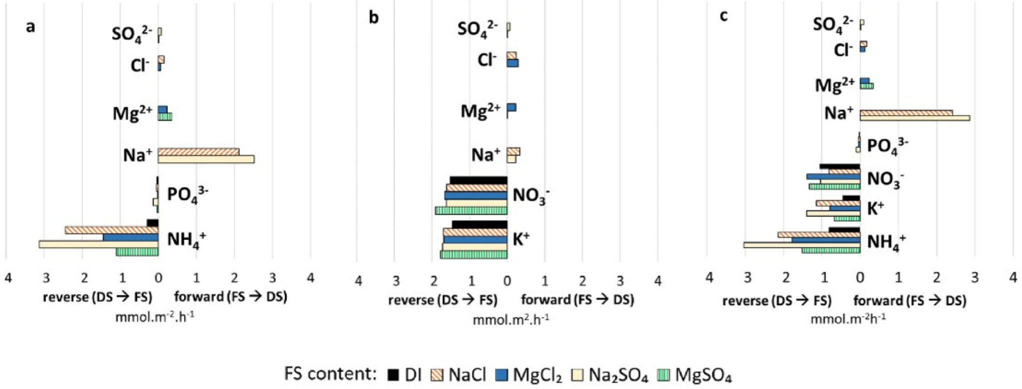

Fig. 5. Solute fluxes (mmol.m^{-2}h^{-1}) for tests with DAP (a), KNO_3 (b) and MIX 1 (c).

water in FS (Fig. 5a and c). Ammonium J_s were slightly higher for blended fertilizers compared to using DAP alone (Fig. 5a and c) and showed a similar trend as when using DI water in FS. Results in Fig. 5a and c also show that the presence of salts in the FS had a strong impact on favoring ammonium passage through the membrane, because of the resulting higher J_s. Ammonium reverse fluxes were up to one order of magnitude higher with salts in FS than with just DI water, the highest being 3.1 mmol m^{-2}.h^{-1} for tests with Na_2SO_4 in FS. This effect was less strong in tests with Mg^{2+} due to its better rejection by the membrane (NH_4^+ J_s lower than 1.8 mmol m^{-2}.h^{-1} for all tests with Mg^{2+} in FS). For KNO_3 ions, nitrate and potassium reverse fluxes were similar for tests with and without salts in FS (Fig. 5b) when tested with KNO_3 alone. For blended DAP and KNO_3 (Fig. 5c), both reverse fluxes of potassium and nitrate were similar regardless of the FS tested, but smaller than with KNO_3 alone. Therefore, it is hypothesized that the J_s of K^+ and NO_3^- are more dependent on DS than FS composition. However, it is worth mentioning that when using blended salts, nitrate reverse fluxes were even lower with Na^+ in FS than when using only DI water (Fig. 5c) due to lower ion exchange. Thus, the presence more than the type of salt in the FS influenced the J_s of nitrate ions. The obtained results show the complexity of ion interactions because the tested DS ions (ammonium, phosphate, nitrate, and potassium) behaved differently and were influenced, to different degrees, by both the presence of salts in FS and the DS composition.

Forward fluxes ($J_{sf,}$ from FS to DS) were minimal for all ions except for Na^+ in tests with DAP and blended salts in DS, with J_{sf} ranging from 2.1 to 2.9 mmol m^{-2}.h^{-1} (Fig. 5a and c). As indicated by Hancock and Cath (2009), feed solutes with larger hydrated radii (*i.e.*, Mg^{2+}), had better FO membrane rejection than monovalent ions (*i.e.*, Na^+). High sodium fluxes (imperfect rejection by FO membranes) are commonly reported (Roy et al., 2016), and in this study its presence influenced ammonium reverse fluxes. This is because Na^+ has higher diffusivity than Mg^{2+} and therefore its transport to the DS facilitates the ammonium transport to FS and vice versa (ion exchange mechanism). The percentage of mass of ion passage from FS to DS (supplementary S2) showed higher Na^+ passages with the pair of monovalent ions (NaCl), because of the retarded sodium diffusion due to the divalent SO_4^{2-} presence in the case of Na_2SO_4 in the FS (solution diffusion mechanism). Similarly, lower anion (Cl^- and SO_4^{2-}) passages were experienced in presence of the divalent Mg^{2+} (supplementary S2). These results point out the importance of FS composition for the performance of the FO process. Concerning draw solutes, divalent ions from FS showed lower forward fluxes, and thus the final FS and DS were less contaminated with ions from the opposite solution when divalent ions were present on both sides of the membrane.

Fig. 6 indicates the distribution of solutes in FS and DS at the end of the tests. A high percentage of draw solutes passed to the feed side, resulting in almost 100% fertilizer losses to FS in some cases (KNO_3). Such observations are of utmost importance as they jeopardize the interest of the FDFO concept. This reinforces the fact that KNO_3 cannot be used alone as DS for fertigation. Comparatively, using DAP or blended fertilizers reduced the losses, which however were still very high for ammonium, nitrate and potassium in most cases as soon as salts were present in the feed solution.

Ideally, osmotic equilibrium should be achieved by an equal EC between original FS and DS solutes without nutrient losses, and not

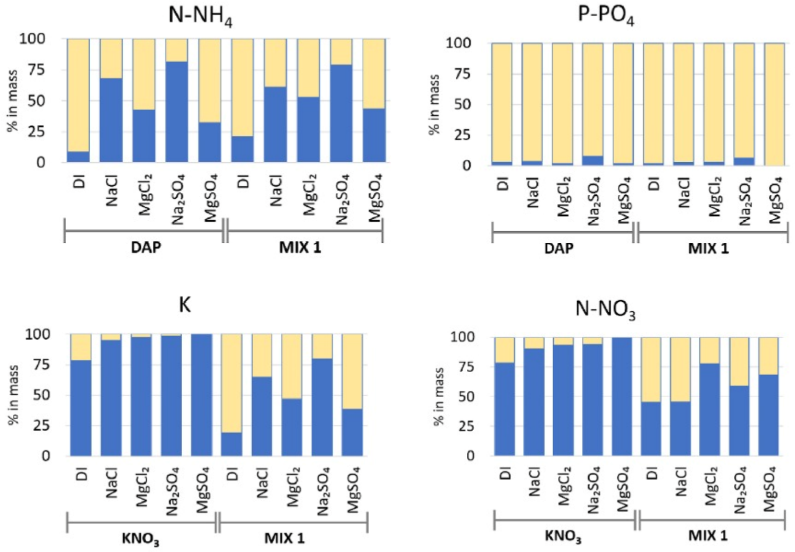

Fig. 6. Percentage of mass of initial DS ions in FS (blue) and DS (yellow) at the end of tests with 0.05 M of initial DS concentration (KNO_3, DAP, and blended, *i.e.*, MIX 1) and 6.5 mM of initial concentration for FS salts when applicable. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

because of large reverse flux of DS solutes to FS, limiting the DS dilution. However, the obtained J_s and nutrient losses were very high, osmotic equilibrium was reached, and water fluxes decreased as a consequence of the salinity buildup in FS caused by the reverse fluxes of DS ions. Existing studies are controversial since some of them point out that the solute fluxes from DS to FS are not influenced by the presence of salts in FS (Hancock et al., 2011), while others indicate the opposite (Phuntsho et al., 2013). In this study, while the presence of salts in FS did not influence PO_4^{3-} behavior, it did clearly influence both J_s and losses of NH_4^+. Although the influence of salts in FS was not clear in terms of reverse fluxes of K^+ and NO_3^-, Fig. 6 shows that it strongly influenced the passage of K^+ and NO_3^- ions to the FS.

Adequate nitrogen and potassium dilution for direct hydroponics application was achieved in some tests with magnesium ions in FS (supplementary S2). For the rest of the cases, due to the high reverse fluxes, nitrogen and potassium concentrations were below the target ranges. In contrast, phosphate reverse fluxes, as well as mass dilution were minimal, and phosphate concentrations in the final DS were well above desired concentrations and toxicity levels. Therefore, the presence of salts in FS plays a fundamental role in the final concentrations of NPK in DS. Additionally, one of the main problems of sodium diffusion in FDFO is its final concentration in the DS, since the DS is intended to be used as a nutrient solution for direct application in hydroponics. Sodium concentrations over 50 $mg.L^{-1}$ are toxic for the plants (Raval and Koradiya, 2016).

Average sodium concentrations in the final DS of tests with NaCl and Na_2SO_4 in FS were above the level of toxicity (supplementary S2). These results indicate that Na^+ forward fluxes may compromise the quality of the final DS and the general efficiency of the FDFO process.

4. Conclusions

This study demonstrated that achieving adequate NPK concentrations for hydroponics by extracting water from reclaimed sources and for direct applications with FDFO process was possible. Using different combinations of KNO_3 and DAP as DS generated promising results for FDFO applications. However, these results were only reached with DI water in FS, which showed the highest osmotic pressure difference between FS and DS, as well as minimal concentration polarization and ion exchange effects. Having real (waste)water as FS might cause decreased water fluxes and increased salt fluxes, which are the opposite of desirable conditions for efficient FDFO applications.

The complexity and the limitations of the FDFO process were especially highlighted when considering operating under conditions close to osmotic equilibrium. A main problem was the loss of the key fertilizer components, from DS to FS, especially when using KNO_3. Additionally, the presence of salts in the feed water could be a limiting factor affecting the achievable dilution rate of the fertilizer due to osmotic equilibrium limitations. Furthermore, the increased reverse salt diffusion of fertilizer when having salts in the feed solution will highly affect the economic and technical feasibility of FDFO applications. Feed ions and especially sodium passage from FS to DS was influenced by ammonium presence, and vice versa, indicating that both FS and DS composition influences the performance of the FDFO process.

Further validation work for specific crops and growth stages should be carried out and the influence of feed (waste)water quality on the process should be studied. Also, more selective membranes, adequate DS composition and concentrations, FS type, and more detailed relations between FS and DS should be carefully evaluated to design future efficient FDFO processes.

Credit author statement

E. Mendoza: Conceptualization, Methodology, Investigation, Writing – original draft, Writing – review & editing, Visualization, Supervision, Project administration. G. Buttiglieri: Conceptualization, Writing – review & editing, Supervision, Project administration, Funding acquisition. G. Blandin: Conceptualization, Methodology, Writing – original draft, Writing – review & editing. J. Comas: Conceptualization, Writing – review & editing, Supervision, Project administration, Funding acquisition.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jenvman.2021.114339.

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ARTICLE 3. Second-Generation Magnesium Phosphates as Water Extractant Agents in Forward Osmosis and Subsequent Use in Hydroponics.

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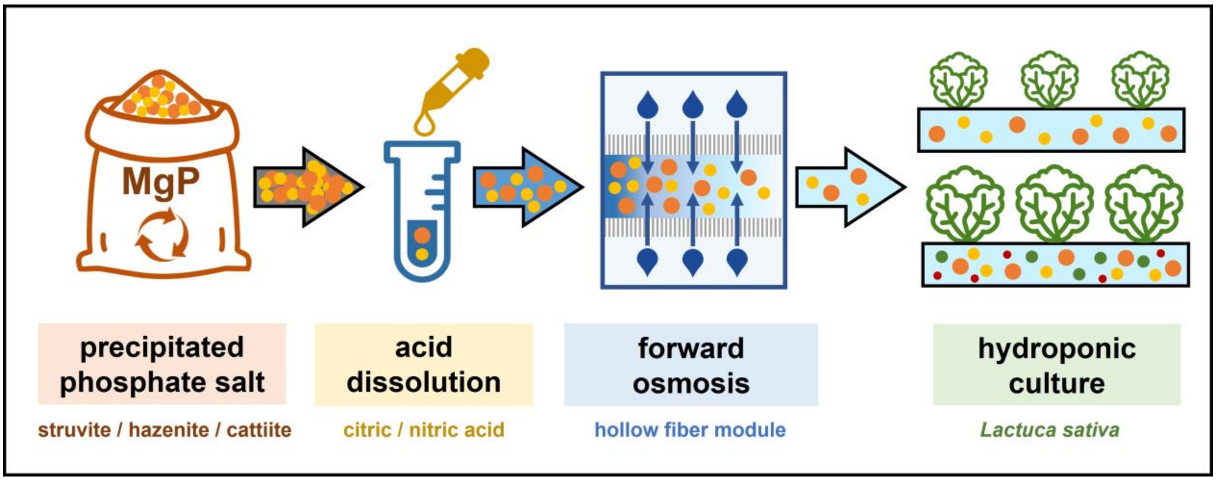

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Second-Generation Magnesium Phosphates as Water Extractant Agents in Forward Osmosis and Subsequent Use in Hydroponics

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Abstract: The recovery of nutrients from wastewater streams for their later use in agricultural fertilization is an interesting approach. Wastewater recovered magnesium phosphate (MgP) salts were used in a forward osmosis (FO) system as draw solution in order to extract water and to produce a nutrient solution to be used in a hydroponic system with lettuces (*Lactuca sativa*, L.). Owing to the low solubility of the MgP salts (i.e., struvite, hazenite and cattiite) in water, acid dissolution was successfully tested using citric and nitric acids to reach pH 3.0. The dilution by FO of the dissolved salts reached levels close to those needed by a hydroponic culture. Ion migration through the membrane was medium to high, and although it did not limit the dilution potential of the system, it might decrease the overall feasibility of the FO process. Functional growth of the lettuces in the hydroponic system was achieved with the three MgP salts using the recovered water as nutrient solution, once properly supplemented with nutrients with the desired concentrations. This is an innovative approach for promoting water reuse in hydroponics that benefits from the use of precipitated MgP salts as a nutrient source.

Keywords: forward osmosis; hydroponic culture; lettuce; nutrient solution; osmotic dilution; precipitated phosphate salt; water reuse

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1. Introduction

Phosphorus (P), along with nitrogen (N) and potassium (K), is an essential nutrient in food production systems. Nowadays, P is mostly obtained from mined phosphate rock, which is a finite resource unevenly distributed around the world, so uncertainties may arise about supply [1]. The European Union (EU) has identified phosphate rock and P as two of the 27 critical raw materials of great importance to the EU economy and with a high risk associated with their supply [2]. As an alternative to mined phosphate rock, wastewater streams are renewable sources of P, and are typically locally available [3]. The recovery of P from wastewater streams (e.g., urban, industrial or agricultural wastewaters) [4,5] and its subsequent reuse, either directly or after intermediate processing, represent a major opportunity to exploit new and more sustainable pathways for the production of P fertilizers. Phosphorus has no substitute but can be reused continuously and is therefore a good example of a critical resource that can be utilized more efficiently within the circular economy framework to support sustainable growth with less pollution. Among the procedures that allow the recovery of P from wastewater streams, the chemically induced crystallization of dissolved phosphate (orthophosphate-P: H_3PO_4 + $H_2PO_4^-$ + HPO_4^{2-} +

PO_4^{3-}) in the form of low soluble salts is one of the most common alternatives [6]. Precipitation is achieved by appropriately supplying metal ions to the liquid phase, frequently magnesium ions (Mg^{2+}) to form magnesium phosphate (MgP) minerals. The most valued precipitated salt is struvite (magnesium-ammonium-phosphate hexahydrate, MAP, $MgNH_4PO_4 \cdot 6H_2O$) [7,8]. Nevertheless, other similar struvite-type salts can be formed in the presence of K^+ and sodium (Na^+), such as K-struvite (magnesium-potassium-phosphate hexahydrate, MPP, $MgKPO_4 \cdot 6H_2O$), Na-struvite (magnesium-sodium-phosphate heptahydrate, MSP, $MgNaPO_4 \cdot 7H_2O$), and K,Na-struvite (hazenite, $Mg_2KNa(PO_4)_2 \cdot 14H_2O$) [9,10]. Newberyite (magnesium-hydrogen-phosphate trihydrate, $MgHPO_4 \cdot 3H_2O$) and trimagnesium phosphates (bobierrite, $Mg_3(PO_4)_2 \cdot 8H_2O$; and cattiite, $Mg_3(PO_4)_2 \cdot 22H_2O$) may also precipitate under certain conditions [11] (Table 1).

Table 1. Magnesium phosphate (MgP) minerals formable in wastewater crystallization processes.

Name	Empirical Formula	Molecular Weight (g/mol)	P Content (wt%)	Mg/P Molar Ratio
Struvite (magnesium ammonium phosphate, MAP)	$MgNH_4PO_4 \cdot 6H_2O$	245	12.6	1.00
K-struvite (magnesium potassium phosphate, MPP)	$MgKPO_4 \cdot 6H_2O$	266	11.6	1.00
Na-struvite (magnesium sodium phosphate, MSP)	$MgNaPO_4 \cdot 7H_2O$	268	11.5	1.00
K,Na-struvite (hazenite)	$Mg_2KNa(PO_4)_2 \cdot 14H_2O$	553	11.2	1.00
Newberyite (magnesium hydrogen phosphate trihydrate)	$MgHPO_4 \cdot 3H_2O$	174	17.8	1.00
Bobierrite (trimagnesium phosphate octahydrate)	$Mg_3(PO_4)_2 \cdot 8H_2O$	407	15.2	1.50
Cattiite (trimagnesium phosphate twenty-two hydrate)	$Mg_3(PO_4)_2 \cdot 22H_2O$	659	9.4	1.50

Concerning water availability, in a recent report, the World Meteorological Organization [12] indicates that more than two billion people currently live under water stress, and that this number is expected to increase, threatening economic and social development worldwide. According to this, increasingly, water is a scarce commodity that is not given enough attention. Therefore, it is important to implement systems that allow its recovery and reuse. In this sense, forward osmosis (FO) is an interesting way to recover and purify polluted water [13,14], such as wastewater or greywater [15,16].

FO bases its extractive potential on the osmotic pressure difference between two solutions that are separated by a semi-permeable membrane, without using mechanical pressure to force permeation through the membrane [17]. The purpose is to extract water from a solution with low salinity (feed solution, FS) to a more concentrated solution (draw solution, DS). Owing to imperfect membrane rejection, during water extraction there are also ion fluxes in opposite directions (from the feed to the draw and from the draw to the feed). These fluxes represent one of the major limitations in the FO systems and entail the need for their quantification. The potential of concentrated fertilizer solutions as water extraction solution has already been tested for the recovery of water containing different contaminants [18–20]. In this way, the use of membranes allows the recovery of water that otherwise could not be used directly for irrigation. Different types of membrane can be used in FO. Unlike cellulose acetate membranes, thin-film composite (TFC) membranes have greater resistance to changes in the pH and temperature [21]. TFC membranes are made up mainly of two parts, the active layer (formed by a polyamide layer) and a porous layer, usually made of polysulfone to avoid mechanical stress. Recent works have explored the potential of other materials to produce FO membranes, such as chitosan [22], which is extracted from crustaceans' shells, or with bamboo pulp [23], reaching superhigh water fluxes (>100 $L/(m^2 \cdot h)$) with both membranes. One of the main causes of loss of osmotic potential in FO is the concentration polarization, which occurs mainly in the support layer due to the accumulation of salts in the porous structure or at the membrane surface [24].

In FO systems, the use of fertilizers as draw solution requires managing them dissolved. Owing to the low solubility of MgPs in water, they need to be dissolved in acidic conditions [7]. Previous experiences have already described the use of citric acid ($C_6H_8O_7$) and nitric acid (HNO_3) for MAP dissolution [25]. Thus, while citric acid (weak tricarboxylic acid, pK_a = 6.4, 4.7 and 3.1) only allows lowering the pH to values near 3.0, nitric acid (strong acid, $pK_a = -1.4$) allows reaching pH values close to 1.0. In the case of using an acid solution as extracting solution in FO, it is advisable to reach pH values not below 2.0–3.0 to preserve the membrane integrity [26].

The lack of land for cultivation, due to dedication to other uses (i.e., industrial, residential), makes hydroponic systems (soilless culture) emerge as a possible alternative. In hydroponics, the plant is in direct contact with water and nutrients. The main components of these waters are N, P and K (Table 2). The specific contents will depend on the type of crop and the applied environmental conditions [27]. This type of controlled cultivation may avoid the loss of crops due to natural events such as high temperature, prolonged periods of rain, drought and storms, allowing for a more stable production [28]. Another factor that can be controlled with hydroponic cultivation is the pollution of the soil caused by traditional crops [29]. Lettuce (*Lactuca sativa* L.) is one of the most popular leafy vegetables and it is combined with many types of food. This plant is a source of vitamin A (organic compounds with unsaturated nutritional forms), vitamin K (fat-soluble vitamins that regulate blood coagulation, bone metabolism and calcium (Ca) levels in the blood) and ascorbic acid, among others [30].

Table 2. Concentration of NPK (mg/L) in standard nutrient solutions for hydroponics, according to previous studies.

Macronutrients			**Mesonutrients**			
N	**P**	**K**	**Mg**	**Ca**	**S**	**Reference**
210	31	234	34	160	64	[31]
168	41	156	36	160	48	[32]
200–236	60	300	50	170–185	68	[33]
168	31	273	48	180	336	[34]

The aim of this work was to assess the use of different MgP products (struvite, hazenite and cattiite) recovered from wastewater streams as draw solution (after acid dissolution) in FO with the subsequent use of the resulting nutrient solution in a hydroponic system with lettuces. This work demonstrated, for the first time, the technical feasibility for the complete treatment line, from the recovery of MgP products [10] to their reuse in hydroponics.

2. Materials and Methods

2.1. Magnesium Phosphates Used as Draw Solution in Forward Osmosis

Three different MgP products were tested as DS (pre-acid dissolution) in a FO system. The compositional characteristics of the salts assayed are listed in Table 3, consisting of: (MgP1, S) struvite coming from the side-stream of an urban wastewater treatment plant; (MgP2, H) hazenite-type material produced from a swine denitrified effluent using newberyite particles as additive [10]; and (MgP3, C) cattiite-type material produced from a swine denitrified effluent using $MgCl_2$ as additive [10]. These three MgP products were non-commercial products. Pictures of them are shown in Table S1 of the Supplementary Materials.

Table 3. Main compositional characteristics of the magnesium phosphate (MgP) products used as draw solution (DS) in the forward osmosis (FO) system.

Ref.	**XRD—Dominant Mineral Phase**	**EA & ICP—Composition (wt%)**					
		N	**P**	**K**	**Ca**	**Mg**	**Na**
S (MgP1)	Struvite	5.3	11.5	0.0	0.9	9.4	0.2
H (MgP2)	Hazenite (w/Newberyite)	0.7	17.1	8.0	0.4	11.7	6.0
C (MgP3)	Cattiite	0.0	10.9	0.1	1.1	10.0	0.1

EA: Elemental Analysis; ICP: Inductively Coupled Plasma; XRD: X-ray diffraction.

2.2. Magnesium Phosphates Dissolution Tests

A dilution ratio of 28 g MgP/L-water (7 g salt in 250 mL water) [25] was initially tested, subsequently applying a four-fold increase up to 112 g MgP/L-water (7 g salt in 62.5 mL water). Two different acids were tested to dissolve the MgP salts: citric acid (C) (4.5 N) and nitric acid (N) (5 N). Dissolution tests were carried out at an acid addition rate of 0.5 mL/min. A titration curve was plotted showing the evolution of the pH against the total amount of protons added. To verify the degree of dissolution of the MgP salts, the remaining total suspended solids (TSS) were measured once pH 3.0 was reached.

2.3. Forward Osmosis Dilution Tests

The FO tests were performed with commercial Aquaporin FO hollow fiber modules (mod. Aquaporin Inside® HFFO6, Aquaporin A/S, Kongens Lyngby, Denmark). These modules, made with inner-selective polyamide based biomimetic active layer, had a total effective area of 0.6 m^2. Deionized (DI) water was used as FS and acid dissolved MgP salts were used as DS. The feed and draw solutions were circulated, respectively, by the shell and bores of the HFFO6 modules (AL-DS) using two peristaltic pumps (mod. 323, Watson Marlow, Falmouth, UK). Both feed and draw solutions were circulated at 0.24 L/min. Experiments were performed with constant feed and draw recirculation speed, leading to continuous DS dilution and FS concentration. The dilution of the DS was performed in two sequential steps: (STEP 1) using 300 mL of DS (acid dissolved MgP) and 5 L of FS (DI water) and operating the system until reaching 5 L of diluted DS; and (STEP 2) using 500 mL of diluted DS produced in step 1 and 5 L of FS (DI water) and operating the system until reaching the osmotic equilibrium.

The water flux (J_w) crossing the membrane from FS to DS was determined by measuring the increase of mass of the DS over time with a balance (mod. PCB 6000-1, Kern, Balingen, Germany). The evolution of the salt content in the FS was determined with an electrical conductivity meter (Crison Instruments SA, Alella, Spain) according to a NaCl-conductivity calibration curve, which was used to calculate the reverse salt flux (J_s) [13]. All data were recorded using a Bluetooth-based system provided by Instrument Works

(Waterloo, Australia) as in former studies [35,36]. Samples of DS at the beginning and at the end of each dilution step were used to assess ion migration across the membrane (from DS to FS).

2.4. Hydroponic System

2.4.1. Experimental Setup and Procedure

A hydroponic system was built with NFT (i.e., nutrient film technique) PVC channels and equipped with four fluorescent LED tubes of 120 cm length (cold white and blue + red, 18W, Osram, Munich, Germany) that were placed 60 cm above the channels. Light cycles of 14 h ON and 10 h OFF were performed to mimic the daily cycle of natural light. Sensors for temperature, relative humidity (mod. Hobo Pendant® U23-001A, Onset, Bourne, USA), and light intensity (mod. Hobo Pendant® UA-002-64, Onset, Bourne, USA) allowed data to be recorded recording at 30-min intervals to monitor the environmental conditions. Lettuce planters were bought in a local market, rinsed to remove the soil, and introduced into the hydroponic system.

Four hydroponic channels were used to test three different nutrient solutions containing dissolved MgP salts, plus one control per experimental cycle. Each channel fitted eight plant pots (distance: 8 cm) filled with inert expanded clay aggregates to support the plants' root system. Two experimental cycles were conducted lasting three weeks each. Weekly, the nutrient solutions were renewed, the number of leaves of the lettuces was recorded and the dry leaves were removed.

To analyze the plant growth and health, three lettuces were selected on the first day of planting and one representative lettuce of average growth was selected per each tested condition on the last day of the test. These lettuces were cleaned with DI water, measured, and dismembered according to their functional parts (i.e., leaves, roots, and shoots). Leaf area was determined using "Easy Leaf Area Free" mobile phone application (last updated 31 July 2015) developed by Easlom and Bloom [37]. Fresh and dry weight (after oven drying at 70 °C for 48 h) [38] were recorded. Concerning nutrient solutions, the final volume, pH, and electrical conductivity were measured weekly. Moreover, samples of the influent water were taken to determine their composition by ion chromatography.

2.4.2. Nutrient Solutions for Hydroponics

The composition of the nutrient solutions obtained through FO depended on the used MgP salt, the applied acidifying agent, and the achieved dilution rates, as will now be discussed. For the correct growth of lettuces, the NPK content in the nutrient solution should be approximately within the reference ranges listed in Table 2. In addition, the excess or deficit of certain ions may be critical for some crops.

The nutrient solutions obtained through FO were tested in two hydroponic experimental cycles planned as follows (Table 4):

- Experimental cycle no. 1. (1) Commercial fertilizing solution (control) made up of $NH_4H_2PO_4$ + KNO_3 + $Ca(NO_3)_2$ + $MgSO_4$; (2) hazenite dissolved with citric acid (HC); (3) hazenite dissolved with nitric acid (HN); and (4) hazenite dissolved with nitric acid and supplemented with KNO_3 (1M) to reach NPK levels similar to those of the fertilizing solution (HN+).
- Experimental cycle no. 2. (1) Control; (2) struvite dissolved with nitric acid and supplemented with KNO_3 (SN+); (3) HN+; (4) cattiite dissolved with nitric acid and supplemented with KNO_3 (CN+).

Table 4. NPK content (mg/L) in the nutrient solutions used in the hydroponic culture of lettuces.

	Experimental Cycle No. 1				Experimental Cycle No. 2			
	Control	**HC**	**HN**	**HN+**	**Control**	**SN+**	**HN+**	**CN+**
NH_4^+-N	23	0	0	0	25	43	0	0
NO_3^--N	168	0	33	105	156	145	124	153
PO_4^{3-}-P	36	83	76	67	37	118	66	89
K^+	187	41	20	153	189	182	250	202
Mg^{2+}	38	81	68	57	38	85	56	116

Reference for MgP salts: S, struvite; H, hazenite; C, cattiite. Reference for acids: C, citric acid; N, nitric acid. +, supplemented with KNO_3.

Additionally, a micronutrient solution containing Cu, Fe, $MnSO_4$, $ZnSO_4$, H_3BO_3 and $(NH_4)_6Mo_7O_{24}$ was added to all the solutions.

In the experimental cycle no. 1, hazenite-derived solutions were chosen since the P concentration was the closest to the reference values (Table 2) and this salt also contributed to the supply of K. During the first cycle, the control condition finished the water in the channel before the scheduled weekly water change in weeks 2 and 3. The same happened in condition HN+ in week 2. Even though more of the respective solution was added to not let the plants dry out, plants were visibly affected, which is why control and HN+ conditions were repeated in the second cycle of the experiment.

In the experimental cycle no. 2, nitric acid dissolved solutions of the three MgP salts considered in this study were tested once supplemented with KNO_3. The salts dissolved in nitric acid were preferred over those in citric acid since they had a contribution of nitrate, one of the main nutrients for plants.

2.5. Analytical Methods

Precipitated salts were analyzed using X-ray diffraction (XRD) and the total content of the main constituents (Na, K, Ca, Mg, and P) was measured after microwave + HNO_3/H_2O_2 digestion using inductively coupled plasma-optical emission spectrometry (ICP-OES) (mod. 5100, Agilent Technologies, Santa Clara, USA). Total N was determined by elemental analysis (mod. 2400 Series II Elemental Analyzer, Perkin Elmer, Waltham, USA).

Water samples were analyzed according to APHA et al. [39]. The pH value was measured with a pH-meter (mod. sensION+ PH3, Hach, Düsseldorf, Germany) and the electrical conductivity was measured with a conductivity meter (mod. EC-Meter Basic 30+, Crison Instruments SA, Alella, Spain). Total suspended solids (TSS) were measured gravimetrically after sample filtration with a glass microfiber filter and subsequent drying to constant weight. The concentration of the soluble cations (i.e., ammonium (NH_4^+), sodium (Na^+), potassium (K^+), magnesium (Mg^{2+}), and calcium (Ca^{2+})), as well as the concentration of the soluble anions (i.e., nitrite (NO_2^-), nitrate (NO_3^-), chloride (Cl^-), sulfate (SO_4^{2-}), and phosphate (PO_4^{3-})), was determined by ion chromatography (mod. ICS-5000, Dionex, Sunnyvale, USA) after filtering samples with 0.2-µm nylon filters.

2.6. Calculations

For the FO tests, the water flux (J_w) in $L/(m^2 \cdot h)$ was calculated with the variation of the DS mass along time, as follows (Equation (1)):

$$J_w = \frac{\Delta m_{DS}}{A \cdot \rho \cdot \Delta t} \tag{1}$$

where Δm_{DS} is the DS mass increase over time (kg), Δt is the time variation (h), A is the membrane area (0.6 m^2) and ρ is the water density (1 kg/L).

Reverse salt flux (J_s) in g/(m^2·h) was calculated based on the FS conductivity (Equation (2)):

$$J_s = \frac{C_{FS,f} \cdot V_{FS,f} - C_{FS,0} \cdot V_{FS,0}}{A \cdot \Delta t} \quad (2)$$

where $C_{FS,0}$ and $C_{FS,f}$ represent initial and final salt concentration (g/L) in FS –NaCl–, respectively, and $V_{FS,0}$ and $V_{FS,f}$ represent initial and final FS volume (L), respectively.

Total ion migration (i.e., the percentage of ions that moved from the DS towards the FS by the end of the experiment in relation to the ion content in the initial DS in the first dilution step) was calculated considering the ratio between theoretical and measured ion concentrations in final DS, as follows (Equation (3)):

$$total\ ion\ migration\ (\%) = \left(1 - \frac{C_{DS,f\_2} \cdot d}{C_{DS,0\_1}}\right) \cdot 100 \quad (3)$$

where: $C_{DS,0\_1}$ and C_{DS,f_2} refer to individual ion concentrations in the DS at the beginning and the end of the dilution process (mg/L), respectively; i.e., the initial concentration in the first dilution step and the final concentration in the second dilution step, respectively. d is the total dilution factor, which is the product of the first dilution by the second.

Growth of the lettuce plants was assessed by considering number of produced leaves, leaf area, fresh and dry weight, as well as growth parameters commonly used elsewhere [38,40,41], and according to the formulas listed below:

$$RGR = \frac{\ln W_2 - \ln W_1}{t_2 - t_1} \quad (4)$$

$$SLA = \frac{(LA_2/LW_2) - (LA_1/LW_1)}{2} \quad (5)$$

where: W is the total dry weight of the plant (g), t is time, LA is the leaf area (cm^2) and LW is the dry weight of the leaves (g). t_1 and t_2 (days) refer to the day of planting and harvesting of each plant, respectively. The relative growth ratio (RGR, g/(g·day)) (Equation (4)) allows knowing the growth rate of a plant regardless of its size. The specific leaf area (SLA, cm^2/g) (Equation (5)) indicates the robustness and/or density of the leaves.

3. Results and Discussion

3.1. Acid Dissolution of the Magnesium Phosphates

The acid dissolution of the three MgP salts (i.e., struvite, hazenite and cattiite) led to similar titration curves depending on the acid used. Figure 1 shows such patterns when considering 28 g/L as the dilution ratio. In the case of using citric acid, the titration curves did not show abrupt changes in the pH value. The slowest pH decrease rate was measured for struvite, which could be caused by the nature of the salt (i.e., the ammonium released behaved like a pH buffer; this was the least hydrated salt). The use of nitric acid did not imply big differences between salts either, struvite again being the salt that offered the most resistance to decreasing the pH. Unlike the previous case, a sharp drop occurred at pH 5.5–3.0, making it difficult to measure a stable pH-value within this range.

Under the dilution ratio of 112 g/L, MgP salts showed good capacity of dissolution at pH 3.0 (data not shown). Thus, undissolved TSS reached 2.5% of the initial solids content as a maximum (Table S1 in Supplementary Materials), confirming the low loss of salts (not dissolved) occurring during the dissolution process. Struvite needed the largest amount of acid for dissolution. For this salt, final TSS analysis only revealed 1.5–1.8% of solids loss. According to these results, almost complete dissolution of the MgP was obtained for all the conditions tested.

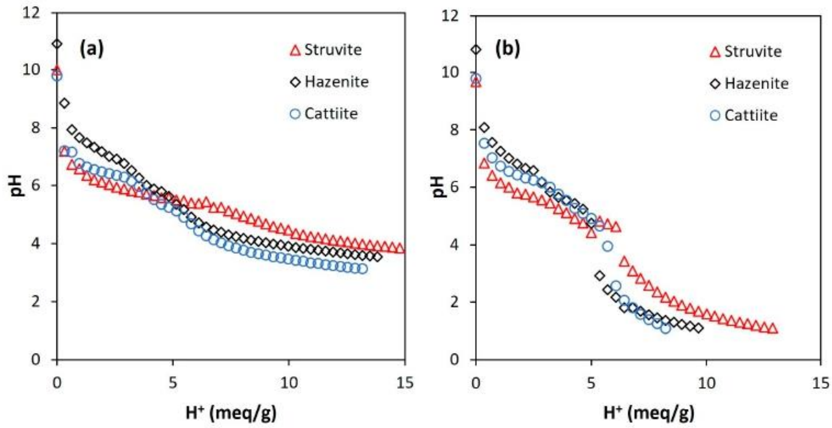

Figure 1. Titration curves for the acid dissolution of the MgP salts (struvite, hazenite and cattiite) using citric acid (**a**) and nitric acid (**b**). Dilution ratio: 28 g salt per liter of water.

3.2. Water Extraction and Nutrients Dilution with Forward Osmosis

3.2.1. Forward Osmosis Dilution Potential

The FO dilution tests were performed in two sequential steps. In the first step, high DS dilution was reached, equivalent to a dilution factor of about 16 times (Figure 2a). In the second step, an additional dilution factor of around four times was achieved (Figure 2b), leading to an overall dilution factor of above 60 times (Figure S1 in Supplementary Materials). By the end of the second dilution step, DS and FS conductivities reached similar values (<1.5 mS/cm), attesting that the system had nearly reached the osmotic equilibrium, and that no more water could be extracted with the nutrient solution. In fact, when looking at the water permeation flux (Figure 2c and Figure S2 in Supplementary Materials), low values were reached even during the first dilution step. This fact can be explained by the rapid dilution of the concentrated DS. Consequently, the DS partly lost the osmotic potential during the first hours of the FO process, leading to low permeation flux, so the overall filtration time took longer than 25 h to reach the targeted volume (Figure S2 in Supplementary Materials). Thus, such long filtration time was inherent to the setup design; from the industrial scale-up point of view, it may result in high membrane area requirements to achieve the proposed dilution in less time.

Interestingly, very low reverse salt fluxes were observed from the DS to the FS (Figure 2d), much lower than in other studies with similar FO membranes [19,42]. These results indicate that most of the ions from the initial DS seemed to remain in the original solution and, thus, they were part of the nutrient solution usable in hydroponics. Comparatively, the MgPs acidified with nitric acid exhibited slightly higher reverse salt flux than when using citric acid. Such behavior could be related to the fact that the nitrate ion is smaller than the citrate ion and so it is more prone to diffuse through the FO membrane [43].

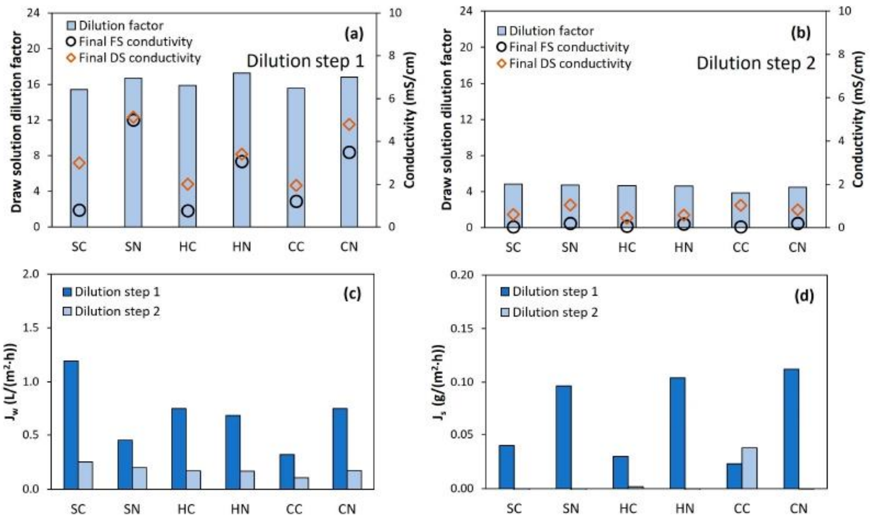

Figure 2. Results for the FO dilution tests. DS dilution factors in step 1 and step 2 of the FO process (**a**,**b**), water flux through the membrane (**c**) and reverse salt flux through the membrane (**d**). Reference for MgP salts: S, struvite; H, hazenite; C, cattiite. Reference for acids: C, citric acid; N, nitric acid.

3.2.2. Total Ion Migration through the Forward Osmosis Membrane

Ion migration from the DS to the FS through the FO membrane is not desirable since it implies loss of valuable nutrients. Thus, ion migration should be kept to a minimum for an efficient FO performance. Overall, in this study, even if calculated reverse fluxes were low, medium to high ion migration was observed for all the tests and ions (Figure 3). Monovalent ions (i.e., NH_4^+, Na^+, K^+ and NO_3^-) migrated to the FS to a greater extent than divalent (Mg^{2+}) and eventually trivalent (PO_4^{3-}) ions. This behavior is attributable to the smaller hydrated radius and the lower electrostatic repulsions with the membrane of the monovalent ions, which passed across the membrane more easily to balance the osmotic pressure between the two solutions. Cation migration was favored by the negatively charged surface of the membrane [44,45], while NO_3^- migration could be explained because of the diffusion mechanism, which would imply the transfer of this anion through the membrane to balance the positive charges. This behavior was clearly observed in the tests with hazenite, where Na^+ and K^+ migration was much higher with nitric acid than with citric acid (Figure 3). This higher migration was due to the high diffusivity of Na^+, K^+ [46], and NO_3^- [47], with the latter one passing through the membrane in similar proportions than cations to balance the positive charges (solution diffusion mechanism). Otherwise, Na^+ and K^+ migration with citric acid was lower since there was not a counter ion (i.e., NO_3^-) able to diffuse through the membrane. For the tests with struvite, high NH_4^+ migration was also found regardless the acid applied, leading also to the highest phosphate migration. In that case, NH_4^+ migration could be explained by the smaller hydrated radius than other cations, which would make it pass through the membrane more easily. The higher Mg^{2+} and phosphate migration observed might be explained by the higher ion contents at the initial DS (struvite was the least hydrated phosphate tested salt). In the case of cattiite, ion migration was lower than for the other MgP minerals (Figure 3) as cattiite only contains Mg^{2+} and phosphate, which are not monovalent, so with a scarcer diffusion through the membrane [48]. These results point out the complexity of the ion transport in FO and the need to mitigate these ion fluxes. The length of batch-operated experiments could also cause significant ion losses, resulting in numerous passages of solutions across the membrane. In this sense, another study showed that, in FO, there is less diffusion when a system is designed to allow continuous operation or with a shorter operating time [49].

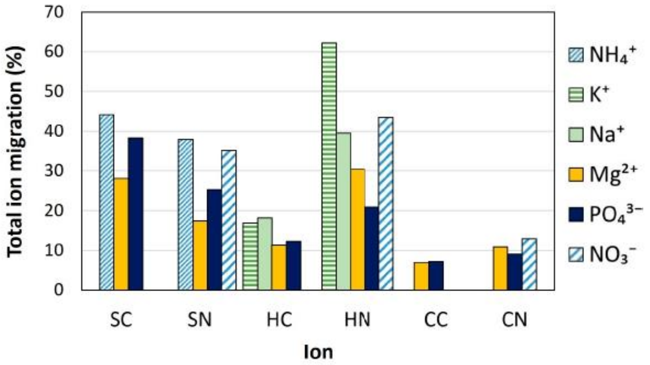

Figure 3. Total ion migration through the membrane (% ions lost to FS in the two dilution steps). Reference for MgP salts: S, struvite; H, hazenite; C, cattiite. Reference for acids: C, citric acid; N, nitric acid. Reference for acids: C, citric acid; N, nitric acid.

3.2.3. Composition of the Diluted Draw Solution for Its Application in Hydroponics

The choice of the best diluted DS as nutrient solution in view of its further application in the hydroponic culture of lettuce depends on different factors, such as FO performance and nutrient composition and concentration. Concerning FO performance, tests with cattiite showed the lowest ion migration (Figure 3), which means less losses of ions to the FS and, thus, more efficient performance. However, cattiite only contains one macronutrient (P) and one mesonutrient (Mg). Struvite tests showed higher nutrient losses, but struvite also contains N, which reduces the need for an external supply of this nutrient. Although hazenite contains K, one of the main nutrients for plants, it also contains Na, which might be toxic at high concentrations. Na concentration in the nutrient solutions assayed reached up to 32 mg/L, whilst it is not recommended to exceed 150 mg Na^+/L, especially when there is Cl^- in the solution [27]. Na^+ migration to FS may be considered as an advantage, since lower Na^+ content will be present in the final DS for use in hydroponics. Regarding the acid used to dissolve the mineral salts, even though in general terms more nutrients were lost using nitric acid, the presence of NO_3^- in the final DS is an advantage since NO_3^- is one of the main nutrients for plant growth.

Concerning the obtained dilution levels, it is important to attain a proper nutrient content for hydroponics (Table 2), i.e., within desired concentration ranges. Low nutrient concentrations will lead to a poor plant growth, but high concentrations might result in plant toxicity. Therefore, optimal composition was selected for those cases in which final nutrient concentrations were within or below the desired ranges for lettuce growth (Figure 4), solving imbalances by adding a nutrient supplement without posing risk to the plant health. HN reached Mg and P concentrations within the required ranges at the end of the DS dilution and also had some K (Figure 4), and thus was selected as the best candidate for further application in hydroponics. HN was followed by SC, although in this case Mg and P concentrations were slightly above the desired ranges. In the tests using struvite (SC and SN), NH_4^+-N concentrations in the diluted DS (34 mg/L for SC and 39 mg/L for SN) were not far from the optimum concentration found in the commercial nutrient solution (about 25 mg/L). The other tested conditions led to higher P and Mg contents than desired (Figure 4) but reaching a slightly higher DS dilution would result in P and Mg concentrations within the appropriate ranges.

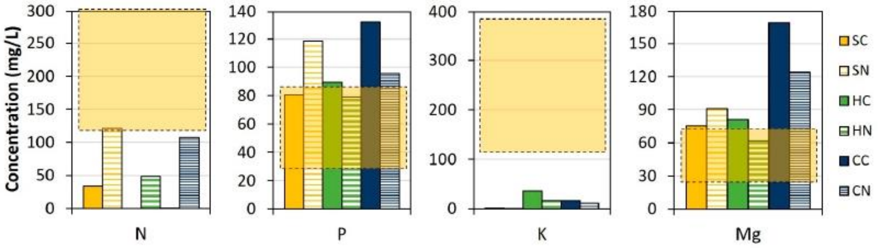

Figure 4. Nutrient concentration after DS dilution by FO in view of its further application in hydroponics and estimated optimal ranges (bars, ±30% values from Table 2) with the optimal ranges (yellow squares). Reference for MgP salts: S, struvite; H, hazenite; C, cattiite. Reference for acids: C, citric acid; N, nitric acid.

Nonetheless, it is not common to achieve such low nutrient concentrations in FO and, thus, the achieved concentrations can be considered as satisfactory. Most of the studies found in the literature, in fact, point out the need to further dilute the DS to be able to apply it in hydroponics [50–52]. Proper DS dilutions with FO were only achieved after applying pressure [53,54], or with higher nutrient losses to the FS [13].

3.3. Hydroponic System

3.3.1. Experimental Conditions

The experiment was conducted in two cycles of three weeks each, with about 3 °C higher temperature in the second cycle (Cycle 1: 24 ± 2 °C; Cycle 2: 27 ± 2 °C), while the light intensity (avg. 4000 ± 1400 lux due to light gradient in the system) and relative humidity (avg. 64 ± 8%) were similar in both experiments. The average N, P, K and Mg concentrations in the nutritive solutions applied in the tested conditions with the ideal ranges are shown in Figure S3. Due to the lacking or low concentrations of some of the main nutrients in the diluted solution from FO, KNO_3 was added as a supplement for the conditions HN+, SN+ and CN+ to reach values in accordance with those found in literature (Table 2).

3.3.2. Plant Growth Analysis

Plants grown in the control condition with commercial nutrient solution showed different growth in both cycles (four more leaves produced in the first cycle but almost 40% higher leaf area produced in the second cycle). This could be due to the rather higher temperature in cycle 2 (where temperatures closer to 20 °C are preferrable for lettuce growth [41,55]) and the fact that the initial plants for each cycle were noticably different in size (e.g., plants had in avg. eight and five leaves at the beginning of cycles 1 and 2, respectively). Consequently, the growth parameters of the conditions tested in the different cycles are compared to their respective control condition and subsequently with each other.

The first cycle included HC, HN, HN+ conditions and control (Figure 5). Condition HC failed to grow lettuces, which may be explained by the lack of nutrients in the solution, with very low N and K concentrations (Figure S3). The control grew about twice as much in terms of produced weight and three times in terms of produced leaf area as both the HN and HN+ conditions (Figure 5), even while frequently finishing the water before the scheduled time. Conditions HN and HN+ performed similarly (RGR of 0.056 & 0.061 g/(g·day), Figure 5), producing fewer leaves that were smaller in size but a little thicker (lower SLA, Figure 5) than control leaves. The results indicate that even if nutrient supply in HN was below the ideal range for hydroponics, the growth of the plants was similar, in cycle 1, to HN+ condition with extra nutrient supply (see picture in Figure S4). However, control plants and HN+ plants that ran out of water at least once were visibly affected by this incidence, which is noticeable also in the rather low RGR (highest RGR in control with 0.071 g/(g·day)) when compared with the literature values e.g., 0.08 (at

10 °C) to 0.14 g/(g·day) (at 20°C) [41] or 0.113 (mean) with −0.036 & 0.295 g/(g·day) (min & max) [56]. As a result, HN+ and control conditions were repeated in the second cycle to confirm wheter the lack of water affected plant growth.

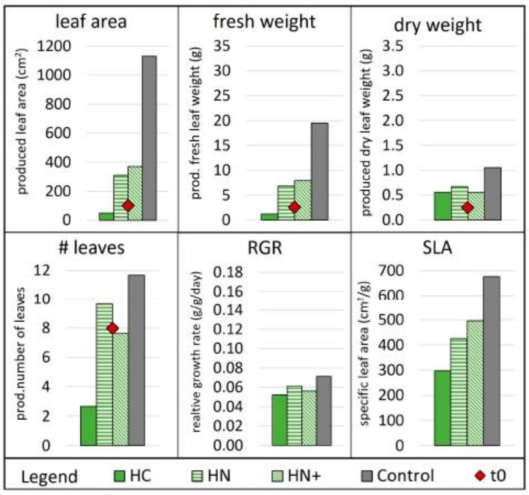

Figure 5. Plant growth parameters in week 3 of cycle 1. Number of leaves, leaf area, fresh and dry weight at t0 are indicated as red dots while the additionally produced quantities after 21 days are indicated as bars. Abbreviations: RGR, relative growth rate; SLA, specific leaf area. Reference for MgP salts: H, hazenite. Reference for acids: C, citric acid; N, nitric acid. +, supplemented with KNO_3.

In the second cycle (SN+, CN+, the repeated HN+, and control) the initial (t0) plants had on average of three leaves and 63% dry mass less than in the first cycle. Nevertheless, plants of all conditions produced higher dry and fresh weight as well as higher leaf area (Figure 6), while growing fewer leaves than cycle 1 (excluding HC, Figure 5). This is also displayed in the observably higher magnitude for RGR of cycle 2 compared with cycle 1 (Figures 5 and 6), as well as RGR of the previously mentioned literature [41,56]. The plants of CN+, SN+ and the control in cycle 2 grew big leaves of increasingly less stable structure along the weeks. The leaves had visually weaker leave blades with elongated and proportionally thin stems and petioles, despite the lower SLA indicating an already higher thickness (dry mass per area) of leaves compared to previous cycle (see picture in Figure S4). An exception to this was condition HN+, which continuously had strong petioles and were stable in structure throughout the leaves, which is surprising since this condition produced the lowest number of leaves but the highest leaf area up to this point. This could be explained by HN+ also having produced the highest dry mass at the same time. On the other hand, SN+ plants showed the optically weakest structure, despite performing similarly to HN+ regarding plant growth parameters, potentially due to the phosphate concentration (118 mg/L), which was higher than the ideal range (30–80 mg/L), which could be toxic to the plants. The water in HN+ briefly ran out again in the third week, but no noticeable effect was observed in this cycle. Conversely, due to the noticably higher RGR of HN+ in the second cycle than in the first one, it can be concluded that the low growth rate of cycle 1 control and HN+ could be related to the drying out, subsequently disproving the prior conclusion in cycle 1 that HN, which did not face the same issue, acheived a comparable growth rate to HN+.

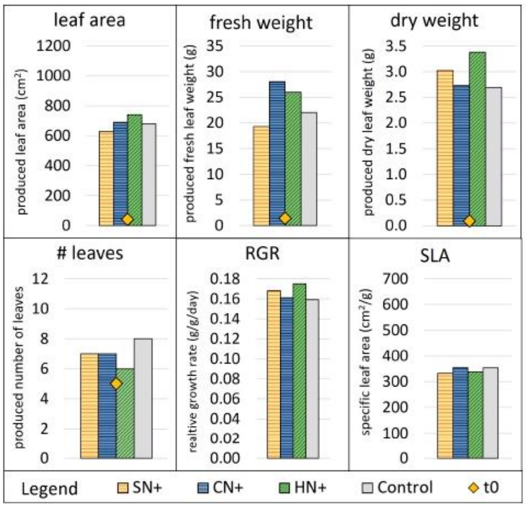

Figure 6. Plant growth parameters in week 3 of cycle 2. Number of leaves, leaf area, fresh and dry weight at t0 are indicated as yellow dots while the additionally produced quantities after 21 days are indicated as bars. Abbreviations: RGR, relative growth rate; SLA, specific leaf area. Reference for MgP salts: H, hazenite. Reference for acids: C, citric acid; N, nitric acid. +, supplemented with KNO_3.

Overall, all experimental conditions in cycle 2 produced similar or higher dry weight than their control plants (Figure 6), even while growing slightly fewer leaves. The same is observed for for the leaf area and fresh weight, with only SN+ performing slightly worse than the control. However, in RGR, all conditions (cycle 2) performed equally as well or slightly better than the control (Figure 6).

Finally, plants grown in all experimental conditions and the control plants were similar in color, though some necrotic edges (i.e., tipburn) were observed in HN+ plants (see picture in Figure S4). The tipburn is usually caused by calcium deficiency, the concentration of which in solution was minimal (data not shown) and it increases with growth rate [57], which can explain why this symptom only appeared in the bigger plants of HN+ condition. Additionally, tipburn could be caused by stress generated by temperatures over 25 °C [58]. These two factors were present in the system and could, therefore, induce tipburn in the lettuces. A more balanced nutrient solution, also including the mesonutrients calcium and sulphate, and a cooler environment should not have induced this symptom in the lettuces.

The described results show that diluted MgP solutions were suitable to grow lettuces in hydroponic cultures. However, only those conditions with KNO_3 supplement showed a comparable growth with the controls. Even if at the end of cycle 2, some plants showed tipburn; this could have been caused by the experimental conditions and by the plants being too close to each other. Additionally, Na^+, which might be toxic for the plants, but is present in hazenite, did not seem to be dangerous for the growth of the plants, since HN+ condition had the plants that performed best, in both cycles. Overall, these are successful results that open the door to decrease the demand of industrially produced P while promoting the valorization of second-generation P.

4. Conclusions

An innovative approach was evaluated as a proof of concept for the use of MgP salts as DS in FO in order to extract water and produce a nutrient solution to be used subsequently in a hydroponic system with lettuces. The main conclusions reached are as follows:

- Wastewater-precipitated MgP salts, such as struvite, hazenite and cattiite were almost completely dissolved in water (at dissolution ratios from 28 to 112 g mineral per liter of water) using citric and nitric acids when final pH was set to 3.0.

- FO allowed reaching a dilution level of the DS close to that required for hydroponics and no further dilution was needed. Ion migration across the membrane (from DS to FS) was not limiting since the desired dilution was achieved. Ion migration tended to compensate the charges, involving preferential pairs such as K^+-Cl^--Na^+, K^+-NO_3^-, and NH_4^+-NO_3^-. Even if reverse fluxes were low, ion migration (which is translated in nutrient losses) was medium to high, especially for monovalent ions, which decreases the economic efficiency and feasibility of the FO technology. In this sense, more selective membranes or different DS are required to reduce these fluxes. Considering the target of FO, it could be interesting to dissolve the MgP salts with sulfuric acid, since it is a divalent ion, which will decrease the migration of other ions through the membrane compared with nitric acid, and at the same time the sulphate can be used by plants, since it is a mesonutrient.
- Functional growth of lettuces in a hydroponic system was achieved with the water recovered using FO. The tested conditions with MgP salts supplemented with KNO_3 produced plants of comparable weight and leaf area as the control condition, with HN+ being the most stable and having the biggest plants, even when compared to the respective control condition. The Na content in hazenite was shown not to be a problem for plant development. The tested MgP salts were proved as an accurate nutrient supply for plant growth, making these by-products valuable fertilizers.

This study was a first proof of concept, moving towards application using real streams. Other challenges such as fouling and limited dilution rate may be observed. Thus, future studies should focus on testing real wastewater streams as feed solution and increasing the efficiency of the FO process by improving water fluxes while reducing reverse salt fluxes.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/membranes13020226/s1. Table S1: View of the MgP products used as DS in FO. Table S2: TSS not dissolved by the end of the acid dissolution test. Figure S1: Total dilution factor in the 2-step FO. Figure S2: Filtration kinetics example. Figure S3: Nutrient solutions tested in the hydroponic experiments. Figure S4: Pictures of lettuce plants.

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ARTICLE 4. Rejection of organic micropollutants from greywater with forward osmosis: A matter of time.

Esther Mendoza, Gaetan Blandin, Marc Castaño Trias, Lucas Leonel Alonso, Joaquim Comas and Gianluigi Buttiglieri

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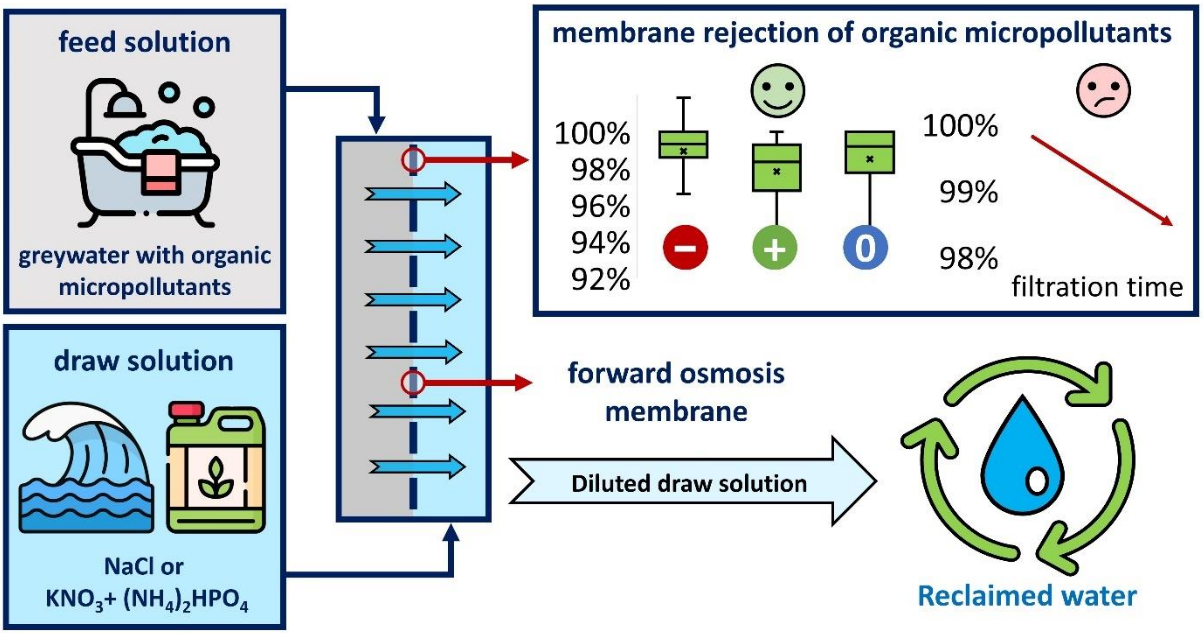

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Rejection of organic micropollutants from greywater with forward osmosis: A matter of time

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ABSTRACT

Forward osmosis (FO) has popularized lately due to its lower fouling propensity, higher pollutant rejection, and potentially lower energy consumption than other membrane technologies. Greywater (GW) is a good candidate for FO treatment for its further reuse due to its lower organic and solids content than other wastewater streams, but it contains organic micropollutants (OMP) that might pose a risk for its reuse. Seawater (NaCl) is widely used as draw solution, but the use of fertilizers instead offers the advantage of applying the diluted draw solution for irrigation. This study evaluated the performance of FO for GW treatment focusing on OMP rejection, by means of tests with fertilizers or NaCl as draw solutions and deionized water or GW as feed solutions. The main GW constituents were well rejected, except for sodium, which diffused to the draw solution. Excellent OMP rejection was obtained (>95% in most cases, average 98.5% rejection at the end of the experiments), which was influenced by experimental conditions and OMP properties. Highest rejections were observed for negatively charged OMP and for neutral/positive charged OMP with large molecular weight. Feed type and contact time between feed and draw solutions had the biggest influence on OMP rejection, which decreased over time and by using GW instead of deionized water as feed solution. The diluted draw solution proved safe for irrigation water reuse purposes although sodium content could be of concern. Further studies on the contact time between the solutions are required to foster further applications of FO, as it clearly influenced the rejection of OMP, aspect that is crucial for safe water reuse applications.

1. Introduction

In the face of escalating global population growth, industrial development, and climate change, the demand for freshwater has reached unprecedented levels, placing tremendous pressure on water resources. In this context, water reuse emerges as a promising and indispensable strategy to cope with this critical situation. Water reuse not only mitigates pollution and prevents environmental pollution but also conserves precious freshwater reservoirs, ensuring a resilient and sustainable water supply for present and future generations. Decentralization and on-site water treatment represent a transformative approach to water management, where treatment can be tailored to meet specific end-use requirements and consequently offer immense potential for water reuse in communities, schools, hotels, etc. Precisely, the segregation of different wastewater streams (e.g., blackwater, greywater) offers the advantage of establishing even more specific treatments for the different uses, and consequently, a more efficient water reuse practice can be achieved. Greywater (GW), coming from showers, kitchens, laundries, and hand basins, is an attractive source for water reuse since it represents up to 75% of the total volume of domestic wastewater [1], but it only contains 30% of the total organic load [2] and low levels of pathogens [3]. Produced GW varies among regions, ranging from 15 to over 200 L per person per day [1,2], which can represent a significant volume for on-site reuse, especially in areas with water scarcity or difficult access to freshwater resources. Hence, segregating, treating, and reusing GW represents an additional water source, and a way towards sustainable urban water systems [4–6]. However, GW may contain hazardous elements, among which special attention must be paid at the presence of organic micropollutants (OMP), a group of heterogeneous compounds, such as pharmaceutical active compounds (PhACs), endocrine

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disruptors (EDCs), industrial chemicals, or pesticides. The presence of OMP in water has become a pressing environmental concern, as it poses risks to ecosystems and human health, requiring urgent research, monitoring, treatment, and mitigation to safeguard water quality and ensure sustainable management of water resources. In a recent review about OMP in GW [7], 350 OMP were found in different GW sources, where surfactants were detected with higher concentrations, followed by personal care products, preservatives, UV filters, and PhACs. Indeed, OMP concentrations in GW were in some cases reported to be higher than in wastewater due to lack of dilution with other water streams [4]. Therefore, the study of the presence, fate and removal of these compounds from GW is crucial to promote safe GW reuse practices.

Membrane technologies showed good performance for water treatment [8], and are widely implemented in water treatment streams thanks to their compactness, which is of interest in the context of on-site GW treatment, where there is generally a limited footprint available. Forward osmosis (FO) technology has emerged in the last years showing better performance than other membrane technologies with respect to pollutant rejection, energy consumption, and fouling propensity [9,10]. A FO process benefits from the difference in salinity between two solutions separated by a dense semipermeable membrane. Due to the osmotic gradient between the two solutions, which is the driving force of the process, the water molecules of the less saline solution (feed solution: FS) are drawn towards the solution with higher salinity (draw solution: DS) [11]. The process is based on osmotic pressure difference and requires less energy to transport the water across the membrane than other pressure-driven membrane processes, like reverse osmosis (RO) [12,13]. An efficient DS produces enough osmotic gradient with the FS to extract water through the FO membrane, and should contain small sized charged ions, have low viscosity, and be non-toxic [14]. The most applied DS is NaCl due to its high osmotic potential and availability (seawater). In most cases, DS then needs a second step, usually coupled with RO, to regenerate the DS while extracting the clean water [12], affecting the overall energy efficiency of the system. An alternative approach is the direct application of the DS without the need of a reconcentration step. This is the case of fertilizer drawn forward osmosis (FDFO), in which the DS is a concentrated fertilizer solution that can be applied for irrigation after its dilution. FDFO approach avoids the need of DS reconcentration, resulting in a simpler and more efficient process, and with the potential of on-site reuse of the diluted DS. As to FS types, the real benefit of FO would be in the use of impaired sources [13], such as brackish water, wastewater, or greywater. Most developed FO membranes are based on the thin film composite (TFC) approach and consist of a thick porous non-selective layer of about 150 μm coated with an ultrathin polyamide separation (active) layer of less than 1 μm [15]. Most common TFC membranes are negatively charged [16]. In general, TFC membranes can achieve higher water fluxes and salt rejection than cellulose triacetate (CTA) membranes [17]. Biomimetic FO membranes, consisting of TFC layer with embedded aquaporin proteins, 100% selective to water molecules [14], have gained popularity in the last years due their good performance in terms of permselectivity (high water fluxes, low salt permeability) in comparison with other FO membranes [18].

Although the concept of forward osmosis as a potential water treatment technology was introduced in the 1970s [19,20], its development has not been as rapid as that of reverse osmosis, due to some issues derived from the nature of the process. First of all, reverse salt fluxes (J_s), which are solute losses from DS to FS, are an important limitation of the FO process [21]. Reverse salt fluxes, in fact, decrease the osmotic gradient between FS and DS, resulting in the case of FDFO in a loss of nutrients, and therefore economic losses. Additionally, forward solute fluxes (J_f, from FS to DS) lead to DS contamination and should be reduced as much as possible. Finally, all FO processes experience concentration polarization (CP) effects, creating a concentration gradient within the porous support layer (internal CP: ICP) or on the membrane surface (external CP: ECP), resulting in water flux reduction [22], and consequently in a critical issue of FO [23], independent on membrane characteristics [24]. Consequently, it is necessary to design processes and develop membranes that limit solute fluxes while maximizing water permeation (i.e., water flux: J_w) with the aim of achieving an efficient FO process for full-scale applicability. Despite the increasing interest in GW, limited research has explored forward osmosis application for GW treatment and reuse. Wang et al. [25] focused on the evaluation of the intrinsic separation properties and antifouling performance of surface modified TFC membranes for GW treatment. In a later study, they obtained rejections close to 99% for GW constituents (total nitrogen - TN, NO_3, NH_4, linear alkylbenzene sulfonate, and Mg) with CTA membranes [26]. Besides, approximately 100% rejection of large organic contaminants and above 80% rejection of sodium dodecyl sulphate were obtained with TFC membranes [27]. Rejections exceeding 90% for eleven GW constituents (ions, lactic acid, glucose, sodium dodecyl sulphate, and sodium dodecyl benzene sulfonate), tested separately and at different concentrations, were reported with aquaporin membranes [28]. In a recently published study, it was found that, with the exception of linear alkylbenzene sulfonates adsorbed onto the FO aquaporin membrane, all other constituents from real GW (chemical oxygen demand - COD, total organic carbon - TOC, TN, NH_4, Ca, Mg) exhibited high rejection rates, which were significantly influenced by the membrane surface morphology and temperature [29]. The existing studies of FO and GW have not considered OMP, which are of significant and crucial concern for water reuse. Therefore, there is a critical knowledge gap regarding the evaluation of GW treatment with FO and its potential to address OMP, prompting the need for comprehensive investigations to ensure safe water reuse practices with FO. Additionally, none of the published studies in FO for GW treatment considered fertilizers as DS, which would increase the efficiency of the process and facilitate the on-site application of the reclaimed GW for irrigation.

Among the studies that evaluated the performance of FO for OMP rejection, it was found that rejection is mainly dependent on their size (steric hindrance), while electrostatic interactions have been reported as the main rejection mechanism for small charged compounds [30,31]. Thus, large OMP present higher rejection rates than smaller ones, while small negatively charged compounds are better rejected than positive or neutral compounds due to their repulsion by negatively charged FO membranes. Positive charged and hydrophobic compounds have a higher tendency to get adsorbed onto the membrane support layer, and the rejection of neutral compounds is driven by their molecular weight to a greater extent than charged compounds [30,32]. Studies with CTA membranes focused on OMP rejection present in saline [33,34], or ultrapure water [35] feed solutions with NaCl as DS. Other studies with CTA membranes used RO concentrate as FS and NaCl [36] or KCl [37] as DS. Worse OMP rejection rates were found for CTA membranes in comparison with TFC [32] or aquaporin membranes [38] due to differences in the transport mechanisms. The OMP rejection with TFC membranes was studied for synthetic secondary effluent [30] or synthetic wastewater [39] as FS and NaCl as DS. The OMP rejection ranged from 93 to nearly 100% with aquaporin membranes with NaCl as DS and milliQ or DI water as FS [40–43]. Similarly, rejection rates higher than 95% for 35 OMP were obtained with aquaporin membranes, NaCl as DS, and DI (or MBR effluent) as FS, in single pass operation [44]. Other studies [24,31,45] also reported very high OMP rejections with aquaporin membranes, different DS types (i.e., NaCl, $MgCl_2$, $MgSO_4$ or glucose), and with DI water, synthetic seawater, or wastewater, as FS. Despite forward osmosis being particularly appealing for cases where draw solution recovery is not required, like FDFO, most studies have employed NaCl as DS. Since the nature of the DS can influence solute fluxes from feed to draw solution [46], it becomes essential to assess contaminant rejection using other relevant DS, such as fertilizers. Zheng et al. [47] reported higher OMP rejection with LiCl than NaCl as DS due to lower reverse salt flux of Li than Na. In contrast, no influence of different J_s in the rejection of OMP was reported in a study comparing the operational behavior of CTA and TFC membranes for OMP rejection

[48]. Several fertilizers as DS ($NH_4H_2PO_4$, $(NH_4)_2HPO_4$, and KCl) were tested separately to evaluate the rejection of 3–4 OMP in FS (DI water or anaerobic membrane bioreactor effluent) with CTA membranes [49,50]. High rejection of polycyclic aromatic hydrocarbons was obtained with NH_4HCO_3 as DS, proved as suitable for irrigation purposes after the dilution [51]. Limited FO studies are available evaluating OMP with TFC or aquaporin membranes and fertilizers in DS, since they used mainly NaCl (also $MgCl_2$ and $MgSO_4$), and none of them utilized GW as FS.

The potential impact of contact time between feed and draw solutions on the diffusion of OMP through the FO membrane and, consequently, their rejection, remains largely unexplored. In general, forward osmosis studies focused on contaminant rejection took less than 4 h and were commonly performed in single pass operation (without recirculation) or with a constant concentration of the DS. Consequently, the osmotic gradient did not decrease as much as in FO processes with recirculation. Reusing water in the context of FDFO requires a substantial dilution of the fertilizer solution, and therefore the initial osmotic pressure of the concentrated DS quickly drops leading to an overall much lower driving force, which is translated in low permeation flux and consequently large filtration time. The large filtration time could lead to significant passage of FS compounds to the DS, due to recirculation of FS solutes in front of the FO membrane and their concentration over time, even if the intrinsic rejection by the membrane is very high [52]. Diffusion of contaminants may then be subject to retarded diffusion, which require longer contact time, but this aspect is currently unknown. In our previous study [53] it was hypothesized that the contact time between FS and DS may influence the solute fluxes across the membrane, but the study did not include OMP, and no further studies considering this aspect were found. Only Li et al. [44] reported stationary rejection of OMP after six days of operation treating MBR effluent with aquaporin membranes, but with DS single pass operation. Therefore, it is important to estimate whether the initially highly rejected OMP by FO membranes can diffuse to the DS when a long filtration time is required, affecting the implementation of FO as efficient barrier to OMP, an aspect that may be critical for the practical applicability of the technology in water reuse scenarios.

This study aimed to evaluate the potential of FO for GW treatment and reuse by analyzing solute fluxes across aquaporin FO membranes, and by studying the influence of time, OMP properties, and feed and draw solution types on the rejection of OMP. To note, there are few studies that have evaluated GW treatment with FO, and including OMP rejection within the context of FDFO represents an innovative approach, since the existing literature is really limited. Furthermore, the evaluation of the impact of contact time between feed and draw solutions on the rejection of OMP in FO represents a novel contribution to the existing body of knowledge in the field. Consequently, the obtained results shed light on crucial aspects for practical applications of the FO technology.

2. Materials and methods

2.1. Chemicals and reagents

The feed solution with a mix of 23 OMP (PhACs and EDCs) contained deionized (DI) water or synthetic GW (Table 1). The selection of OMP for this study was based on those commonly found in GW or wastewater, and with different physicochemical properties: molecular weight (MW), dissociation constant (pka) at feed pH (6), and $LogK_{ow}$ (Table S1). Additionally, whenever possible, transformation products of some of the OMP were analyzed (Table S1).

Draw solutions were prepared using NaCl (Sea salt, >99.4% NaCl, from Vicens i Batllori S.L., Banyoles, Spain), or a blended mix of fertilizers (i.e., KNO_3 and $(NH_4)_2HPO_4$: DAP, from Scharlab, Sentmenat, Spain), which were selected among the most widely used worldwide [54] and providing N, P, and K for plant growth.

2.2. Forward osmosis experimental setup

Lab scale tests were carried out with commercial FO hollow fiber modules (Aquaporin Inside HFFO2, Aquaporin A/S, Denmark). The FO module had a total effective area of 2.3 m^2 and an estimated pore size of 0.733 nm [41]. The module was positioned vertically with the DS and FS circulating in counter-current and with the FS facing the active layer of the membrane (*FO mode*).

Four conditions were tested in a set of duplicate experiments, with FS containing either DI water or synthetic GW, and with DS containing 0.5 M NaCl or 0.25 M of each of the fertilizer salts (KNO_3 and DAP: fert). From now on, tested conditions are referred to as "FS content-DS content": DI-NaCl, DI-fert, GW-NaCl and GW-fert. Initial volumes were 60 L for FS and 2 L for DS, with average flow rates of 60 $L.h^{-1}$ for FS and 37 $L.h^{-1}$ for DS. Experiments were performed in batch mode, with constant FS and DS recirculation aiming to 50% FS recovery (30 L extracted from the FS). A balance connected to a programmable logic controller registered the DS mass every minute, to then calculate the water flux crossing the membrane (J_w, from feed to draw). GW was filtered prior to entering the FO module (50 µm, mesh cartridge) to reduce the clogging. Before and after the tests, the system was rinsed with at least 50 L of DI water in single pass operation and check flow tests (FS: DI water, 10 L; DS: NaCl at 0.5 M, 2 L) were performed prior to each test, without water fluxes decreasing.

2.3. Calculations

The water flux (J_w, $L.m^{-2}.h^{-1}$) was calculated following Eq. (1):

$$J_w = \frac{\Delta V_{FS}}{A * \Delta t} \tag{1}$$

with ΔV_{FS} as the decrease in the volume of FS over time (L, determined by the complementary decrease of DS volume, due to the location of the balance in the draw), A as the membrane area (2.3 m^2), and Δt as the time variation (h). 1 $kg.L^{-1}$ was assumed as the density of both solutions.

The reverse salt flux (J_s, $mmol.m^{-2}h^{-1}$) of each DS ion to FS was calculated by Eq. (2):

$$J_s = \frac{C_{FSf} * V_{FSf} - C_{FSi} * V_{FSi}}{A * \Delta t} \tag{2}$$

with C_{FSf} and C_{FSi} as final and initial ion concentrations in FS ($mmol.L^{-1}$), respectively; and V_{FSf} and V_{FSi} as final and initial FS volume (L), respectively.

Table 1
OMP spiked in the feed solution and synthetic GW recipe (adapted from Hourlier et al. [55]).

Organic micropollutants (20 $\mu g.L^{-1}$)				Synthetic GW	
Acetaminophen (**ACE**)	Ibuprofen (**IBU**)	Furosemide (**FUR**)	Carbamazepine (**CBZ**)	**compound**	**$mg.L^{-1}$**
Sulfamethoxazole (**SFX**)	Trimethoprim (**TRI**)	Methylparaben (**mPar**)	Desvenlafaxine (**DVLF**)	Lactic acid ($C_3H_6O_3$)[a]	100
Naproxen (**NPX**)	Erythromycin (**ERI**)	Bisphenol A (**BPA**)	Venlafaxine (**VLF**)	Sodium dodecyl sulphate ($NaC_{12}H_{25}SO_4$)[b]	50
Ketoprofen (**KTP**)	Irbesartan (**IRB**)	Ranitidine (**RAN**)	Caffeine (**CAF**)	Glycerol ($C_3H_8O_3$)[b]	200
Diclofenac (**DCF**)	Atenolol (**ATE**)	Bezafibrate (**BZF**)	Iopromide (**IOP**)	Sodium hydrogen carbonate ($NaHCO_3$)[a]	70
Indomethacin (**IND**)	Metoprolol (**MTP**)	Gemfibrozil (**GMF**)		Sodium sulphate (Na_2SO_4)[b]	50

[a] purchased from Scharlab; [b] purchased from Merck.

The OMP membrane rejection and the OMP concentration in the permeate were calculated in time periods (i.e., after 10 and 60 min and at the end). In the following equations, *(t)* refers to the values at 10, 60, or at the end of the test, while *(t-1)* refers to the values from the previous samples: t_i, 10, or 60 min.

The OMP membrane rejection (%) was calculated considering the amount of OMP (with mass balances) in the DS at the time *t* compared to the amount of OMP in the FS at the time *t-1*, according to Eq. (3):

$$Rej(t) = 100 \times \left(1 - \frac{C_{DS(t)} * V_{DS(t)} - C_{DS(t-1)} * V_{DS(t-1)}}{C_{FS(t-1)} * V_{FS(t-1)}}\right) \tag{3}$$

with C_{DS} as OMP concentrations in DS (μmol.L^{-1}), and V_{DS} as DS volume (L).

The OMP concentration in permeate (mmol OMP.L^{-1}) was calculated with the following Eq. (4):

$$OMP \quad in \quad permeate = \frac{C_{DS(t)} * V_{DS(t)} - C_{DS(t-1)} * V_{DS(t-1)}}{V_{PERM(t-1)}} \tag{4}$$

where V_{PERM} is the permeated water coming from FS to the DS (FS volume – DS initial volume).

2.4. *Sample collection and analytical methods*

Filtered samples (0.2 μm, nylon) from FS and DS were collected at the beginning and at the end of each test to analyze ions by ion chromatography. TOC was analysed by catalytic oxidation on non-filtered samples according to Standard APHA methods [56]. Samples from FS and DS were collected at the beginning, after 10 and 60 min, and at the end of each test and filtered (0.45 μm, PVDF) to analyze OMP. EDCs and PhACs were analyzed by means of direct injection into UPLC-QqLIT-MS/MS, adapted from Becker et al. [57] and Gros et al. [58], respectively. The matrix effect of GW was applied in the FS samples and used to correct the OMP concentrations obtained using the calibration curves in methanol (MeOH) at 10 and 25 μg.L^{-1}. Matrix effect of each OMP was determined by comparing the concentrations obtained using the calibration curve un MeOH with those obtained in the GW matrix and applied to all FS samples. Some compounds were discarded for matrix issue: GMF in GW-fert 1 and GW-fert 2, FUR in GW-NaCl 1, IND in GW-NaCl 1 and GW-fert 2, and TRI in GW-NaCl 2. Information about OMP detection and quantification limits is indicated in Table S1.

3. Results and discussion

3.1. *General performance*

3.1.1. *Water fluxes and operation time*

The operated batch loops led to continuous DS dilution and FS concentration due to water permeation through the FO membrane, reducing the osmotic gradient between the two solutions, and consequently reducing the water fluxes [59]. The highest water fluxes were recorded at the beginning of the tests, followed by a sharp decline with time (Fig. 1). Highest recorded water fluxes in DI-NaCl (Table 2) were slightly below those set by the membrane manufacturer (11 ± 1.5 L.m^{-2}.h^{-1} with 0.5 M NaCl in DS and DI water as FS, on single pass operation). Similar J_w was reported in the literature with similar modules from the same manufacturer [43,45]. The water fluxes with GW in FS did not decrease from one test to the next one, as confirmed by the very small error bars in Fig. 1a. Therefore, a satisfactory membrane performance was assumed, leaving out potential fouling during the tests. The low water fluxes obtained after the first minutes of operation compromise the economic viability of the process. High water fluxes are required for an economically viable FO process, but it implies lower DS dilutions, which is a limitation of the FDFO approach [60]. Kim et al. [61] reported that the process could be economically feasible, but only when applying extra pressure on the FS with the aim of enhancing water fluxes. It is thus necessary to improve process design to achieve more efficient performance as means of higher water fluxes.

Initial J_w in tests with GW as FS were lower than in those with DI water (Table 2). GW contains ions (mainly Na^+ and SO_4^{2-}) that increase the osmotic pressure in the FS, reducing the osmotic gradient between FS and DS and, consequently, the water flux [62]. As a result, tests with GW took twice as long as tests with DI water to achieve the desired 50% recovery (i.e., 6.7 and 14 h for DI and GW, respectively, Table 2) due to the lower initial J_w. Additionally, solute fluxes, which will be discussed later, could affect the osmotic driving force and consequently the length of the experiments. The increase in FS electrical conductivity (EC) was due to salt fluxes of ions from the DS and due to FS concentration (only in samples with GW as FS), while the reduction of EC in the DS was due to dilution and the loss of solutes to the FS (Table 2). The final EC in FS was lower than in DS (Table 2), and since EC is linearly related with osmotic pressure [63], the osmotic equilibrium was not reached. Therefore, the process could have continued since the system had the capacity to obtain greater FS recovery (water extracted from the FS) than the experimentally established (50%) and consequently higher DS dilution, primary parameter in the case of FDFO.

Table 2
General performance results with average of the duplicate tests.

condition	t (h)	Initial J_w (L.m^{-2}.h^{-1})	Feed EC (mS/cm)		Draw EC (mS/cm)	
			Initial	Final	Initial	final
DI-NaCl	6.7	10.0	0.04	0.3	45.5	3.4
DI-fert	6.7	10.5	0.04	0.6	53.9	3.8
GW-NaCl	14.5	7.6	0.17	0.7	45.5	3.8
GW-fert	14.0	7.5	0.17	0.9	53.9	5.1

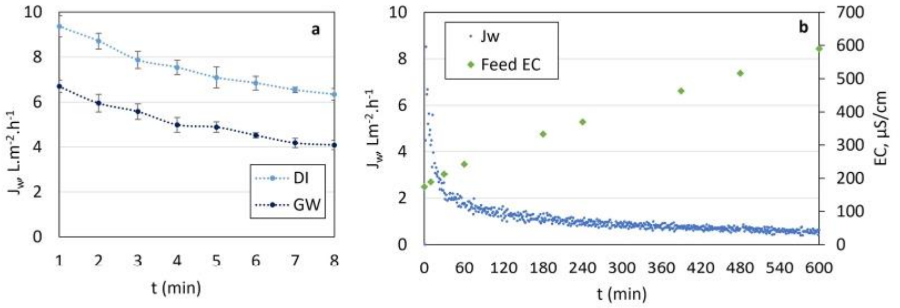

Fig. 1. a) Initial water fluxes for tests with DI water or GW in feed solution (average and standard deviation of 4 tests per feed type); b) Water flux and feed electrical conductivity (EC) over time (example of GW-NaCl test).

3.1.2. Reverse salt fluxes

The obtained J_s ranged from 3 to 120 mg.m^{-2}.h^{-1}, equivalent to 0.1–6.7 mmol.m^{-2}h^{-1} and were lower with GW than with DI for all ions (Table 3). The J_s of this study were smaller in comparison with other studies with aquaporin membranes and NaCl, (around 1–2 g.m^{-2}.h^{-1}, [40,64]) or fertilizers as DS (from 2 up to 10 g.m^{-2}.h^{-1} [65,66]), indicating satisfactory membrane performance regarding J_s.

FS more than DS type determined both the water fluxes and the reverse salt fluxes, as already reported [67], as well as the required time to achieve the established FS recovery (50%). The ions clearly crossed the membrane in the tests with NaCl in DS in molar equilibrium (Table 3) to compensate for charges (solution diffusion mechanism [46]). Reverse salt fluxes were nearly the same, regardless of the FS type (Table 3), although higher J_s were found in tests with DI because of the higher osmotic gradient, which also increased the flux of draw salts [66]. However, since the tests with GW took longer to achieve the desired recovery, ion migration at the end of the tests was higher than for DI as FS (Table 3). The higher ion migration in tests with GW in FS was due to interactions between feed and draw salts, favouring the passage of DS ions through the membrane towards the FS. The fact that ion migration with GW was higher than with DI water, despite the lower J_s, underscores the importance of also reporting values of ion migration, especially batch processes where the DS is valuable, as in the case of FDFO.

Overall, a low to medium ion migration was observed: the fertilizers are valuable compounds in the case of FDFO and, hence, it is crucial to minimize their losses. With fertilizers as DS, the ion migration was similar for the cations (i.e., NH_4^+ and K^+), whose passage was favoured by the negatively charged membrane surface [68], while the anions (i.e., NO_3^- and PO_4^{3-}) passage was explained by the solution diffusion mechanism to balance charges in the FS [69]. NO_3^- fluxes and migration were much higher than those of PO_4^{3-}, since the latter is trivalent and bigger, and so suffering higher electrostatic repulsion with the membrane than NO_3^- [70,71].

3.1.3. Membrane rejection of main GW constituents

Average GW composition was 161, 42.9, and 11.5 mg.L^{-1} for C (TOC), Na, and S-SO_4, respectively (Fig. 2). The rejection of main GW constituents was satisfactory in both cases, with very high TOC and sulphate rejection, but low sodium rejection (Fig. 2), which must be improved to avoid DS contamination. Only two existing studies evaluated GW treatment using aquaporin membranes, albeit on a smaller scale compared to this study. Specifically, these studies involved FS volumes of 4 L (60 L were used in this study), smaller membrane surface areas than in this study (hollow fiber membranes of 2.3 m^2) and employed NaCl as DS. In the study conducted by Wang and Li [28], they achieved rejections close to 100% for GW constituents tested separately with a 200 cm^2 flat membrane, which are slightly higher than the obtained in this study. Chen et al. [29] tested real GW with a 28 cm^2 flat membrane and obtained slightly lower rejections than in this study, but exceeding 75% for all analyzed GW constituents, except for linear alkylbenzene sulfonates, which were adsorbed onto the membrane. Our comprehensive evaluation on a larger scale with different feed and draw solution types provides valuable insights into the effectiveness and versatility and drawbacks of aquaporin membranes for GW treatment. The results still are in line with other studies evaluating GW treatment with other FO membrane types, which reported over 90% rejection for GW constituents [25–27] although not analyzing sodium. In fact, Xiao et al. [27] reported lower rejection of sodium dodecyl sulphate than of the other contaminants present in GW in their experiments with TFC membranes, which are also negatively charged. The rejection of the other GW constituents was similar for both DS types (Fig. 2), showing that the DS type did not influence the rejection of those compounds, in agreement with Phuntsho et al. [67], but in contrast with other studies [72].

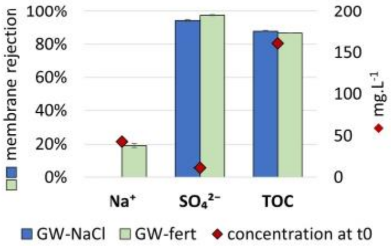

Fig. 2. GW constituents' rejection (bars) and concentrations at the beginning of the tests (dots). The rejection of Na is not shown in the tests with NaCl in the DS because reverse Na fluxes were higher than forward fluxes of Na and the rejection of Na would have appeared as negative.

3.2. Behaviour of organic micropollutants

The average rejection of OMP in all tested conditions and time periods (10 min, 1 h, and at the end of the test) was 99.3%, very high and in line with reported OMP rejections from 80 and up to 100% in the literature with the same membrane type [24,31,38,40–45]. The rejection was above 95% in most OMP and tested conditions, with only 3 samples with rejections below 90% for some OMP (in GW-fert). The OMP concentrations in the diluted DS were on average 1.05 ± 0.8 µg.L^{-1} (Fig. 3), indicating satisfactory treatment and potential reuse feasibility of the diluted DS for fertigation. Only five compounds were detected with concentrations above 3 µg.L^{-1} (ATE, MTP, RAN, ACE, and BPA). Out of seven analysed transformation products (TP), only metoprolol acid (MTPA, TP of metoprolol) and 1-hydroxy-ibuprofen (1-OH-IBU, TP of ibuprofen) were found in some FS and DS samples, at very low concentrations (average 0.04 and 0.06 µg.L^{-1} for 1-OH-IBU and MTPA, respectively). Thus, a non-significant degradation of the OMP can be assumed.

Among the existing studies that employed the same membrane type as in this study (i.e., aquaporin), the majority used DI or milliQ water as FS. This choice avoids the presence of salts in the FS, thereby simplifying the process, as the interaction between different salts in both solutions can potentially impact process development [46]. Only three studies involving aquaporin membranes have been identified, in which *water with some salinity* was used in the FS. Specifically, Sanahuja-Embuena et al. [24] utilized artificial seawater (3.5% NaCl), Xie et al. [31]

Table 3
Average reverse salt fluxes and ion migration.

——	J_s, mmol.m^{-2}h^{-1}				ion migration, %			
	DI-NaCl	GW-NaCl	DI-fert	GW-fert	DI-NaCl	GW-NaCl	DI-fert	GW-fert
Na^+	4.1 ± 0.2	3.3 ± 0.2			6.4 ± 0.1	10.0 ± 0.7		
Cl^-	4.1 ± 0.2	3.0 ± 0.2			6.3 ± 0.1	10.0 ± 0.6		
NH_4^+			6.2 ± 1.2	5.0 ± 0.1			9.2 ± 0.6	14.0 ± 0.1
K^+			2.6 ± 0.5	2.2 ± 0.0			7.8 ± 0.4	12.7 ± 0.2
NO_3^-			6.7 ± 1.2	2.6 ± 0.1			19.8 ± 1.1	16.8 ± 1.3
PO_4^{3-}			0.1 ± 0.0	0.1 ± 0.0			0.4 ± 0.1	0.7 ± 0.0

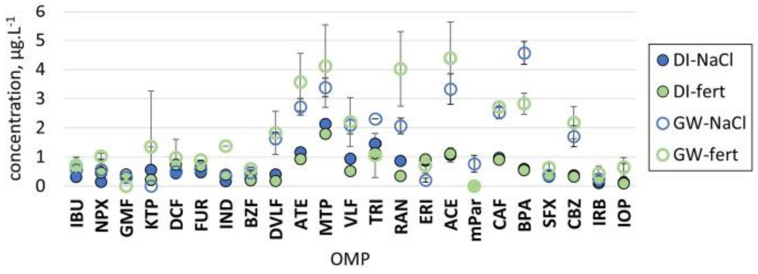

Fig. 3. OMP concentrations in diluted DS at the end of the experiments, average, and standard deviation.

employed synthetic wastewater (NaCl + $NaHCO_3$), and Li [44] uniquely employed real water (i.e., MBR effluent). Consequently, further investigations with impaired water as FS are needed to comprehend the intricate interactions between different feed and draw solutes and their influence on the behaviour of OMP. Furthermore, there is a need to explore solutions with a broader diversity of salts, as in this study, especially with respect to GW, which constitutes a significant proportion of domestic wastewater (up to 75%, [1]) and possesses considerable potential for reuse.

3.2.1. OMP rejection over time

The average membrane rejection was 99.9%, 99.7%, and 98.5% after 10 min, 60 min, and at the end of the tests, respectively (Fig. 4a).

Even if the rejection was certainly high in any case, the contact time between feed and draw solutions played a fundamental role in the rejection of OMP. It is hypothesized that higher OMP concentrations could have been found in the diluted DS with longer operation time. Sanahuja-Embuena et al. [24], in fact, obtained 99.4% caffeine rejection in tests with NaCl (0.5 M) in DS and DI water in FS (i.e., same as in DI-NaCl) and with the same FO membrane module after 45 min of operation. This result is in line with the caffeine rejections obtained after 10 and 60 min in this study (over 99%), but the rejection decreased to 97.5% at the end of the experiment (around 7 h). Considering the same or very similar configuration between the two studies, the only variable would be the contact time between FS and DS, which led to more recirculation of both solutions, which decreased the rejection of OMP. The obtained results are in contrast with Li et al. [44], which reported constant rejection and no OMP adsorption after 24 h of operation with aquaporin membranes, but with constant DS concentration and thus higher water fluxes.

The membrane rejection had a strong decreasing linear correlation with time ($R^2 > 0.9$ in most cases), depending on the condition and the tested OMP (Fig. S1). Only 3 calculations are provided for membrane rejection (at 10, 60 mins, and end of the tests) and many DS compounds were below the detection or quantification limits, which could affect the obtained linearity. At any case, the rejection of OMP clearly decreased over time for all OMP and tested conditions, to varying degrees (0.1–10.5% difference in rejection between 10 min and the end of the tests), with the decline being most pronounced for small MW positive and neutral compounds (ATE, MTP, ACE) in tests with GW in FS.

The calculated OMP concentration in the permeate should be constant or decrease, as water fluxes decrease along the process. This is the case of the tests carried out with DI water as FS (Fig. S2), where the OMP concentration in the permeate slightly varied along the process, with increasing, decreasing, or stable concentrations (examples in Fig. 5). However, linearly ($R^2 > 0.9$) increasing OMP concentration in permeate was found for most compounds with GW as FS (Fig. S3). Small MW positive and neutral compounds showed the highest concentrations in permeate, and also the highest increases over time, up to 20 nmol.L^{-1}. Conversely, OMP concentrations in permeate for all negative compounds (except for KTP in GW-fert), and large MW positive (ERI) and neutral (IRB, IOP) compounds did not exceed 4 nmol.L^{-1}. The obtained results with GW in FS are the closest to the real application of the FO technology and show that even if water fluxes decreased substantially (Fig. 1), the concentrations of OMP in the permeate increased over time. OMP concentration in the permeate increased over time faster than the water fluxes and, therefore, it may be driven by other factors other than water flux only. Additionally, OMP concentration in permeate could have been subject to retarded diffusion, with permeate concentrations increasing over time.

3.2.2. Effect of feed and draw types on OMP behaviour

The rejection and fluxes were very similar at the beginning and after 60 min. From now on, hence, the focus will be on the rejection values obtained at the end of the tests to find out further relations or tendences.

The differences on average OMP rejection at the end of the experiments were more noticeable between FS types than between DS types (Fig. 4b). Average OMP rejection with DI water as FS was 2% higher than with GW (i.e., 98.5% and 96.6%, respectively), while it was 0.5% higher with NaCl as DS compared to fertilizers (i.e., 97.8% and 97.3%, respectively). Therefore, in our case, the FS type more than the DS type influenced the OMP rejection. Indeed, 20 and 21 out of 23 compounds (for tests with NaCl and fertilizers as DS, respectively) were better rejected with DI than with GW in FS (Fig. 6), although in most cases with

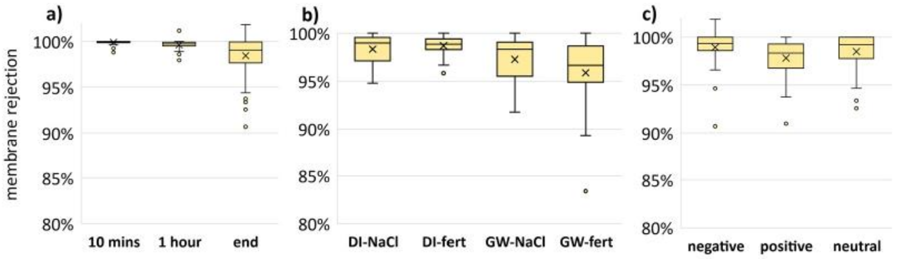

Fig. 4. Membrane rejection of OMP: a) after 10, 60 min, and at the end of the experiment; b) for the different tested conditions at the end of the experiment; for negative, positive, and neutral OMP at the end of the experiments.

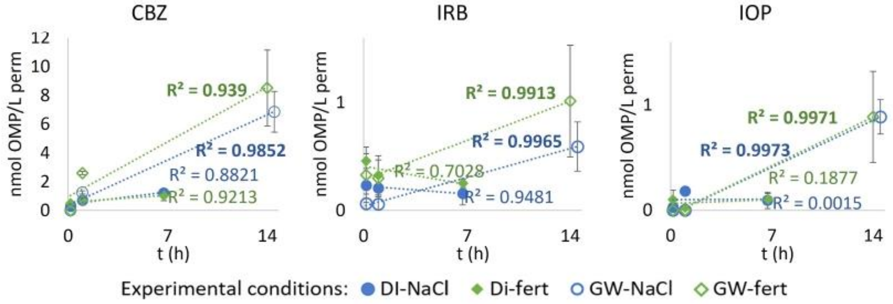

Fig. 5. Average calculated OMP concentration in permeate. Examples of compounds with increasing (CBZ), decreasing (IRB), or stable concentrations (IOP) with DI water in FS and increasing concentrations with GW in FS.

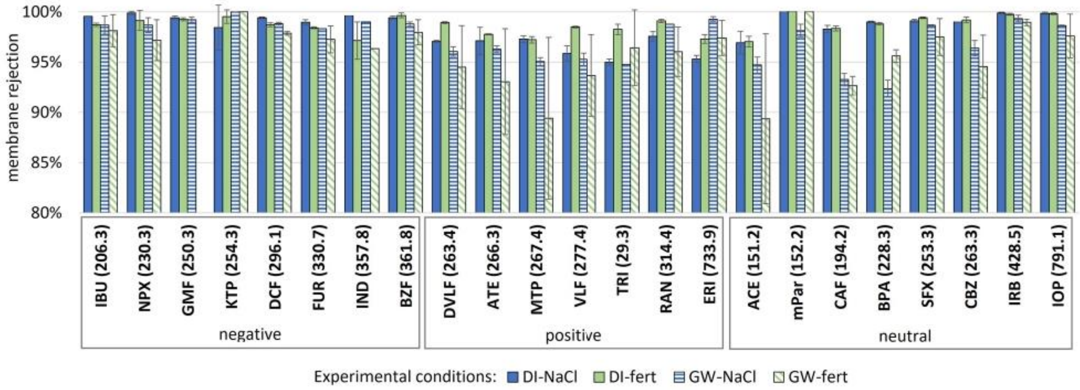

Fig. 6. Membrane rejection of OMP at the end of the tests, average (bars) and standard deviation (error lines). The OMP are divided in negative, positive, and neutral (pH 6), and with increasing molecular weights in each group (in brackets, g.mol^{-1}).

differences below 2%. Lower rejections in tests with GW as FS might be related to the enhanced forward flux of the OMP, eased by the flux of GW constituents, and by the longer contact time between the solutions. Comparing the OMP rejection between the different DS, negatively and positively charged compounds were better rejected with NaCl than with fertilizers in DS (Fig. 6). OMP rejection with DS inducing higher J_s was reported in the literature [31,49] as well as the opposite relation [47], although testing only individual salts in the DS. In the present study, the highest and lowest J_s values were obtained with fertilizers in DS: nitrogen compounds (NH_4 and NO_3) had the highest J_s while phosphate the lowest (Table 3). The higher diffusivity of the nitrogen compounds could have enhanced the transport of OMP due to higher J_s values. Additionally, the differences in OMP rejection related with the DS types could be explained by the higher speciation of the DS when fertilizers were employed, an aspect that has not been analyzed previously, because no studies were found evaluating the influence of alone or blended solutions on the transport of OMP in FO. Majeed et al. [73] indicated that more ionic speciation drives higher fluxes, which could have eased the OMP transport across the membrane in this study.

3.2.3. Effect of OMP properties on OMP behaviour

The rejection mechanisms of OMP in FO are a combination of steric exclusion, electrostatic interactions, concentration polarization, and membrane and solute characteristics [24]. Various studies reported electrostatic interaction as the main OMP rejection mechanism with negatively charged membranes [30,47]. Negatively charged compounds usually have the highest rejection rates due to their repulsion by the membrane, positively charged compounds are attracted by the membrane and then diffuse to the DS, and neutral compounds are governed by steric hindrance [32,48]. Our tests confirmed the importance of electrostatic interactions since negatively charged compounds were the best rejected (average 98.8%), followed by neutral (97.6%), and positive ones (96.4%), with more dispersed rejections in positive and neutral compounds (Fig. 4c). Additionally, the physicochemical properties of the OMP (i.e., MW, $LogK_{ow}$, and pKa) have a large impact on OMP transport in FO [30]. In this study, large MW neutral and positive compounds were rejected to a higher degree than the smaller ones (Fig. 6), in accordance with studies using the same membrane [31]. Previous studies report strong linear correlations between OMP rejection and MW and, to a lesser degree, to $LogK_{ow}$ [30,32]. In contrast, Zheng et al. [47] found a weak correlation between OMP rejection and MW. In this study, linearity (R^2 >0.8) between the rejection of neutral OMP and MW was found only for some of them and in DI-NaCl (Fig. S3). No linear relations were here obtained for $LogK_{ow}$ or pKa or MW and OMP membrane rejection, only a tendency of higher rejection at higher $LogK_{ow}$ and MW and lower pKa (Fig. S4). The compounds presenting the lowest rejection were those with highest pKa (above 9) and small MW, as expected from the literature. Iopromide, with pKa of 11 but also with the largest MW of 791 g.mol^{-1}, had one of the lowest forward fluxes due to size exclusion.

Finally, OMP can be adsorbed on the membrane, especially small positively charged OMP due to their attraction by the negative membrane support layer. The biggest differences in rejection between 10 min and the end in tests with GW in FS (Fig. S1) were precisely for the smallest MW positive compounds (DVLF, ATE, MTP, VLF) and some neutral compounds of comparable MW (ACE, CAF). These compounds might have been attracted by the membrane, adsorbed, and then diffused to the DS. In fact, the adsorption of these compounds was reported in previous studies [30,32]. However, the differences in rejection over time were less pronounced for neutral compounds because their main diffusion mechanism is steric hindrance and might have been less influenced by time.

3.3. Evaluation of forward osmosis for greywater treatment and implications for water reuse

In this section, the focus is on the results of tests with GW as FS and their potential applicability for (grey)water reuse in decentralized scenarios. The concentrated GW could be treated for example by an anaerobic membrane bioreactor, yielding biogas as a valuable byproduct [74]. Nevertheless, the sodium reverse fluxes will increase the salinity, inhibiting the activity of microorganisms and posing a limitation to the process [59]. If further on-site treatment of the concentrated FS would not be possible, it could simply be discharged to the municipal water network, but still, the GW volume to be discharged would be the half of the produced, in the tested conditions. As the system did not reach the osmotic equilibrium, the recovery could have increased and consequently the final GW volume to treat or discharge would be lower. Envisioning the potential application of this approach on a larger scale (numerous houses, schools, hotels, etc.) will lead to substantial reductions in the volume of wastewater requiring treatment at municipal wastewater treatment plants. Additionally, a more concentrated wastewater could facilitate the recovery of valuable nutrients through precipitation processes or enable the production of biogas within the plant. Reverse salt flux with GW-fert could contaminate the FS. NO_3 and PO_4 can cause eutrophication if discharged at high concentrations [54]. In this study, only NO_3 would be of concern since PO_4 migration was almost negligible (Table 3). Nevertheless, a recently published review about smart utilization of J_s pointed out that reverse salt fluxes, inevitable in FO, can benefit the FO process by improving the filtration efficiency and anti-scaling properties, as well as promoting nutrient recovery [75]. A previous study included microalgae in the FS [76], to further treat wastewater while taking up the nutrients coming from the DS. However, a better option would be J_s reduction, increasing the process economic efficiency and reducing draw constituents' losses. Therefore, more selective membranes are required to minimize the solute fluxes. In this sense, membrane surface modification is an option that improves process performance. For example, incorporating charcoal-based carbon nanomaterial [77] or metal-organic frameworks [78] in the structure of the FO membrane resulted in higher permeability and salt rejection, thus increasing selectivity, and improving overall process performance.

To produce drinking water, the diluted DS with NaCl should be reconcentrated and FO coupled with other technologies, like RO, reducing the required hydraulic pressure to apply in RO [79]. The diluted DS with fertilizers could be applied for irrigation of the surrounding areas, and the low observed OMP concentrations (Fig. 3), which are usually smaller in real GW, make its reuse safe. Sulphate migration to the DS, although minimal, would not be a problem, yet an advantage as it is also a required nutrient for the plants. Thus, the only concern would be the presence of sodium, a toxic element for the plants. The final concentrations obtained in this study are too high for irrigation and further dilution would be necessary, as reported previously [54,80,81]. Further FS dilution until DS osmotic equilibrium could be applied in the future with final lower sodium (and OMP) concentration. However, it is possible, that sodium migration further increases in time, hence this issue should be carefully considered in case of diluted DS application for irrigation. Another option would be further DS dilution with fresh water with anyway significant freshwater saving amounts for irrigation purposes.

With the proposed setup, individual house application can also be foreseen because FO has the capacity to treat the daily produced GW to reuse the diluted DS for irrigation of the surrounding areas.

4. Conclusions

This study demonstrated the promising potential of forward osmosis for effective greywater treatment and reuse. The FO membrane proved to be an excellent barrier against the 23 OMP evaluated, achieving an average rejection of 98.5% in all tested conditions. However, it is evident that recirculation of feed and draw solutions led to increased OMP diffusion through the membrane, resulting in reduced rejection over time. Longer contact times between solutions intensified OMP diffusion, particularly for smaller positive and neutral compounds, revealing time as a crucial factor inversely affecting the rejection of OMP. Thus, further studies on FO for water reuse should consider this aspect.

The obtained diluted DS proved to be safe for reuse, due to high rejections of main GW constituents and very low OMP concentrations. However, to ensure its suitability of the diluted DS for irrigation purposes, improvements are required to avoid DS contamination, by increasing sodium rejection. Comparable OMP rejections were observed when using fertilizers and NaCl as DS, reinforcing the prospects of FDFO applications, where the diluted DS can be directly applied for irrigation without the need for DS recovery, thereby enhancing process efficiency and facilitating on-site GW reuse.

Water reuse implies social and environmental benefits: it increases water availability for communities, reduces the dependence on freshwater sources, and consequently mitigates the stress on freshwater resources. Additionally, the high rejection rates of OMP could ensure safe water reuse for irrigation and a resilient and sustainable water supply for future generations. However, the low water fluxes and the high reverse salt fluxes of some of the draw solutes (especially of nitrate) compromise the economic viability of the FO process. Minimizing solute fluxes to prevent DS contamination is of utmost importance for safe water reuse practices. Consequently, a comprehensive assessment of the various mechanisms, membrane properties, and configurations is crucial to maximize water fluxes while minimizing solute fluxes to optimize FO performance for full-scale applicability.

CRediT authorship contribution statement

Esther Mendoza: Conceptualization, Methodology, Validation, Formal analysis, Investigation, Writing – original draft, Writing – review & editing, Visualization. **Gaetan Blandin**: Conceptualization, Methodology, Writing – review & editing, Supervision. **Marc Castaño-Trias**, **Lucas Leonel Alonso**: Formal analysis, Writing – review & editing. **Joaquim Comas**, **Gianluigi Buttiglieri**: Conceptualization, Writing – review & editing, Supervision, Project administration, Funding acquisition.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jece.2023.110931.

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ARTICLE 5. From shower to table: fate of organic micropollutants in hydroponic systems for greywater treatment and lettuce cultivation.

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From shower to table: fate of organic micropollutants in hydroponic systems for greywater treatment and lettuce cultivation

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ABSTRACT

This study evaluated the dual functionality of hydroponic systems to grow edible crops while treating greywater (GW) containing 20 organic micropollutants (OMPs). Various conditions with differing nutrient contents were tested: raw GW, GW with struvite, and GW with commercial nutrient solution. System performance was assessed with plant growth and standard parameters and OMP removal. After 4-week exposure, all conditions produced healthy-looking plants, proving GW as a viable hydroponic growth medium. However, only the condition with commercial solution yielded plants comparable to the biotic control, indicating the necessity of nutrient supplementation. Effluent from conditions with well-developed plants met the requirements of the European water reuse legislation (EU 2020/741) for scenarios B–D (food crops not in direct contact with the reclaimed water and industrial crops), and had the highest OMP removal, showcasing the effectiveness of the system for OMP treatment. Estimated calculations of OMP detected in leaves (10/20 OMP detected, predominantly positive and small) resulted in calculated potential human health risks through lettuce intake for two compounds: atenolol and epoxycarbamazepine. These findings support a continued evaluation of the behavior of other OMPs and their transformation products in water–plant systems, and their consideration in legislation on water reuse and food safety.

Key words: edible plants, emerging contaminants, endocrine-disrupting compounds, greywater reuse, hydroponics, pharmaceuticals

HIGHLIGHTS

- Hydroponic system successful for greywater treatment and lettuce cultivation.
- Greywater is a viable medium for hydroponics but needed nutrient supplement.
- Effluent complied EU 2020/741 for reuse scenarios B, C, and D.
- Variable and moderate OMP removals, detecting 10 compounds in lettuce leaves.
- Although only atenolol and epoxycarbamazepine posed individual ingestion risks, cumulative exposure risks are expected.

1. INTRODUCTION

The escalating stress on global freshwater resources due to climate change and population growth necessitates a paradigm shift in current water management. Water reuse emerges as a crucial strategy, particularly for agricultural irrigation. Agricultural activities, in fact, are expected to surpass 70% of the total water withdrawals by 2050 (UNESCO & WSSM 2020) while food and water demand are expected to increase by more than 50% by 2050 (Karan *et al.* 2018). However, water reuse implementation remains limited, with a scarce number of countries considering this practice in their legislation. The European Union recently published the legislation (EU) 2020/741 on minimum requirements for water reuse in agriculture. Greywater (GW), defined as the fraction of domestic wastewater (WW) excluding toilet WW, constitutes 50–80% of the total domestic WW load, with daily volumes ranging from 15 to 200 L/person (Oteng-Peprah *et al.* 2018; He *et al.* 2022). GW emerges as an

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excellent candidate for reuse since it is considered low strength WW, with lower organic and pathogen levels than the total WW load (Oteng-Peprah *et al.* 2018), thus its treatment seems simpler and its reuse safer (Donner *et al.* 2010). Additionally, GW contains valuable nutrients for plant growth, including phosphates and nitrogen compounds (Prodanovic *et al.* 2017), making it an excellent candidate for irrigation (Misra *et al.* 2010). Indeed, studies have shown enhanced nutrient levels in plants irrigated with reclaimed GW compared to tap water (Rodda *et al.* 2011). Consequently, GW application in agriculture may reduce reliance on chemical or commercial fertilizers, the availability of which could be at risk in the near future, and also promotes more sustainable agricultural practices and resource management.

In recent years, on-site decentralized GW treatment and reuse practices have popularized, particularly for non-potable purposes like toilet flushing and irrigation, especially in water deficient areas (Noutsopoulos *et al.* 2018). Among the different options, nature-based solutions (NBSs) have gained importance due to lower operational costs, durability, and co-benefits (Vymazal 2007; Boyjoo *et al.* 2013). These systems have the capacity to achieve high removal rates of a wide spectrum of water contaminants (Ramprasad & Philip 2018) with the combined action of plants (root adsorption and plant uptake), substrate (adsorption), and microorganisms (biodegradation). Notable examples of NBS encompass green roofs, retention ponds, vegetated pavements, or constructed wetlands (CWs). NBSs have shown good performance for GW treatment, with CW among the most popular NBS. The effluent of different CWs (vertical and horizontal flow configurations, and GROW-Green Roof-top Water Recycling System) treating light domestic GW was of comparable quality to other low and high technologies, with removals exceeding 87% for BOD_5, total suspended solids (TSS), and microbial indicators (Williams *et al.* 2008). Similarly, removals over 88% were reported for standard parameters and nutrients (TN, TP) with the GROW system treating GW from a student residence (Ramprasad *et al.* 2017). The vertECO technology (hydroponic system including diverse ornamental plants) achieved removals higher than 90% for most standard parameters from hotel GW while the removal of organic micropollutants (OMPs) was reported to be variable, and greater than 95% for several compounds (Zraunig *et al.* 2019). Additionally, no detriment to the plants was reported in a study testing different CW configurations treating synthetic GW, with COD removals surpassing 87% in all cases (Comino *et al.* 2013). Incorporating edible plants into NBS enhances circularity by simultaneously addressing GW treatment (Gattringer *et al.* 2016; Xu *et al.* 2020) and food production (Barbosa *et al.* 2015; Bliedung *et al.* 2020). Among the diversity of NBS for WW treatment, hydroponic systems (soilless culture) are also widely recognized for their role in food production, by optimizing water and nutrient utilization, resulting in higher yields, less water consumption, and lower specific greenhouse gas emissions compared to conventional agricultural crops in soil (Barbosa *et al.* 2015; Martinez-Mate *et al.* 2018). The versatility of these systems offers a valuable option to promote sustainable water management, particularly in space-constrained urban environments, as they can be installed indoors, outdoors, on vertical surfaces, and other locations for simultaneously treating GW while producing edible goods. Indeed, Sangare *et al.* (2021) obtained 64% greater mass and 60% more leaves in hydroponic lettuce cultivation in raw GW compared to those grown in well water. Nutrient supplementation required for optimal lettuce growth in hydroponics can be provided, at least partially, by GW/WW (Da Silva Cuba Carvalho *et al.* 2018). In parallel, recovering P and N from WW as fertilizers holds significant promise. The application of struvite ($MgNH_4PO_4{\cdot}6H_2O$), a byproduct derived from the precipitation of magnesium, phosphate, and ammonium from WW streams, resulted in similar plant growth and nutrient uptake compared to synthetic fertilizers in hydroponic culture (Carreras-Sempere *et al.* 2021; Halbert-Howard *et al.* 2021; Arcas-Pilz *et al.* 2022). Consequently, struvite can be considered a sustainable fertilizer with the capacity to replace those synthetic in terms of N, P, and Mg. In the case of hydroponics, although nutritional requirements vary among plant species, growth stages and environmental conditions (Resh 2022), the required concentrations generally vary between 140 and 260 mg/L for N, 30 and 60 mg/L for P, and 30 and 50 mg/L for Mg (Trejo-Téllez & Gómez-Merino 2012). Hydroponic systems, hence, can offer a sustainable approach to GW treatment, compared to other conventional treatment options (Magwaza *et al.* 2020), and may benefit from both GW streams and struvite addition for nutrient supplementation, increasing the circularity. Nevertheless, such urban agriculture applications with GW/WW, promoting plant growth and sustainable agricultural practices, are still largely lacking.

Ensuring safe water reuse, especially in applications that directly impact our food supply, is of utmost importance, and therefore efficient WW treatment strategies are required. Remarkably, the ubiquitous presence in water streams of OMPs, such as pharmaceuticals (PhACs), pesticides, endocrine-disrupting compounds (EDCs), or industrial chemicals, is a point of concern for water reuse applications (Verlicchi *et al.* 2023). Also reclaimed WW/GW for irrigation may introduce contaminants in the food chain (Riemenschneider *et al.* 2016). Various studies, in fact, have highlighted the wide array of OMP present in GW (Eriksson *et al.* 2002), at different concentrations (from pg/L to mg/L). Up to 350 OMPs are identified across diverse GW sources, not completely removed during the treatment, and posing potential risks to the environment when released via irrigation (Glover *et al.* 2021). Additional risks to human health arise when plants irrigated with reclaimed water are consumed (Keerthanan *et al.* 2021). Consequently, comprehensive investigation into the occurrence and behavior of OMP in GW is needed, with the goal of integrating them in the water reuse legislations (Gulyas *et al.* 2011). The European Watch List (WL) under the Water Framework Directive is a mechanism aimed at evaluating potential water contaminants, and the risk they may pose to aquatic ecosystems in surface water. The first WL (EU 2015/495) was published in 2015 (European Union 2015) and the last one (EU 2022/1307, European Union 2022) included only 26 compounds of concern. Thus, while serving as a valuable tool for monitoring potentially hazardous compounds in various environmental matrices, it is limited due to the scarce number of considered compounds. Hence, it is necessary to study a broader array of contaminants that may pose risks to both environmental ecosystems and human health.

Some OMP enter the plants through the roots and then are gradually taken up by the shoots and fruits with the transpiration flow (Vo *et al.* 2018; Chuang *et al.* 2019), while their degradation within the plants is attributed to complex biochemical processes (Carvalho *et al.* 2014). Plant-specific characteristics such as species, lipid content or transpiration rates also affect the OMP uptake (Ravichandran & Philip 2021), with leafy crops exhibiting the highest propensity for OMP uptake, followed by root vegetables and cereals (Christou *et al.* 2019b). Additionally, the OMP behavior in the aqueous matrix and their interactions with the plant system are influenced by physicochemical properties of the OMP, with hydrophobicity (usually expressed as log K_{ow}) considered the most important property (Carter *et al.* 2014). In addition, other properties such as charge and molecular weight (MW) of the OMP have shown to influence their behavior in water and their ability to translocate to edible parts of crops (Goldstein *et al.* 2014; Chuang *et al.* 2019). Therefore, it is of particular importance to study the OMP in hydroponics with greater plant uptake potential due to the absence of soil (Dodgen *et al.* 2013). While numerous studies have explored OMP accumulation in edible plants in hydroponic systems, they have often focused on a limited number of compounds and always using tap or deionized (DI) water with added nutrients (Wu *et al.* 2013; Chuang *et al.* 2018, 2019; Tian *et al.* 2019; Leitão *et al.* 2021b). Previous studies have reported no stress symptoms and adverse effects on plant growth due to OMP exposure (Calderón-Preciado *et al.* 2012; Chuang *et al.* 2019), while others indicated the opposite (Bartha *et al.* 2010; Carter *et al.* 2015) or attributed different effects on the plants depending on the type of OMP (Leitão *et al.* 2021a). On the other hand, the studies with edible plants in raw or treated GW (Eregno *et al.* 2017; Sangare *et al.* 2021) or WW (Da Silva Cuba Carvalho *et al.* 2018; Bliedung *et al.* 2020) have mainly focused on the removal of standard parameters, but have not included OMP. Only Kreuzig *et al.* (2021) evaluated lettuce grown in treated WW, and reported OMP removal rates ranging from 3 to 100%, along with the detection of two out of nine tested compounds in the plant leaves. No studies on GW hydroponic systems for edible plants cultivation and evaluating OMP behavior and removal are available in the literature.

Finally, it is of crucial importance to perform human health risk assessment (HHRA) studies to calculate the potential human exposure to OMP through irrigation, as well as to quantify the potential adverse effects based on the exposure concentrations (Piña *et al.* 2020). In this sense, the exposure to OMP through ingestion of various crops irrigated with raw and treated WW was reported as safe in most cases, with OMP concentrations in edible parts below the acceptable safety thresholds (Carter *et al.* 2014; Hyland *et al.* 2015; Riemenschneider *et al.* 2016; Martínez-Piernas *et al.* 2019). Similarly, studies with edible crops (lettuce, spinach, cucumber, peppers, and collards) grown in hydroponic systems using OMP-spiked DI/tap water with added nutrients have consistently demonstrated negligible risk (Shenker *et al.* 2011; Dodgen *et al.* 2013; Wu *et al.* 2013). However, other studies raised concerns about the potential risks of consuming crops irrigated with reclaimed WW due to the presence of OMP (Bartha *et al.* 2010; Keerthanan *et al.* 2021). Importantly, even though individual OMP exposure is typically considered safe, the risk derived from the exposure to numerous compounds increases because of cumulative exposure (Glover *et al.* 2021). Consequently, more studies considering the potential for plants to grow in reclaimed or raw WW, and particularly GW, as well as the risks associated with the exposure to OMP are thus necessary.

The objective of this study was to evaluate, as a proof of concept beyond the legislation constraints (i.e., cultivation of edible plants in raw GW/WW is currently forbidden), the capability of hydroponic systems to integrate

GW treatment and lettuce production by means of plant growth and contaminant removal. Furthermore, the study aimed to delineate the pathway of OMP from GW to the edible parts of plants, by evaluating their removal in the system and by assessing the associated risks to human related to OMP exposure through the consumption of plants grown in GW.

2. MATERIALS AND METHODS

2.1. Chemicals

2.1.1. Synthetic GW solution

Synthetic GW (modified from Hourlier *et al*. 2010, Supplementary material, Table S1) simulated water typically originated from baths, showers, and wash basins (light GW). All synthetic GW constituents were of reagent-grade quality, and were purchased from Scharlab (L(+)–Lactic acid, $NaHCO_3$, KNO_3, and $(NH_4)_2HPO_4$) or from Merck (glycerol, α-cellulose, $NaC_{12}H_{25}SO_4$, and Na_2SO_4). Struvite ($MgNH_4PO_4{\cdot}6H_2O$), purchased from Merck, was dissolved in approximately 100 mL of GW with around 10 mL of citric acid (1M) until reaching a pH around 3, and it was then mixed with the rest of the GW solution, causing a pH rise to values close to those of real GW (see Table 3 with the characteristics of the GWS influent). The commercial standard nutrient solution (CNS), designed for hydroponic applications, was obtained from *GroHo Hidroponía* (www.groho.es), and included five stock solutions with macronutrients (KNO_3, $Ca(NO_3)_2$, $MgSO_4$, $NH_4H_2PO_4$) and micronutrients (Fe [6%], Cu, $MnSO_4$, H_3BO_3, $(NH_4)_6Mo_7O_{24}$, and $ZnSO_4$).

2.1.2. Organic micropollutants

A selection of 20 OMP (Table 1, including the compounds acronyms) was made based on those commonly found in GW and with different physicochemical properties (i.e., pKa, log K_{ow}, MW). OMP were of analytical quality grade and purchased from LGC Group, except iopromide and venlafaxine, purchased from Merck. Individual stock solutions (1 or 10 g/L) were prepared in methanol and stored in amber glass vials at −20 °C. Caffeine stock (1 g/L) was prepared in milliQ water due to its low solubility in methanol and stored at 4 °C. The OMP mixture was prepared in methanol and spiked into the GW solution (presented in Section 2.2.1.) attaining at

Table 1 | OMPs analyzed in the experiment with their acronyms

Compound	Acronym	Use	Compound	Acronym	Use
Acetaminophen	**ACE**	Analgesics/anti-inflammatory drugs	Atenolol	**ATE**	β-Blocking agents
Diclofenac	**DCF**		Metoprolol	**MTP**	
Ibuprofen	**IBU**		Carbamazepine	**CBZ**	Psychiatric drugs
Indomethacin	**IND**		Desvenlafaxine	**DVLF**[a,b]	
Naproxen	**NPX**		Venlafaxine	**VLF**[a]	
Ofloxacin	**OFX**[a]	Antibiotics	Iopromide	**IOP**[c]	X-ray contrast agent
Sulfamethoxazole	**SFX**[a]		Caffeine	**CAF**[c]	Stimulant
Tetracycline	**TET**		1-Hydroxy-IBU	**1OH-IBU**	TP of IBU
Trimethoprim	**TRI**[a]		2-Hydroxy-IBU	**2OH-IBU**	
Gemfibrozil	**GMF**	Lipid regulators and cholesterol lowering drug	10,11-Epoxycarbamazepine 2OH-Carbamazepine	**EpCBZ** **2OH-CBZ**[c]	TP of CBZ
Ranitidine	**RAN**	Histamine H2 receptor antagonist	Metoprolol Acid	**MTPA**	TP of MTP and ATE
Bisphenol A	**BPA**[c]	Plasticizer	N-Acetyl- SFX	**N-AcSFX**	TP of SFX
Methylparaben	**mPar**[c]	Preservative	N-Desmethyl-VLF	**N-VLF**	TP of VLF

TPs were not spiked.

[a] Compounds included in the last published Watch List (EU 2022/1307).

[b] Also VLF TP and named O-Desmethyl-venlafaxine.

[c] Compounds not analyzed in plant tissues (not included in the analytical protocol).

20 μg/L of each OMP in the GW solution, except for MTP (50 μg/L, due to an error in the individual stock solution). Additionally, all possible transformation products (TPs) of the spiked OMP that are included in the available analytical protocol (Section 2.5) were also searched (Table 1). Further details of the selected OMP are indicated in Supplementary material, Table S2.

2.2. Hydroponic system

The hydroponic laboratory-scale system consisted of modular units, where each module contained four plastic (PVC) rectangular canals (5.5 cm × 8.0 cm × 100 cm), accommodating six lettuces per canal (24 lettuces per module, Figure 1). Plastic netted pots (Ø 5.5 × 4.9 cm height) with light expanded clay aggregates (LECAs) as inert substratum were introduced in the canals to accommodate the plants. Each module was connected to a reservoir on the top of the system, feeding the system by gravity. Abiotic controls were carried out in hydraulically disconnected canals and fed manually (Figure 1). A series of LED light tubes (18W, Osram, cold white and blue + red – full spectrum) were positioned 65 cm above the canals, ensuring uniform light distribution. Three sensors (Hobo® Pendant U23-001A HOBO) placed in different parts of the system recorded relative humidity and temperature at 30-min intervals.

2.3. Experimental setup

Lettuce planters *(Lactuca sativa)*, with 6–9 leaves were acquired from a local store and carefully rinsed with DI water to eliminate any soil particles adhering to their roots before the experiments. The canals were half filled with 1.8 L of water and replaced once a week. The experiment lasted 4 weeks, in line with other studies on hydroponics with edible crops (Mathews *et al.* 2014; Arcas-Pilz *et al.* 2022; Clyde-Smith & Campos 2023). The photoperiod was 14 h/day, in line with previous studies on hydroponics (Benzarti *et al.* 2008; Herklotz *et al.* 2010). The recorded average temperature was 20.1 ± 1.6 °C and the relative humidity was 52.1 ± 6.0%.

Three distinct experimental conditions were investigated, differing in nutrient composition: the baseline condition involving solely GW (GWB), GW supplemented with struvite (GWS), and GW supplemented with the CNS (GWN). Additionally, a biotic control (CTRL) was established, involving the lettuces grown in CNS dissolved in DI water. Abiotic controls (with GW and the netted pots filled with LECA but without plants) were used to assess abiotic processes such as degradation, transformation, and adsorption onto LECA. All system components and LECA were cleaned with soap, bleach, and thoroughly rinsed with DI water before the experiments.

2.4. Plant growth evaluation

Number of leaves and visual appearance of each lettuce were registered weekly, recording wilting, discoloration, number of leaves as well as number of lost leaves, and overall comparison of impression (e.g., leaf thickness, color and physical strength indicated through the leaves ability to hold itself up) between CTRL and GW conditions. Other growth parameters were only obtained at the beginning and end of the experiment (4 weeks) due to the destructive nature of the sampling. For this, two representative plants of each condition were rinsed with DI water, separated into roots and shoots (leaves), and weighted to obtain the wet mass. The leaf area (LA) was

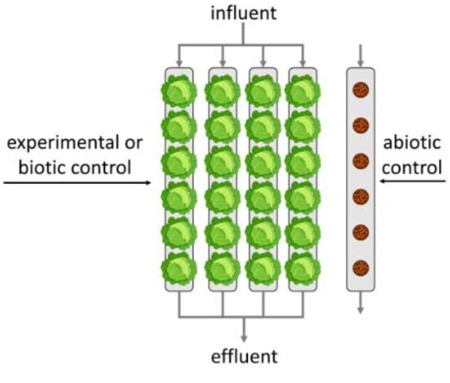

Figure 1 | Diagram of the experimental design for each of the tested GW. Each condition had a four-canal modular unit with six lettuces/canal. A separate canal with the same GW but without plants was used as the abiotic control. Lettuce vector was retrieved from vecteezy.com.

assessed using the app ‘Leafscan’ (version 2.1.1; updated August 30, 2020). After oven drying at 70 °C for 48 h, the samples’ dry mass was obtained. The leaf dry matter content (LDMC; mg/g) and water content (%) were calculated. Additionally, the plant growth was evaluated with plant growth parameters based on the leaf area, mass production, and leaf morphology (Eregno *et al.* 2017; Fraile-Robayo *et al.* 2017; Gent 2017, 2016; Sangare *et al.* 2021):

- Relative growth rate (RGR; g/g*day), indicating the proportionate growth of the plant independent of its initial size.
- Net assimilation rate (NAR; g*cm^2/day), increase in dry matter per unit leaf area, indicating the efficiency of using the produced plant material for photosynthesis.
- Specific leaf area (SLA; cm^2/g leaf dry weight), ratio of the leaf area to the dry weight of the leaves, indicating leaf thickness/density.
- Leaf weight ratio (LWR; g/g), indicating the proportion of leaves to the whole plant and thus the dry weight involved in assimilation.

More details of the calculations and formulas are indicated in Supplementary material, Section S1.

2.5. Sampling and analyses

2.5.1. Liquid samples: analyses of standard parameters and OMP

Influent and effluent water samples from the hydroponic system were taken weekly and analyzed in duplicate, within the same week, for physicochemical parameters: (a) ions (NO_3^-, PO_4^{3-}, SO_4^{2-} Na^+, NH_4^+ and K^+; 10 mL, filtered with nylon syringe filter 0.2 μm) by ion chromatography (ICS 5000 from DIONEX); (b) COD, BOD, TSS, TOC (1 L, unfiltered) according to Standard APHA methods (American public health association *et al.* 2012). Samples for OMP analyses (2 mL, filtered with syringe filter PVDF 0.45 μm, stored at −20 °C until analysis) were analyzed by direct injection into UHPLC-MS/MS. EDCs (methylpraben and bisphenol A) and caffeine were analyzed according to Becker *et al.* (2017), while PhACs were analyzed according to Gros *et al.* (2012). Limit of detection (LOD) and limit of quantification (LOQ) are provided in Supplementary material, Table S2.

2.5.2. Plant samples: analyses of OMP

Immediately after harvesting, the lettuce leaves were rinsed with DI water and freeze-dried for 1 week. The freeze-dried samples were ground with a stainless-steel coffee grinder and stored until analysis (−20 °C). Sample preparation involved extraction by QuEChERS and dSPE PSA-C18 clean-up adapted from Montemurro *et al.* (2020) with more information provided in Supplementary material, Section S2. Matrix-match calibration curves and recovery experiments were performed with the use of laboratory-grown lettuce, free of micropollutants. The analyses of PhACs were performed by UHPLC-MS/MS according to Castaño-Trias *et al.* (2023). Recovery values in the lettuce matrix (%), as well as LOD and LOQ are provided in Supplementary material, Table S2.

2.6. Statistical analyses

The coefficient of determination (R^2), calculated with Microsoft Excel, was used to evaluate linearity between plant growth (expressed as number of leaves) in relation to pollutant/nutrient removal or water loss per week. Then, IBM-SPSS 28.0 software package was used to perform Principal Component Analysis (PCA) on the growth parameters obtained at the beginning and end of the experiments. The differences in number of leaves were assessed through univariate with a between subjects’ analyses, as they were recorded weekly. The differences between the OMP removals across conditions were analyzed through a univariate Generalized Linear Model with a between subjects’ factor. Further details and formulas are indicated in Supplementary material, Section S3.

2.7. Human health risk assessment

The target group for the risk assessment was the European adult population with an average body weight of 70 kg. The Hazard Quotient (HQ) was determined by comparing the estimated daily intake (EDI) of the OMP when consuming 50 g of the produced lettuce leaves (Eregno *et al.* 2017), over a reference value, that represents an exposure level at which no adverse health effect is expected. In this study, the reference values were generated from the lowest daily therapeutic dose (LDTD) for the PhACs (applying a literature safety factor (SF) or a default SF by Snyder *et al.* (2010), or the threshold of toxicological concern (TTC, Kroes *et al.* 2004) in the case of TPs. If

TTC was not available for the TP, the parent compound TTC was used for indicatory evaluation since TP potentially express higher toxicity than the parent compound. A $HQ > 1$ suggests that there is a potential risk to human health through the consumption of the produced lettuce leaves, thus more detailed toxicological studies would be required (e.g., De Santiago-Martín *et al*. 2020; Margenat *et al*. 2020; Tadić *et al*. 2021). Applying the state-of-the-art additivity assumption (NRMMC 2008), the combined exposure to all analyzed compounds was assessed with the Hazard Index (HI), which is the sum of the HQ of each compound. In case the concentrations exceeding the range of the available calibration curves (i.e., for DVLF, ATE, MTP, VLF, MTPA, and EpCBZ), the corresponding highest calibration curve points, different for each of the compounds, were used for calculating the risk assessment. The obtained values represent the minimum level of exposure (i.e., the lower bound of the compounds' concentration in the leaves) and used to calculate the minimum risk for each of the compounds. Thus, the presented results gave an idea of potential risks although the real accumulated concentration must be assumed to be higher. More detailed explanations, formulas and values are provided in Supplementary material, Section S4.

3. RESULTS AND DISCUSSION

3.1. Plant development

3.1.1. Plant development and nutrient uptake over the experiment

All lettuces (24 per condition) survived the 4-week experiment with a healthy appearance at harvest (see Supplementary material, Figure S1). The plants grown with conventional nutrient solution (i.e., GWN and CTRL) produced healthy looking leaves (i.e., no extraordinary discoloration/rotting, self-supporting physical strength) and thin, light-colored roots, resembling those cultivated in hydroponics using standard nutrient solutions (Lei & Engeseth 2021). In contrast, plants growing in GW or GW supplemented with struvite (GWB and GWS) produced smaller, but thicker leaves (see Chapter 3.1.2) and visibly thicker roots, a strategy known to enhance nutrient uptake (Vaillant *et al*. 2004; Eregno *et al*. 2017) as the available nutrients were probably not sufficient in GWB and GWS compared to GWN. Likewise, Da Silva Cuba Carvalho *et al*. (2018) reported the potential of WW to achieve comparable lettuce growth and nutrient absorption to tap water supplemented with fertilizers, but they also indicated that lettuces grown in WW without nutrient supplementation failed to meet market standards. Yellowish discoloration of a single leaf occurred in week 4 of some GWB and specially GWS plants, probably indicative of stress resulting from salinity and pollutant exposure (García-Valcárcel *et al*. 2016; Ramprasad & Philip 2018).

The number of leaves increased in all conditions, with 8, 6, 15, and 20 leaves produced by the end of the experiment for GWB, GWS, GWN, and CTRL, respectively. Statistical analyses (p-value < 0.01) revealed significant differences between number of leaves across all treatments, in line with Ramprasad & Philip (2018), who reported slightly more leaves in the control of *Phragmites australis* grown in hydroponics with nutrients and GW constituents (sodium dodecyl sulfate, propylene glycol, and trimethyl amine). Similarly, Rababah & Al-Shuha (2009) reported typical lettuce growth in WW effluent with nutrient supplementation in hydroponics, although control lettuces exhibited greater size, like it was observed for GWN in comparison with CTRL. Regarding the influence of the presence of OMP in water on plant development, the existing literature is not conclusive, since some studies reported negative effects (Bartha *et al*. 2010; Carter *et al*. 2015), while others did not report any effect (Calderón-Preciado *et al*. 2012; Chuang *et al*. 2019). It is hypothesized that the plants were more affected by other GW constituents (Misra *et al*. 2010), with a much higher concentration than OMP (30–200 mg/L vs. 0.02 mg/L, Supplementary material, Table S1). Furthermore, the tested OMP concentration in this study was lower than in the previously mentioned studies (20 vs. 50–100 μg/L). Although the GWN lettuces grew slightly less, their development and appearance were comparable to the control. This result places GW as a suitable medium for irrigation, particularly in decentralized systems and in water scarcity scenarios. Alternative irrigation resources are essential to create more resilient and circular systems, and the use of GW with adequate nutrient supplementation can help reduce that pressure while increasing food security. However, ideally, irrigation with GW should be able to be combined with freshwater to diminish the negative effects of its constituents on plant development.

The relationship between nutrient removal and water loss (evaporation and transpiration) exhibited linearity with the number of leaves and nutrient removal for GWN and CTRL (Figure 2), indicating enhanced nutrient and water uptake to support plant growth. In contrast, no linearity was found for GWB and GWS, as these lettuces showed poorer growth. Interestingly, while nutrients in GWB and GWS were scarce, they were not

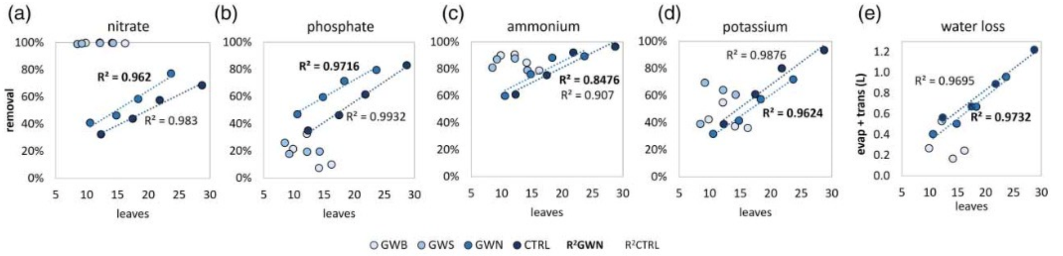

Figure 2 | Relation of the number of leaves with the nutrient removal (nitrate, phosphate, ammonium, and potassium: a, b, c, d, respectively) and the water loss (evaporation (evap) and transpiration (trans), e).

completely depleted (except for nitrogen), and although the number of leaves increased in these conditions, the relation with the nutrient and water uptake was not linear like in the other conditions, indicating inadequate growth. Additionally, the presence of sodium might had affected plant growth. Sodium concentration in this study (around 38 mg/L, Table 3) was similar in all the conditions and below the reported toxicity levels of 50 (Raval & Koradiya 2016) or 87 mg/L (Da Silva Cuba Carvalho *et al.* 2018), but early stage plants might be more sensitive. Literature indicates that the presence of sodium can stimulate the growth of roots due to salt stress, leading to lower water content and fresh biomass as well as darker color of the leaves (Bartha *et al.* 2015). Hence, the darker color of GW lettuces as well as the poor growth and thick roots of GWB and GWS can be related to both the lack of nutrients (especially N) and the stress induced by the salts present in the GW. Particularly, sodium can inhibit the plant uptake of potassium (of similar size and charge) because of competitive uptake (Vairavan *et al.* 2007). The obtained results are in line with a previous study on cucumbers grown in hydroponics with treated GW amended with nitrified urine and nutrient supplementation, where slightly lower growth was obtained compared to the control, and it was attributed mainly to the presence of sodium (Wdowikowska *et al.* 2023).

3.1.2. Plant growth assessment

A holistic interpretation of the plant growth indicators reduces possible misinterpretation of results. A consistent pattern emerged in terms of the calculated parameters (RGR, NAR, and LWR). The smallest values were observed for GWS, closely followed by GWB, with GWN exhibiting markedly higher values, while CTRL displayed slightly lower values (Table 2). Specifically, RGR (indicative of plant material increase over time) were similar for GWN and CTRL (grown with the same nutrient solution), while GWS and GWB lettuces did not receive additional nutrients and grew similarly (Table 2). The RGR of CTRL and GWN plants were in line

Table 2 | Plant growth parameters (leaf fresh and dry weights, # of leaves, and leaf area refer to the values measured at the end of the experiment), average, and standard deviation

Parameter	Unit	GWB	GWS	GWN	CTRL
Leaf fresh weight	g	2.7 ± 0.7	3.4 ± 0	25.0 ± 0.5	24.8 ± 4.7
# of leaves		18 ± 1.4	13 ± 0	23.5 ± 0.7	27 ± 0.0
Leaf area	cm^2	112.1 ± 25.9	149.7 ± 2.1	990.5 ± 22.4	1,055.9 ± 124.9
Leaf dry weight	g	0.3 ± 0.1	0.4 ± 0.0	1.4[a]	1.1 ± 0.2
Root dry weight	g	0.09 ± 0.02	0.12 ± 0.03	0.18 ± 0.0	0.16 ± 0
LDMC	mg/g	124.8 ± 3.5	102.2 ± 0.6	57.3[a]	43.5 ± 0.3
Water content in leaves	%	87.5 ± 0.4	89.8 ± 0.1	97.1[a]	95.6 ± 0.0
RGR	g/g/d	0.04 ± 0.01	0.03 ± 0.0	0.07[a]	0.06 ± 0.0
NAR	$mg/cm^2/d$	0.14 ± 0.03	0.10 ± 0.01	0.16[a]	0.10 ± 0.02
SLA	cm^2/g	344.9 ± 0.2	349.1 ± 3.1	492[a]	665.4 ± 30.7
LWR	g/g	0.78 ± 0	0.77 ± 0.02	0.84[a]	0.76 ± 0.0

[a] Standard deviation not included as there was a mistake on the measurement of the dry weight of one of the lettuces of GWN, thus only the value of one sample was used to calculate the parameters.

with the literature for medium sized lettuces grown in hydroponics under varying temperature conditions (Gent 2016). Regarding the morphology, all GW plants yielded thicker and denser leaves, as indicated by their lower SLA compared to CTRL (Table 2). The NAR evidenced that the GWN condition produced the highest dry weight, using its available dry mass more efficiently for growth and maintenance. This is further underscored by LWR, with the GWN condition displaying a higher proportion of leaves to roots most likely caused by the more abundant access to essential nutrients compared to CTRL (Hopkins 2009; Eregno *et al.* 2017). On the other hand, GWB or GWS produced fewer and smaller but thicker leaves than GWN, which is a typical morphological change characteristic of plants adapting to resource-poor conditions (Eregno *et al.* 2017). This observation is supported by the higher LDMC, lower water content (95–97% for CTRL and GWN, 87–90% for GWS and GWB), and lower SLA.

PCA applied to the initial values of the plant growth assessment (Supplementary material, Table S3) extracted three components, collectively representing 97% of the variance. Most parameters clustered on the first component (where fresh weight was the parameter with the higher factor loadings), displaying strong correlations among them, while number of leaves and LDMC fell on different components and therefore were not redundant (Supplementary material, Table S3). Therefore, the general linear model with repeated measures design was employed focusing only on these three components (total fresh weight, number of leaves, and LDMC). Tests of within-subjects effects highlighted that time was always the most significant factor for variability (Supplementary material, Table S4). The treatment (condition*time) was significant because there were different time effects (i.e., observed more growth or less).

For the first component (fresh weight), nutrient content revealed two distinct trends: plants growing with commercial nutrient solution (GWN and CTRL) exhibited similar results, while plants with lack of nutrients (GWB and GWS) yielded significantly lower estimated marginal means, displaying similarities between themselves (Supplementary material, Figure S2(a)). This emphasizes that nutrient content significantly influenced plant growth and weight. For the second component (LDMC, Supplementary material, Figure S2(b)), significant differences emerged only between GWB and CTRL, at the end of the experiments, and all conditions exhibited decreased LDMC at the end of the experiment, except for GWB. Regarding the third component (leaves, Supplementary material, Figure S2(c)), there were evident differences among all conditions. Nevertheless, the second and third components displayed greater variations among conditions, suggesting that they were less influenced by nutrient content and possibly affected by GW and/or the presence of OMP.

Limited studies have reported successful struvite application for the hydroponic growth of tomatoes (Carreras-Sempere *et al.* 2021; Halbert-Howard *et al.* 2021) and lettuce (Arcas-Pilz *et al.* 2022; Mendoza *et al.* 2023), although it was blended with other fertilizers. Struvite, in fact, is a sustainable fertilizer but rarely introduced in the literature. In this study, struvite application was not successful and the growth of the lettuces from GWS was comparable to those from GWB rather than GWN (Table 2). This could be attributed to the low water solubility of struvite, requiring pH values below 4 for near complete dissolution (Carreras-Sempere *et al.* 2021), while higher pH was applied in the current study (see GWS influent, Table 3), which exceeded 6 after 48 h, suggesting struvite reprecipitation, potentially reducing its availability to the plants. Carreras-Sempere *et al.* (2021) dissolved the struvite with HNO_3, also contributing to NO_3 input, while Arcas-Pilz *et al.* (2022) applied struvite directly in water, resulting in 50–70% undissolved struvite. In our study, struvite was dissolved with citric acid to investigate whether the Mg, P, and NH_4 supplied by struvite, along with nutrients in the GW could sustain lettuce growth. Dissolving it in HNO_3 would have led to a better nutrient balance but disguising the effects of struvite. The calculated struvite amount was based on the PO_4 content in the CNS, and successful dissolution was confirmed by PO_4 concentrations in the influent control, closely resembling those in GWS (Table 3). Notably, TSS and turbidity in the GWS effluent were higher compared to other GW conditions, possibly due to struvite precipitation, and the addition of citric acid elevated the carbon content, resulting in higher COD and TOC influent values in GWS compared to the other two GW conditions. These factors could have had a potential negative impact on plant development.

3.2. GW treatment

3.2.1. Main GW constituents and nutrients

The removal of TSS, TOC, and Na was constant with minimal weekly variability (see small standard deviation values in Table 3, in contrast to Sangare *et al.* (2021), who reported reduced removal efficiencies over time due to the accumulation of pollutants in plant tissues. Linear correlation was not found between TSS, TOC, or

Table 3 | Concentration of the standard parameters and nutrients present in the different conditions and their removal

	influent concentration, mg/L				effluent concentration, mg/L				removal, %			
	GWB	GWS	GWN	CTRL	GWB	GWS	GWN	CTRL	GWB	GWS	GWN	CTRL
EC (μS/cm)	324.3 ± 9.1	461.3 ± 8.7	2017.5 ± 15.5	1703.8 ± 47.5	223.5 ± 17.7	326.1 ± 19.9	1707.8 ± 105.8	1607.6 ± 157.3	–	–	–	–
pH	7.1 ± 0.4	4.8 ± 0.2	6.2 ± 0.2	5.6 ± 0.3	7.0 ± 0.1	7.0 ± 0.2	6.9 ± 0.4	5.4 ± 0.5	–	–	–	–
turb	1.2 ± 0.5	5.4 ± 2.7	5.3 ± 1.4	3.7 ± 0.9	6.0 ± 3.0	15.3 ± 4.1	4.6 ± 3.7	3.5 ± 3.1	–	–	–	–
COD	594.0 ± 34.2	789.7 ± 93.1	628.9 ± 31.0		65.0 ± 9.0	116.5 ± 10.6	49.3 ± 27.3	65 ± 9.0	90.7 ± 1.1	88.1 ± 1.9	95.4 ± 2.5	
BOD	309.5 ± 31.8	346.0 ± 19.9	318.3 ± 24.4		25.4 ± 7.3	60.2 ± 10.8	22.5 ± 9.0		93.1 ± 1.6	86.0 ± 3.0	95.9 ± 0.7	
TOC	180.7 ± 7.6	237.8 ± 11.7	162.1 ± 3.7	14.4 ± 1.5	26.6 ± 2.9	34.5 ± 4.4	14.3 ± 4.8	17.6 ± 7.2	87.8 ± 1.7	88.3 ± 1.2	94.6 ± 1.1	41.9 ± 3.5
TSS	52.6 ± 12.8	68.8 ± 25.8	66.0 ± 12.8		12.3 ± 4.5	20.5 ± 7.4	15.2 ± 17.2		80.4 ± 6.6	75.4 ± 7.4	87.5 ± 10.1	
Na	38.3 ± 0.8	38.0 ± 0.2	37.2 ± 0.2		39.5 ± 1.7	40.2 ± 1.4	50.9 ± 8.2	12.9 ± 4.7	14.7 ± 8.8	14.6 ± 3.3	14.5 ± 7.3	
N-NH$_4$	21 ± 1.0	25.3 ± 0.7	43.4 ± 0.5	29.7 ± 0.4	3.5 ± 1.3	5.2 ± 1.5	13.8 ± 6.3	9.2 ± 5.8	86 ± 5.6	83.7 ± 4.2	78.4 ± 13.4	81.2 ± 15.2
K	11.9 ± 0.3	12.2 ± 0.1	191.2 ± 3.8	196.9 ± 3.5	8.2 ± 1.7	6.3 ± 2.3	144.3 ± 28.7	106.5 ± 55.8	42.5 ± 13.4	58.2 ± 14.8	50.5 ± 16.9	68.2 ± 22.1
N-NO$_3$	4.4 ± 0.1	4.8 ± 0.2	174.0 ± 5.6	168.4 ± 5.1	0.1 ± 0.0	0.1 ± 0.0	117.2 ± 28.2	158.1 ± 9.8	99.8 ± 0.2	99.4 ± 0.3	55.8 ± 15.6	50.6 ± 14.6
P-PO$_4$	18.5 ± 0.5	35.4 ± 0.4	57.1 ± 1.5	38.9 ± 1.1	18.4 ± 1.3	34.8 ± 1.7	30.9 ± 7.7	30.5 ± 6.4	17.8 ± 10.8	20.6 ± 3.7	64.4 ± 14.0	56.4 ± 19.3
S-SO$_4$	10.8 ± 0.3	17.2 ± 12.8	58.5 ± 1.9	56.0 ± 8.4	16.8 ± 0.8	16.4 ± 0.5	84.3 ± 14.5	90.9 ± 44.3	0 ± 0	31.7 ± 36.7	10.1 ± 5.5	22.1 ± 9.3

Shaded cells correspond with the parameters used to evaluate the effluent's compliance with the requirements of the different reuse scenarios of EU 2020/741.

Na removal and plant growth (number of leaves), suggesting that increased plant growth did not necessarily enhance pollutant uptake. Similar removals of TSS and organics were observed for abiotic controls (Supplementary material, Table S5) due to abiotic degradation and/or adsorption onto the LECA and, thus, the uptake by the plants is estimated to be minimal. High BOD, COD, TSS, and TOC removal were achieved in all conditions (85–96%, Table 3), in line with studies on hydroponics cultivation of honeysuckle with the same GW recipe of this study (Xu *et al.* 2020) and of lettuce with raw dishwasher GW, reporting also high nitrate and ammonium removals (Sangare *et al.* 2021). In contrast, sodium removal remained consistently low and uniform (Table 3), in line with Ramprasad & Philip (2018), reporting 20% sodium removal after a 35-day hydroponic experiment with *P. australis*, primarily accumulating in the roots through adsorption. Additionally, sodium dodecyl sufate, (typical GW constituent applied also in this study) is considered recalcitrant (Ramprasad & Philip 2018), hence high sodium removal was not expected. Comparable BOD and TSS removals were reported in various types of CWs treating GW (Williams *et al.* 2008; Ramprasad *et al.* 2017; Zraunig *et al.* 2019). Furthermore, obtained nutrient removals (i.e., N and P) from raw GW without extra supplementation (i.e., GWB condition) were in line with the results obtained in previous studies on hydroponic systems with edible plants for WW treatment, gathered in a recent review (Mai *et al.* 2023), hence confirming the efficacy of the proposed system.

3.2.2. Fate and removal of OMP

3.2.2.1. OMP removal in the system. The OMP removal over the 4-week period in the systems with plants displayed considerable variability across all conditions, leading to removals from 0 to 100% (Figure 3(a)). The average weekly removal was 62, 49, and 65% for GWB, GWS, and GWN, respectively, confirming the literature on hydroponic systems or other types of CWs for the treatment of WW (Kahl *et al.* 2017; He *et al.* 2018; Wolecki *et al.* 2019) or GW (Zraunig *et al.* 2019). The average OMP removals in the corresponding abiotic controls for GWB, GWS, and GWN were 51, 46, and 47%, respectively (Supplementary material, Table S5), indicating that OMP were removed through abiotic processes (adsorption onto LECA) or experienced abiotic degradation (e.g., hydrolysis or oxidation-reduction), as already reported (Dodgen *et al.* 2013; Bartha *et al.* 2015; Zhang *et al.* 2016). Therefore, the presence of plants improved the removal of most OMP to some extent, as generally reported in the literature (Dodgen *et al.* 2013; Chuang *et al.* 2019), but in contrast with Cardinal *et al.* (2014). GWB and GWN exhibited similar OMP removal patterns although GWN had a higher median and slightly higher average than GWB (Figure 3(a)), suggesting a removal efficiency improvement with healthier and more robust plants, consistent with previous reports (Dodgen *et al.* 2013; Chuang *et al.* 2019). Conversely, GWS presented the lowest OMP removal rates, despite having similar lettuces to GWB (Supplementary material, Figure S1, Table 2). Hence, not only plant development, but other particular characteristics of the GWS condition (higher turbidity and greater organic content, as previously mentioned, Table 3) resulted in a more complex matrix that could hinder the interactions between the OMP and the system and, consequently, decreasing their removal.

Highest removal (>90%) was recorded for RAN, OFX, TET, ACE, mPar, and BPA, while DCF, DVLF, VLF, and TRI showed the lowest removals (<30%), and the remaining compounds intermediate removal (Figure 3(b)). It should be highlighted, in fact, that very few studies are available in regarding some of the here considered OMP in hydroponics and/or GW. Comparing to literature, CBZ was removed to a greater extent than reported in

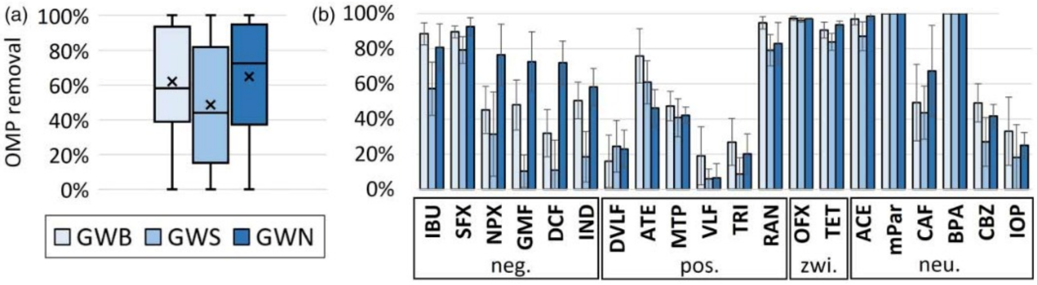

Figure 3 | OMP removal, average per condition (a) and individual removal (b). Compounds in (b) are ordered from lowest to highest MW in each of the groups. Below the compounds, the corresponding ionizable form at solution pH (7): negative (neg.), positive (pos.), zwitterionic (zwi.), and non-ionizable/neutral (neu).

studies with CW with non-edible plants (Kahl *et al.* 2017; Ravichandran & Philip 2021). Both CBZ and CAF removals (around 50%) are in line with Chuang *et al.* (2019), who evaluated their uptake by hydroponically grown lettuces. IBU removal (60–80%) happened to a lower extent than in hydroponic systems with non-edible plants (Zhang *et al.* 2016). It is worth mentioning that due to an error, MTP concentration in the synthetic GW was even higher than the average spiked (around 50 μg/L vs 20 μg/L) and thus the concentrations found in the effluent as well as the possible metabolization might be higher than with other compounds due to this higher concentration. Precisely, the intermediate removal for ATE and MTP was lower than the only available study considering these compounds (31–35% in hydroponic systems with *Iris pseudacorus*, Brunhoferova *et al.* 2021).

The removal of certain OMP remained consistent across various matrices and plant growth stages. There were not statistically significant differences on the removal of ten OMP (SFX, DVLF, MTP, VLF, TRI, ACE, mPar, CAF, IOP, and mPar) among the three experimental conditions ($p < 0.05$, Supplementary material, Table S6). This implies that their removal was not influenced by differences in the tested solutions (nutrient concentration, salinity, turbidity, carbon content, etc.) nor by plant development (no linearity between leaves and OMP removal). On the other hand, the removal of some OMP was influenced by the condition. Pairwise comparison (Supplementary material, Table S6) indicated significant differences in OMP removal for five compounds (i.e., DCF, NPX, RAN, TET, ATE) between GWB and GWN, with higher removals for DCF, NPX, and TRI in GWN, and for RAN and ATE in GWB (Figure 3(b)). GWB presented significant differences in OMP removal for more compounds with GWS (eight compounds) than with GWN (five compounds), despite having similar plants as GWB. Other issues, as mentioned before, might have influenced plant development and OMP removal in GWS.

On the relation between the removal of OMP and their properties, no direct linear correlation was observed with log K_{ow}, MW, or pKa, implying that OMP removal was not determined by a single property but by a complex interplay of factors. Neutral OMP with higher propensity of diffusion through plant cells (Chuang *et al.* 2019; Ravichandran & Philip 2021) were in general removed to a greater extent than charged compounds. Zwitterionic OFX and TET were highly removed also in the abiotic controls (Supplementary material, Table S5), indicating their degradation could be attributed to abiotic processes or adsorption onto the LECA. Compounds of smaller size and negative charge (IBU, SFX) demonstrated superior removal compared to larger ones, and the most pronounced differences between GWN and other conditions were observed for hydrophobic compounds, most likely due to the interactions with the roots.

The TPs of CBZ (i.e., EpCBZ and 2OH-CBZ) along with 1OH-IBU, N-AcSFX, and N-VLF were generally not detected in the effluent samples, and only 2OH-IBU was found at low concentrations (<4 μg/L), suggesting that substantial degradation of the parent compounds did not occur in the aqueous solution, although the formation of other not analyzed TP cannot be excluded.

3.2.2.2. OMP uptake by lettuces. Ten out of the 20 analyzed compounds in lettuces leaves were either not detected or were below LOD or LOQ limits. The remaining compounds, including DVLF, ATE, MTP, VLF, MTPA, and EpCBZ, were frequently detected above the highest point of the respective calibration curves (Table 4). It is possible that the high concentrations of MTP and MTPA found in lettuces leaves were related with the higher spiked concentration of MTP in comparison with the rest of OMP of this study. The other compounds (i.e., IBU, TRI, OFX,) ranged from 0.02 to 0.87 μg/g dry weight (dw, Table 4). Correspondingly, Wu *et al.* (2012) detected 12 out of 20 OMP in lettuces leaves grown in hydroponic solution without detecting IBU, SFX, NPX, and DCF. Similar levels were reported by Kreuzig *et al.* (2021) for lettuce grown in treated WW (0.032–0.135 μg/g for ACE, CBZ, and DCF). In contrast to this study, where no NPX was found in leaf

Table 4 | OMP concentrations in lettuce leaves, μg/g dw

	Condition	**IBU**	**DVLF**	**ATE**	**MTP**	**VLF**	**TRI**	**OFX**	**MTPA**	**EpCBZ**
μg/g dry weight (dw)	**GWB**	<LOQ	>0.51[a]	>1.01[a]	>0.82[a]	>1.28[a]	0.87 ± 0	<LOQ	>0.99[a]	0.84 ± 0.06
	GWS	<LOQ	>0.51[a]	>1.01[a]	>0.82[a]	>1.28[a]	0.74 ± 0.04	0.08 ± 0.01	0.58 ± 0.03	>1.06[a]
	GWN	<LOD	>0.51[a]	>1.01[a]	>0.82[a]	>1.28[a]	0.41 ± 0.01	0.17 ± 0.05	0.35 ± 0.03	1.03 ± 0.01

Not detected: NPX, GMF, DCF, IND, TET, ACE, 1OH-IBU, 2OH-IBU, N-AcSFX, N-VLF. SFX and RAN were analyzed but not recovered.

[a] Compound detected at concentrations exceeding the range of its available calibration curve.

tissue, its accumulation in lettuce tissue in hydroponic culture was reported elsewhere (Calderón-Preciado *et al.* 2012). While CBZ and SFX were not found in lettuce leaves of this study, they were commonly detected in previous studies (Herklotz *et al.* 2010; Chuang *et al.* 2019; Manasfi *et al.* 2021).

Although results of this study show very high removal for the most studied antibiotics (Figure 3(b)), they were either non-detected or detected at low concentrations within the leaves (Table 4), most likely because they tended to accumulate in the roots, where usually higher OMP concentrations are found (Chuang *et al.* 2019). In this line, hydrophobic DCF and NPX (log $K_{ow} = 4.51$ and 3.18, respectively), were removed to a significantly greater extent with well-developed plants (GWN) compared to other conditions, despite not being detected in leaf tissues, and not being removed in the abiotic control (0 and 4.6% removal for DCF and NPX, Supplementary material, Table S5). Their hydrophobic nature lead to their accumulation in the roots, with more lipid content than other plant tissues (Dodgen *et al.* 2013; Christou *et al.* 2019a). In contrast, although positively charged compounds did not exhibit overall superior removal, some of them (ATE, MTP, MTPA, VLF, and DVLF) were detected at higher concentrations in lettuce leaves, due to their greater potential to be transported with the transpiration stream (Ravichandran *et al.* 2021). Indeed, high translocation potential of some positive compounds, including MTP, was reported after being detected in all samples from lettuces grown in soil irrigated with WW (Manasfi *et al.* 2021).

As regards to TPs, they are relevant to be considered in treated water as well as in terms of plant uptake in future studies. MTPA, a metabolite of both ATE and MTP, was not spiked in the influent, but detected in both lettuce leaves (Table 4) and the effluent (average 9.5 μg/L and up to 22.9 μg/L), confirming ATE and/or MTP transformation into MTPA (Rubirola *et al.* 2014). The other TP of concern in this study is EpCBZ, detected in all lettuce samples, exceeding the calibration curve in two of the tested conditions (Table 4). As indicated previously, its parent, CBZ, is typically detected at high concentration in leaves, but it was not detected in this study. In this case, since EpCBZ was not found in any effluent sample, it is postulated that CBZ underwent metabolization within the plant, as previously reported (Kodešová *et al.* 2019). No studies were found evaluating the uptake of VLF and DVLF in edible plants, and it is important to note that DVLF is a pharmaceutical, but also a TP from VLF, and for this reason the possible metabolization cannot be ensured. Both compounds (VLF and DVLF) were spiked because they are present in the last published WL and because there are scarce studies evaluating them. Only Petrie *et al.* (2017), who spiked different concentrations of several OMP, including VLF and DVLF, found VLF in *P. australis* at concentrations up to 50 ng/g dw, while DVLF was detected at very low concentration (usually < LOQ).

To summarize, OMP can follow diverse pathways from GW to the edible parts of the plants as a function of the characteristics of OMP, plant type and growth medium. Results from this showed no linear relation between the removal of contaminants and their properties, although it must be taken into account that more contaminants have been evaluated than in other studies, and that some trends can be observed. Smaller OMP, as well as hydrophobic ones, were eliminated to a greater extent, while most of the compounds detected in high concentrations in the leaves were positively charged. This study holds significant importance as it sheds light on the concentrations in edible plant tissues of certain OMP which have seldom been investigated or remain unexplored, particularly VLF, DVL, and MTP, detected here at high concentrations.

3.2.3. Effluent quality for reuse applications

The reuse potential of the system effluent was assessed according to the European Union's reuse legislation (EU 2020/741), considering all parameters (i.e., turbidity, TSS, and BOD) except for microbiological indicators (synthetic GW without bacteria). In any case, previous research on NBS for WW treatment and reuse reported the need for an additional disinfection step to meet legislative criteria when scaling up these systems and with real GW (Winward *et al.* 2008; Arden & Ma 2018). EU 2020/471 stipulates four scenarios for the use of reclaimed water for irrigation. GWN met the turbidity limit of class A (5 NTU), however both BOD and TSS limits only met the limits suitable for classes B to D (crops not in direct contact with the reclaimed water and industrial crops). The remaining conditions also met the TSS limits for scenarios B to D (35 mg/L) and although GWB effluent approached the BOD standards for these scenarios (25 mg/L, Table 3), they did ultimately exceed the required limits for turbidity and BOD. Consequently, only the effluent from GWN had enough quality for reuse regarding the European legislation, for scenarios B to D, whose TSS and BOD requirements are the same, and the difference lies in the concentration of *E. coli,* but this parameter was not included in this study. These findings underscore that the success of the GW treatment system falls on the optimal growth of plants, which enhances removal processes and consequently results in compliance with existing legislation. Prior studies confirmed effluent from NBS for GW treatment complied with Spanish legislation (Zraunig *et al.* 2019) and with USEPA standards for reuse (Ramprasad & Philip 2018).

On the effluent quality regarding OMP, attention should be paid to those compounds with lower removals as well as those that carry greater risks for human and environmental health. Antibiotics are of special interest due to the potential for contaminated vegetables to foster antibiotic-resistant pathogens within the human organism (Keerthanan *et al.* 2021), but most of them were highly removed in this study, showing promising results. It is important to mention that the OMP concentration in this study (20 μg/L) was higher than that typically found in real GW streams for most of the tested compounds (median 0.4 μg/L for PhACs in GW, Glover *et al.* 2021), and thus their concentrations would be much lower in the effluent of a real application. Nevertheless, in several cases the spiked concentration was in the same order of magnitude and, even, concentrations of compounds such as ACE, IBU, DCF and CAF in real GW were reported to be up to one order of magnitude higher than in this study (Zraunig *et al.* 2019; Glover *et al.* 2021), thus the results obtained from these compounds can be considered comparable/similar to those systems using real GW. The outcomes of this study indicate that it is apparent that even when the effluent from a system aligns with the provided quality limits, numerous parameters remain without specific regulation in the current legislation, as it is the case of OMP.

3.3. Human health risk assessment

The only tested condition that produced lettuces of marketable size (comparable to the control) was GWN (GW supplemented with CNS). Accordingly, the risk assessment is here discussed for GWN only, as a proof of concept, although the generated data of the other conditions is also indicated in Table 5.

HHRA was only evaluated for those compounds that were detected in lettuce leaves (Table 4). OFX, MTPA, and TRI produced HQ from 0.004 to 0.04, all below the threshold of 1, indicating that risk through the individual compounds is not expected. Similarly, the HQ of MTP, VLF, and DVLF ranged from 0.09 to 0.29 (Table 5). The assessed risk using the highest quantifiable concentration (Table 4) was only indicative of whether the upper end of the quantifiable concentrations would already indicate a potential risk, but the actual concentration and therefore the potential risk must be assumed to be higher. On the other hand, most OMPs studied here are present at lower concentrations in real GW, and therefore, their concentrations in lettuce are expected to be lower in real applications than those found in this study. As regards to the compounds found in some cases at higher concentrations in real GW (ACE, IBU, and DCF), they were always not detected, or at LOQ level, in the lettuces' leaves.

The HQs of both ATE and EpCBZ were substantially above the threshold of 1 (Table 5), indicating high potential risk. Notably, these results are related to compounds classification as potentially genotoxic, warranting a

Table 5 | Risk assessed for compounds quantified in the lettuce leaves, expressed as Hazard Quotient (HQ, potential risk of individual compounds) and Hazard Index (HI, potential risk of mixture)

	Hazard characterization				**Hazard quotients (HQ)**[a]		
OMP	**LDTD/TTC, μg/day**	**SF**	**Ref. value μg/kg BW/day**	**Source**	**GWB**	**GWS**	**GWN**
ATE	25,000	30,000	0.012	a	7.571	6.135	3.443
EpCBZ	0.15[b]	n.a.	0.002	b	35.055	36.054	19.663
MTP	25,000	3,000	0.120	c	0.615	0.498	0.280
MTPA	90.00[b]	n.a.	1.286	b[c]	0.069	0.033	0.011
OFX	400,000	3,000	1.900	c	–	0.003	0.004
TRI	80,000	3,000	0.380	a	0.207	0.142	0.044
VLF	37,500	3,000	0.180	d	0.640	0.518	0.291
DVLF	50,000	3,000	0.237	e	0.194	0.157	0.088
Hazard Index (HI)[a]					**44.352**	**43.541**	**23.823**

LDTD was applied for parent compounds (i.e., ATE, MPT, OFX, TRI, VLF, DVLF) and TTC for transformation products (i.e., EpCBZ and MTPA). Shaded cells indicate that the compound was detected in concentrations exceeding the calibration curve used for quantification. In these cases, the EDI was calculated for the upper bound of the analytically quantifiable concentration, representing the lower bound of the compound's concentration in the leaves.

Sources: **a**: Snyder *et al.* 2010, **b**: Malchi *et al.* 2014, **c**: Semerjian *et al.* 2018, **d**: https://www.drugs.com/dosage/venlafaxine.html (SF: Snyder *et al.* 2010); **e**: https://www.drugs.com/dosage/desvenlafaxine.html (SF: Snyder *et al.* 2010).

n.a.: not applicable.

[a] HQ & HI ≤ 1: no risk expected; HQ & HI ≥ 1 possible risk must be analyzed in more detail.

[b] Transformation product: TTC applied.

[c] The TTC value of MTP (parent compound of MTPA) was applied for the risk assessment.

higher SF of 30,000 (Snyder *et al.* 2010) applied to the LDTD for ATE and the lower TTC value of 0.0021 μg/person/day (Malchi *et al.* 2014) for EpCBZ. The obtained HQ of ATE and EpCBZ were up to two orders of magnitude higher than those reported in edible crops grown in soil irrigated with WW (Prosser & Sibley 2015), as OMP are usually taken up to a lesser extent in soil due to more interactions and richer microbiological environment in soil than in hydroponics. As regards to TP, for example, EpCBZ presents a higher health risk to the consumer than its parent compound (CBZ, Malchi *et al.* 2014). Therefore, this study confirms the importance of considering these compounds in future related studies as well as in legislations.

Even if the exposure to individual OMP indicates risk for two compounds, cumulative exposure could pose additional risk for the other compounds due to the presence of multiple OMP in real GW (Glover *et al.* 2021). Hence, the HI index (Table 5) shows that the five compounds mentioned above (MTP, VLF, DVLF, ATE, and EpCBZ) were primarily contributing to HI (97%). Excluding ATE and EpCBZ (over the limit of 1 already by themselves) the HI for cumulative risk was of 0.72 with MTP and VLF contributing about 40% each, and DVLF 13%. Other quantified compounds contributed in a minor way (6 and 1% for TRI and MTPA, respectively). In contrast, in the literature negligible dietary uptakes of DCF, BPA, and NPX were reported for lettuce and collards (Dodgen *et al.* 2013), as well as negligible risk related with the consumption of lettuces exposed to 20 OMP (Wu *et al.* 2013), in both cases grown in hydroponics with 21 days exposure to the OMP, which were applied at smaller concentration than in this study (0.1–5 μg/L). Please note that DCF in this study was spiked in the water but not detected in the lettuce. In any case, attention should be paid to the uptake and translocation potential of MTP, VLF, DLVF and even more of ATE and EpCBZ.

CONCLUSIONS

The findings of this investigation offer a comprehensive exploration of GW treatment using hydroponic systems, encompassing treatment efficacy, plant growth and health, and the fate of OMP, including potential human risks arising from their presence in GW. The results underscore the potential of GW as a hydroponic growth medium for edibles, particularly lettuce. However, results emphasize the necessity for adequate nutrient supplementation when utilizing GW medium for hydroponics, as only those lettuces grown in GW fortified with commercial nutrient solution (GWN) exhibited growth comparable to control plants. Plant development was slightly affected, most likely due to GW salinity rather than OMP presence.

The system demonstrated effective removal of standard parameters from GW, surpassing 85% in all cases, except for sodium. Only GWN effluent met physicochemical quality requirements for reuse scenarios B, C, and D (food crops not in direct contact with the reclaimed water and industrial crops) set by European water reuse legislation (EU 2020/741). Furthermore, the study showcased effectiveness in OMP removal, aligning with the performance of other NBS. However, the variability in OMP removal and the low removal rates for certain compounds suggest the need for system optimization. Notably, the condition with better-developed roots (GWN) exhibited higher removal rates, particularly for hydrophobic OMP, but also displayed the lowest OMP concentrations in leaves, indicating effective plant development and OMP removal, albeit with the lowest uptake.

HHRA for the condition with robust plant growth (GWN) revealed that five out of the ten detected compounds (20 analyzed) are unlikely to pose adverse health effects under the exposure scenario of chronic ingestion of 50 g of lettuce per day. Conversely, ATE and EpCBZ demonstrated considerable potential for human health risks, whereas VLF, DVLF, and MTP may raise concerns in the context of cumulative risk of chemicals in water reuse applications.

This study provides valuable insights into OMP in the context of water reuse, edible production, and food safety. Despite effluent compliance with water reuse parameters, the low removal rates of certain OMP underscores potential issues upon effluent discharge or reuse. Consequently, it is strongly recommended to consider these compounds in future water reuse regulations, along with their TPs, which, as demonstrated in this study, may entail even greater risk than the parent compounds. Future research should prioritize optimizing these systems for enhanced removals without increasing the risks derived from plant ingestion. Finally, studies applying real GW and expanding the spectrum of evaluated OMP are required to ensure safety in reuse applications.

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DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

CONFLICT OF INTEREST

The authors declare there is no conflict.

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4. General discussion

4.1. Feasibility of forward osmosis and hydroponics for greywater treatment and reuse

The examination along this thesis of FO and hydroponics (Articles 2, 3, 4, 5) has revealed the potential for their implementation as decentralized systems for GW treatment, producing effluents of reuse quality, as evidenced in the sections dedicated to this matter in Articles 4 and 5. Both technologies offer versatility in configuration, adapting to a variety of spaces and GW volumes and characteristics, hence becoming excellent candidates for decentralized systems for GW treatment and reuse. While NBS would require more extensive area and longer operation times, membrane technologies are susceptible to fouling [59,88,304], thereby potentially rising maintenance and operational costs. However, it is noteworthy that the *fertilizer-drawn forward osmosis* (FDFO) approach, extensively explored in Articles 2, 3 and 4, emerges as particularly advantageous due to its simplicity and lower energy requirements and costs attributed to DS recovery [152,162]. Results of Article 4 demonstrated similar general process performance (water fluxes, operational time) and OMP rejection between tests utilizing NaCl (traditional draw solute) and those employing fertilizers. Consequently, utilizing fertilizers as draw solutions improves FO efficiency by allowing direct utilization once diluted with GW/WW, proving especially attractive in decentralized scenarios. The findings across Articles 2 to 5, concerning the performance of these two distinct technologies, are consistent with prior research on treatment performance. However, the obtained results enable also to elucidate several barriers to the implementation of these systems, which will be thoroughly discussed, along with some strategies to enhance their performance.

4.1.1. Treatment performance

This thesis investigated two distinct approaches: FO, an intensive grey system reliant on physical processes, and hydroponics, an extensive green system involving diverse physicochemical and biological treatment processes. Specifically for FO, the primary objective was to mitigate contaminant passage across the membrane from the FS (GW), thereby preventing pollution of the DS. The dense FO membrane (usually negatively charged) serves as a physical barrier primarily impeding contaminants through size exclusion, followed by electrostatic interactions. Accordingly, small positively charged and hydrophobic compounds exhibited greater affinity for the membrane, while negatively charged compounds are repelled and neutral compounds demonstrate increased permeability due to reduced interactions with the membrane [170,217]. Indeed, results of Article 4 show that the FO membrane acted as an excellent barrier against GW constituents (except for sodium), including OMP. As a result, FO produces high-quality water on the DS side, but it yields a concentrated FS containing contaminants, as it was presumed that most pollutants experienced minimal degradation. One potential mitigation strategy involves treating the concentrated FS by anaerobic bioreactor, which enhances biogas production [206,224,305] while potentially producing permeate of sufficient quality for reuse, although the bacterial community could be affected by the salinity buildup in the concentrated solution [306]. Another option is integrating algae into the FS. For instance, incorporating *Chlorella vulgaris* to the FS has shown effective nitrogen and phosphorus remediation, along with organic load removal [181].

Previous studies on FO and OMP reported linear relationships between OMP rejection and their Log K_{ow} or molecular weight [170,217], though such correlations were not observed with the tested OMP (Article 4), possibly due to the high rejections resulting in very low OMP concentrations in the draw solution, the similarity of some OMP (e.g., minimal hydrophobic OMP), or the involvement of multiple mechanisms. Nonetheless, discernible trends were observed, in agreement with prior investigations. Results of Article 4 show OMP rejections getting higher with increasing molecular weight and Log K_{ow}. With regards to their charge at feed pH, negatively charged compounds exhibited the highest rejection, and small neutral and positively charged compounds were the most influenced by the contact time between feed and draw solutions, resulting in sharper reductions in rejection with time.

In comparison to FO, the hydroponic technology adopted in this study avoids the generation of a concentrated solution with pollutants. With hydroponics, the treatment lies on the removal of contaminants from GW through various processes including root and substrate adsorption, degradation, whether biotic or abiotic (e.g., hydrolysis or oxidation-reduction), and plant uptake, with potential further degradation within plant tissues and substrates [292]. While this approach appears simpler for decentralized options, the study of the removal mechanisms of the different contaminants stands out as a complex topic. The findings of Article 5, in fact, underscored the intricate interactions of OMP with the water-plant system, highlighting the complexity of their behavior within hydroponic environments. Results of Article 5 align with the performance of other NBS [22,250,307,308]; and hypothesized that removal of main GW constituents was primarily attributed to abiotic processes [309]. Conversely, the removal of some OMP increased with the presence of plants [107,297]. In line with the literature, the more hydrophobic OMP (e.g., diclofenac and naproxen) exhibited greater removal with more developed plants, presumably being accumulated in the roots due to their higher lipid content compared to other tissues [289]. Despite the inability to conduct analyses on the roots, comparisons with abiotic controls provided insights into the role of plants in OMP removal, supplemented by extensive literature documenting greater contaminant accumulation in roots than in aerial plant parts [235,288]. Nevertheless, further studies should also analyze the OMP in roots to elaborate a more detailed pathway of the contaminants from the GW to the different parts of the plants.

4.1.2. Limitations and challenges for implementation

Despite demonstrating satisfactory performance, notable limitations were observed that reduce process efficiency. In the case of FO, key challenges include low water fluxes and solute fluxes, as discussed across Articles 2, 3, and 4. Additionally, factors such as concentration polarization and fouling contribute to the limitations of FO. These aspects were beyond the scope of this thesis, but they should be considered in future studies. Low water fluxes compromise process efficiency, requiring longer operation times or increased membrane area, thereby escalating costs, while high solute fluxes can diminish the driving force of the process and contaminate the opposing solution [184]. Specifically, fertilizer losses obtained in Articles 2 and 3 were not reported before, likely resulting from reaching osmotic equilibrium conditions, uncommon in FO studies yet crucial for optimizing the technology, particularly for dilution purposes like FDFO.

Previous FO studies [177,196] and results of this thesis (Articles 2, 3 and 4) obtained higher reverse solute fluxes (RSF, from DS to FS) at higher concentrations of DS and of monovalent ions, which exhibit greater permeability due to weaker interactions. Thus, mitigating RSF could involve using divalent DS ions such as sulphate, phosphate, magnesium or calcium. Regarding forward solute fluxes (from FS to DS), sodium fluxes from GW to DS pose significant concerns due to its toxicity to plants and soil, as highlighted in Articles 2 and 4. Additionally, while OMP concentrations in the DS were very low (on average 1.05 ± 0.8 µg/L), rejection of OMP decreased with contact time between feed and draw solutions, which implies that higher OMP concentrations should be found in a more diluted DS, with the proposed setup in Article 4. These findings present an important novelty and strategies aimed at mitigating this phenomenon should be further evaluated, especially in approaches requiring high DS dilutions, as in FDFO. Furthermore, by employing a single-pass approach [226,310], which avoids recirculation, FS would remain *unconcentrated*, thereby maintaining a higher osmotic potential between FS and DS, consequently preserving water fluxes. However, this approach would necessitate a larger FS volume, resulting in lower FS recovery, which might not be suitable for reuse applications.

Particularly important for the FDFO approach are the challenges in achieving proper fertilizer dilution for direct application in irrigation, with most FDFO studies indicating the need of consecutive DS dilution [176,206,208]. One of the most noticeable novelties of this thesis is precisely this achievement, in Article 2 within one step and in Article 3 with two steps, although with high nutrient migration to the FS, which reduces the efficiency of this approach. Future studies should focus on achieving proper dilutions with minimal losses to optimize the process. An easily applicable option for simple decentralized treatment systems would involve alternative water sources, particularly rainwater, to further dilute the DS until reaching the required nutrient concentrations or even to dilute the GW of the FS to increase the osmotic potential.

Another crucial factor not addressed in the articles but essential for the implementation of FO technology is its energy efficiency. Theoretically, the absence of applied hydraulic pressure in FO reduces energy costs while providing better fouling control than high-pressure-driven membranes [154]. However, this remains unclear, with studies reporting a decrease in specific energy consumption for FO compared to conventional membrane processes [158,159], while others indicate the opposite [199,311]. The literature highlights that energy associated with DS recovery poses a significant barrier to FO implementation, with a 40-50% higher energy consumption compared to RO for desalination purposes [162]. Nevertheless, the FDFO approach used in this thesis eliminates the need for DS recovery by applying the DS directly for irrigation, potentially making FO more energy-efficient in this context [162]. Indeed, literature indicates that the specific energy of the FO process itself, excluding DS recovery, is relatively low [154], reported to range from 0.2 to 0.55 kWh/m^3 based on an evaluation of 15 pilot-scale studies [162]. Given these mixed findings, further studies are necessary to comprehensively evaluate the energy efficiency of FO, and particularly of FDFO in varied practical applications, to fully understand its potential advantages and limitations.

The limitations of hydroponics primarily involve the inadequate removal of certain pollutants. Consequently, strategies are required to enhance removal rates, ideally through approaches that are simple, cost-effective, and suitable for decentralized systems. Studies in water-plant systems have demonstrated that adsorption on the substrate and interaction with the bacterial community are the main routes of contaminant removal [72,307]. Therefore, increasing the adsorption surface in the hydroponic system would likely enhance the performance of the system. A sustainable example is coco coir, which exhibited superior removal of pollutants (including OMP) from GW with green walls [129,247,312]. Thus, future experimental designs should incorporate a variety of media and optimize system performance with different media types or combinations. Alternatively, integrating larger plants, could lead to improved performance due to more developed leaves and roots, following the results of Article 5. Additionally, different system configurations could incorporate both aerobic and anoxic conditions to enhance the removals [67,229]. A simpler option would be the reduction of contaminant concentration through the dilution of GW with rainwater [127,128], although this approach is difficult to be resilient, particularly in regions without constant rainwater. Another limitation of NBS is the larger footprint requirements compared to membrane technologies. For practical applications, integrating NBS into the structure of buildings (i.e., green walls or green roofs) is recommended to optimize the available space, which is limited in most urban scenarios. Despite the slower treatment rates compared to intensive technologies, NBS systems are generally easier and cheaper to maintain and offer additional benefits. Notably, promoting biodiversity [238], creating a fresher environment [25,236,237], improving air quality, reducing noise [239] and projecting a green image in tourist establishments [240] are among the co-benefits associated with the implementation of NBS.

Overall, while both FO and hydroponics show promise as decentralized systems for GW treatment, each technology has its limitations that hinder their implementation. However, by combining these technologies (as suggested in the next section 4.2.), their strengths can complement each other, potentially increasing overall efficiency.

4.1.3. Implications for water reuse and circular economy

The capacity to cultivate food on-site irrigated with GW (raw or treated) presents additional advantages, transitioning towards more circular approaches. On the characteristics of the reclaimed water for irrigation purposes, the diluted DS with fertilizers had superior quality compared to the effluent from the hydroponic system, attributed to the high rejection of OMP and GW constituents. In contrast, the effluent from the hydroponic system presented a greater concentration of GW contaminants, including OMP. Nevertheless, this effluent remained suitable for reuse, as OMP are not contemplated in most water reuse guidelines and regulations [89].

The results of Article 4 (FDFO for GW treatment) suggest that employing diluted DS in hydroponics for the cultivation of edible plants should pose minimal risks, given the very low OMP concentrations found in the diluted DS (on average 1.05 ± 0.8 µg/L). However, the sodium concentration emerges as a potential concern, as indicated in Article 5 (hydroponics in GW), where it may affect plant growth [270]. In this context, cultivating more tolerant plants could lead to improved growth outcomes. For instance, although sodium ions induced stress symptoms in cucumbers grown in GW, they also promoted flower formation with minimal differences observed compared to cucumbers grown in reference nutrient solutions [277]. Additionally, planting alternative fruit crops, such as berries, is advisable to ensure safety as literature indicates that fruits tend to accumulate fewer OMP compared to leafy crops [85,294,295]. Hence, future studies should explore various types of plants and further investigate the effects of pollutants on plant physiology.

On the capability and safety of eating edibles grown in GW, the proposed hydroponic system in Article 5 served as a proof of concept, primarily addressing the pathways and risks associated with OMP. The concentrations of OMP in real GW would likely be lower than in the tested synthetic GW, reducing the potential risk for human health, that was, at any case, attributed to only two compounds in Article 5 (i.e., atenolol and epoxy-carbamazepine). Notably, the presence of certain OMP in the effluent from the hydroponic system, and even in lettuce leaves, particularly those from the EU Watch List (venlafaxine and desvenlafaxine), raises concerns. The results of Article 5 point out the importance of assessing the risks to human health related to the presence of OMP in edible crops and the necessity of performing such evaluations with a wider range of compounds. Precisely, real GW may contain a more diverse array of OMP [90] including other types of emerging contaminants like pesticides, microplastics or PFAS that should be evaluated in future studies, as well as the risks associated with cumulative exposure, which may arise [304]. Conversely, in real applications, GW would need (pre)treatment to comply with legislative requirements for edible crop cultivation, thus further preventing a fraction of the pollution from reaching the plants. Furthermore, while negligible concentrations of certain TPs from the OMP were detected in FO experiments, detectable levels were found in the hydroponic effluent, likely due to chemical reactions within the system and longer retention time (a week for hydroponics versus 15 h for FO) as well as in lettuce leaves. Further evaluation of TPs, often understudied, are required as they may pose greater risks than the parent compounds [99].

The paradigm shift towards circular economy, explored in this thesis, includes the utilization of byproducts from WW treatment, in line with newly established regulatory standards set by the European Commission on quality criteria for byproducts like fertilizers (EU 2019/1009) [313]. In this thesis, magnesium-phosphate (MgP) salts (i.e., struvite, cattiite, hazenite) were used both as DS (Article 3) and fertilizers applied in hydroponics (Articles 3 and 5). Notably, the utilization of these salts as draw solution is novel and they were barely applied in hydroponics [44–46]. As regards to FO, a proper dilution was obtained, supplemented by the osmotic potential of nitrate ions from the nitric acid present in the DS. The successful cultivation of lettuces using diluted DS with MgP products exemplifies the viability of these compounds as substitutes for conventional fertilizers. Nevertheless, the findings emphasize the importance of proper nutrient supplementation for optimal yields, alongside the selection of strong acids like nitric or sulfuric for salt dissolution, which can contribute with additional nutrients for plant growth. In contrast, the dissolution of the MgP products in citric acid did not provide such satisfactory performance in neither FO nor hydroponics (Articles 3 and 5). While dissolving these salts might seem inefficient in some cases, it is important to point out that especially phosphate is an indispensable, yet critical raw material, hence promoting a new sustainable approach to its extraction and utilization, such as its recovery from wastewater, is imperative.

While this thesis focuses on hydroponics, other methods that efficiently use water and nutrients, requiring minimal land and consequently increasing circularity could also be promoted. One such method, closely related to what was evaluated in this thesis, is bioponics, where recycled organic waste (e.g., animal manure, agro-industrial waste) is applied as nutrient-rich solution for plant growth, effectively acting as a nutrient recycling process and reducing the demand for synthetic mineral fertilizers [314]. In this line, organoponics technique consists of growing crops in beds filled with soil amended with manure, earthworm composts, and sugarcane residues, which enhance soil health and provide rich sources of mineral nutrients for plant growth [315]. Another emerging practice is aquaponics, which has earned global attention in recent years [316]. This approach combines aquaculture and hydroponics, using water from fish tanks to grow crops [317]. Studies have demonstrated the profitability and effective plant development of aquaponic systems with crops such as lettuces [317] or water spinach [318]. Aquaponics is particularly promising for addressing health disparities and food security in urban environments and isolated areas with limited water and land resources [319].

Overall, within the urban environment, it is recommended to advocate for the integration of edible gardens that can benefit from the use of impaired sources such as GW or rainwater, which, when properly treated and supplemented with nutrients, can serve as excellent growing medium. Furthermore, studying the contributions of sustainable fertilizers, such as MgP precipitates employed in this thesis, holds promise for advancing sustainable development paradigms in agricultural practices.

4.2. Decentralized systems for GW treatment and reuse in touristic accommodations

In the context of this thesis, the imperative to improve water management practices and implement water reuse strategies in the tourism sector is emphasized. Specifically, hotels, characterized by a higher proportion of bathrooms compared to residential settings, generate substantial volumes of light GW that could be effectively treated and reused within hotel premises. Findings of Article 1 show that while conventional water-saving measures such as dual flushing, flow reducers and tap aerators are widely applied, only a small percentage of respondents (9.9%) implemented strategies related to water reuse, therefore showing a big room for improvement. The necessity of adopting water reuse practices becomes particularly pronounced in water-scarce regions like the Mediterranean, where tourism serves as a significant economic driver. Implementing measures to enhance circularity and resilience in these establishments becomes imperative to alleviate the pressure on freshwater resources stemming from tourism. The outcomes of this thesis elucidate the strength, as well as the limitations, of both FO and hydroponic systems in treating and reusing GW. Hence, a promising avenue to maximize efficiency and results can be their combination, not only minimizing the space requirements associated with sole NBS but also reducing the costs and maintenance associated with sole membrane systems. With the goal of promoting circularity and safe water reuse practices, particularly in the context of food production within touristic accommodations, two options are here proposed.

A first proposed setup entails treating primarily settled and filtered GW (to prevent membrane clogging) with FO and then use the diluted DS in hydroponic systems for cultivating edible crops to be consumed within the hotel premises (Figure 4 up). Hydroponic cultivation is advisable for their numerous advantages and versatility in adaptation, offering efficient water use, enhanced growth and reduced pest-related risks [85,262], while eliminating the risks for soil quality derived from salinity and sodicity. Applying the diluted DS in the hydroponic system would significantly mitigate (or eliminate) the potential risks related to OMP presence in raw GW and their uptake by food crops (Article 5), given the very low OMP concentrations in the diluted DS observed in Article 4. Article 5 underscores the importance of adjusting and supplementing the hydroponic solution with the required nutrients for optimal plant growth and, ideally, from sustainable sources (e.g. as vinasse, a byproduct of bioethanol production, as source of nitrogen and potassium [46]). Furthermore, as shown in Article 3, alternative fertilizers such as MgP salts recovered from WW exhibited favorable performance as DS, aligning with sustainable and recommended practices. Drawing insights from the findings on FDFO studies in this thesis concerning the high nutrient losses to the FS, an alternative approach would be to benefit from the RSF by introducing algae into the FS. This configuration, termed an osmotic photobioreactor, uses fertilizer salts from the DS as nutrients for algae, consequently reducing their presence in the FS [181]. Successful outcomes utilizing the same FO membrane employed in this thesis, along with tertiary effluent containing microalgae in the FS [320], underscore the efficacy of this approach. Furthermore, concentrating the FS facilitates the recovery of precipitated compounds in the membrane, as demonstrated in recent FO studies involving N and P recovery from urine [321–323], or textile dyes and struvite from WW [324,325]. In addition, the effluent from the hydroponic system can be repurposed for irrigation, washing of surrounding areas, or toilet flushing, thereby closing the loop on water reuse and nutrient utilization within the hotel. This circular approach not only addresses water scarcity concerns but also offers a sustainable method for obtaining edible goods and using alternative water streams and fertilizers.

A second viable option entails an exclusive NBS-based approach, where raw GW (pre-settled) is treated by ornamental plants before edible crop irrigation (Figure 4 down). As an example, the vertECO technology, a four cascading stages NBS system deployed at Hotel Samba for a decade (Figure 2 in the introduction), demonstrated remarkable efficacy for GW treatment and the removal of diverse OMP [22], while offering the potential for 40-50% water savings [258,259]. The proposed configuration aims to reduce contaminant loads in water destined for crops, mitigating potential risks associated with alternative water sources. In this sense, although vertECO reduced the microbiological load [258], a disinfection step was required to comply with water reuse legislations [259], which is also commonly reported in studies with NBS for water reuse [243,244]. Among the different options for disinfection, chlorine is not advisable as it can negatively affect the plants. Therefore, alternative technologies like solar-powered ultraviolet disinfection or activated carbon derived from sustainable sources (e.g. coconut shell, wood or coffee grounds) represent more suitable and environmentally friendly choices for this application.

This second option was tested in the framework of this thesis, incorporating several edible crops (tomato, lettuce, broccoli, fennel, lavender, and mint) in a hydroponic system with real GW. Preliminary assessments revealed a satisfactory growth of all plants, with no discernible signs of toxicity or nutrient deficiencies. This research was interrupted by the COVID-19 pandemic (preventing results publication), but it suggests that hotel pre-treated GW provided adequate nutrient richness to edible plants without adversely affecting their growth, aligning with the principles of the food-water nexus and circular economy. Furthermore, in comparison to membrane technologies, the implementation of NBS requires less specialized personnel, ease of maintenance and provides co-benefits. Indeed, recent research underscored that, despite the estimated vertECO payback period exceeding that of a MBR, a comprehensive assessment considering co-benefits (amenity, vehicle of sustainable communication, habitat creation and potential thermal regulation) resulted in higher overall ratings for vertECO [259]. However, the implementation of this approach may raise concerns regarding the risks associated with the proximity of raw GW to hotel guests, necessitating cautious action.

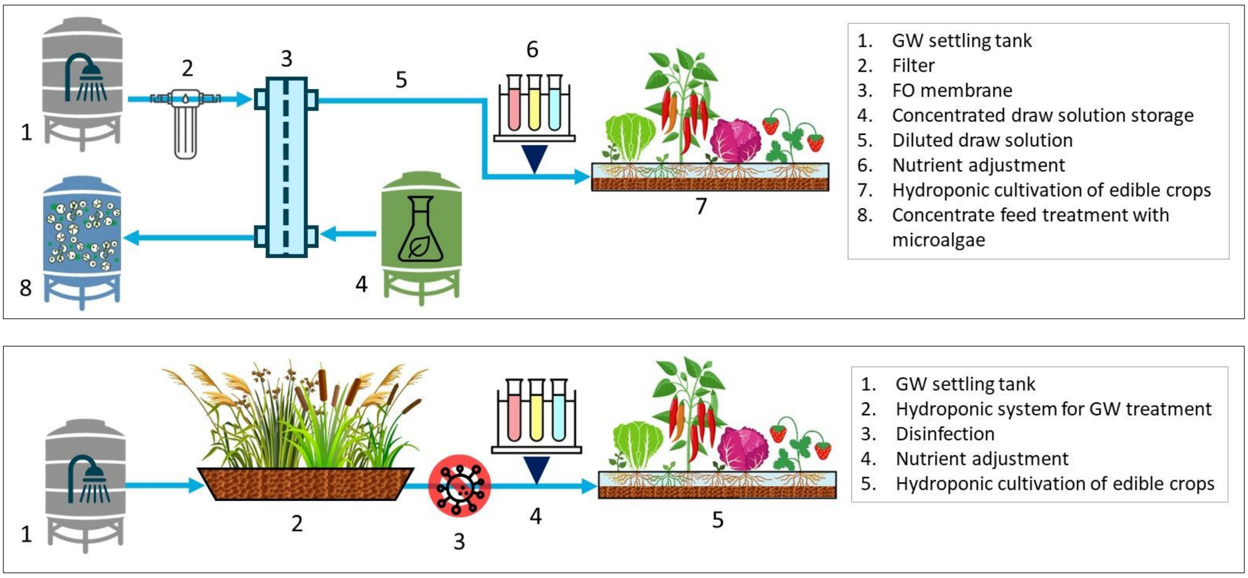

Figure 4. Proposed configurations for the implementation of decentralized treatment systems for GW reuse in hotels.

Several factors, encompassing logistical, economic and intended reuse purposes will determine the implementation of a specific technology or combination of various. Moreover, the economic benefits of water reuse in hotels extend beyond mere resource efficiency, with the perceived environmentally friendly image of hotels positively influencing consumer preferences [326]. Finally, while the proposed solutions have been predominantly discussed in the context of hotels, their applicability extends to various decentralized scenarios, including residential buildings, schools, airports, gyms, or other settings with significant GW generation. Efforts should be directed towards the implementation of decentralized systems for GW treatment and reuse including membrane systems combined with NBS, due to the ease of maintenance and the associated co-benefits.

4.3. Barriers to the implementation of decentralized systems for greywater treatment and reuse

In addition to the inherent technical limitations of the technologies, other barriers difficult the on-site implementation of GW treatment and reuse systems. Firstly, the installation of GW separation necessitates a complex and costly process, involving infrastructural modifications, the incorporation of dual piping systems, and the provision of space for storage tanks and treatment technologies, demanding regular inspection, monitoring and maintenance [121,304]. Nevertheless, these expenses can be mitigated by considering the incorporation of the dual piping system during the building design phase, alongside the potential cost savings stemming from reduced freshwater usage through GW reuse for applications like toilet flushing or irrigation. The application of GW treatment and reuse systems in hotels may encounter comparatively fewer challenges, as elucidated in Article 1, where a substantial number of hotels featured decentralized treatment systems for pool water. The preexistence of trained personnel managing water treatment systems in these establishments could facilitate the incorporation of decentralized systems for other water streams, minimizing logistical impacts on hotel management.

The findings of Article 1 corroborate that a lack of financial means is a predominant barrier to respondents' willingness to improve their water-related infrastructure. Other studies emphasize on the positive correlation between the reduction in costs and the increase of acceptance towards water reuse practices [64,327,328]. In this line, public perception emerges as a crucial factor, with studies raising concerns regarding water quality, human health and environmental implications associated with GW reuse [304]. While public acknowledgment of water reuse exists, preferences often lean towards reclaimed water being designated for activities not involving personal contact [60]. Geographical circumstances further influence this perception, with people from arid regions exhibiting a more convinced attitude towards water reuse [329]. Hence, comprehensive education and awareness campaigns about the importance of water conservation and the potential benefits of GW reuse are essential [121].

Finally, the complexity of legal and bureaucratic requirements, coupled with legislation gaps, frequently pose further challenges for the implementation of water reuse practices. Many countries lack a legal framework for water reuse and particularly for GW, hindering the development and implementation of reuse practices [64]. While less administrative concern could ease implementation, it may pose environmental and public health risks, if overly permissive [304]. Furthermore, limitations in existing water reuse legislation are evident and the promotion of other reuse scenarios, beyond traditional toilet flushing or irrigation, is required, particularly in the urban environment. As indicated in the introduction, European reuse legislation (EU 2020/741) exclusively contemplates irrigation purposes for reclaimed water, whereas Spanish legislation (RD 1620/2007) encompasses wider range of reuse scenarios beyond irrigation, even allowing for unspecified uses (i.e., quality class 5.4, Table 6), rendering this practice more versatile and attractive. This divergence is illustrated in Table 6 with the effluent of only one of the conditions of Article 5 (GWN) having enough reuse quality for the European legislation (irrigation scenarios B to D, food crops not in direct contact with the reclaimed water and industrial crops). In contrast, varied scenarios were permitted under Spanish legislation for the effluents from the various conditions tested in this thesis (Article 5), including crops in direct contact with reclaimed water (Table 6). This is because Spanish legislation does not require BOD_5, the only parameter above the limits. It is therefore important to update the reuse legislation in accordance with current and future needs and scientific advances. For this reason, a public consultation was opened at the end of 2023 to review the Spanish legislation on water reuse. Both, the promotion of water reuse through economic incentives and the establishment of more rigorous objectives, were considered as crucial [330]. Precisely, one of the proposed modifications was the integration of the requirements of European reuse legislation with the scenarios of the Royal Decree. Increasing the number of parameters was also considered, including those of Royal Decree 817/2015 (45 substances, mostly industrial chemicals, metals and pesticides) and the indicators of Royal Decree 1514/2009 (As, Cd, Pb, Hg, NH_4, Cl^-, PO_4, SO_4, NO_2, trichloroethylene, tetrachloroethylene, electrical conductivity). These updates are necessary to promote safer reuse of water, while expanding its implementation, which will be increasingly necessary.

Notably, while water reuse practices are imperative, attention must be paid on the assessment of associated chemical risks, which might not be sufficiently considered in the regulatory context [83]. On the quality indicators for GW reuse, a recent review reported several parameters including conventional (e.g., solids, BOD, COD, N, P), as well as microbiological indicators and heavy metals [304]. Of special interest for this thesis are the OMP, generally not considered in reuse legislations [89], despite their ubiquity in water bodies. Precisely, a recent study conducted in 2020, which reviewed 70 regulations and guidelines for agricultural water reuse worldwide, emphasized the absence of OMP in most texts while underscoring the importance of addressing these compounds [89]. In this line, the *European Watch List of substances for Union-wide monitoring in the field of water policy* meticulously evaluates potential water contaminants and their associated risks to aquatic ecosystems in surface water. The latest version of this list, published in 2022 (EU 2022/1307), includes 26 compounds of concern, some of them included in Articles 4 and 5 of this thesis (i.e., ofloxacin, sulfamethoxazole, trimethoprim, venlafaxine and desvenlafaxine). While this list serves as a valuable tool, it is not specifically designed for reuse purposes, and its scope may be limited because of the number of compounds. An alternative approach, recently (2023) described by Verlicchi et al. [92] offers a promising path for addressing this challenge. They proposed a list of 30 indicators of emerging concern for the reuse of reclaimed water for irrigation, based on occurrence, persistence, bioaccumulation potential and toxicity. While comprehensive investigation into a diverse array of OMP is necessary, this methodology facilitates quality assessment using a limited set of indicators. Many of the proposed indicators align with PhACs included in this thesis (i.e., bezafibrate, carbamazepine, epoxy carbamazepine, diclofenac, erythromycin, furosemide, gemfibrozil, ibuprofen, iopromide, irbesartan, sulfamethoxazole, tetracycline, trimethoprim and venlafaxine), as well as bisphenol A (EDC). Thus, the findings obtained in this thesis contribute to expanding the body of knowledge on these compounds.

Table 6. Quality class of the different tested conditions from the effluents of the hydroponic system regarding the Spanish legislation RD 1620/2007. Microbiological indicators (E. coli, Legionella, Salmonella, intestinal nematodes) are not indicated since they were not included in the synthetic GW.

Type of use	Quality class	Effluent condition	
		GWB & GWN	**GWS**
Urban	1.1 Residential: irrigation and toilet flushing.		
	1.2 Services: irrigation and street washing.	■	
Agricultural irrigation	2.1 Edible parts in direct contact with the reclaimed water and eaten raw/fresh	■	
	2.2 Edible parts in direct contact with the reclaimed water, but not eaten raw/fresh; crops for consumption by animals producing milk or meat; aquaculture	■	■
	2.3 Woody crops; ornamental flower crops and non-food industrial crops	■	■
Industrial	3.1 Process and cleaning except for the food industry	■	
	Process and cleaning in the food industry	■	■
	3.2 Cooling towers and evaporative condensers		
Recreational	4.1 Irrigation of golf courses	■	
	4.2 Bodies of water in which public access to the water is not allowed	■	■
Environmental	5.1 Aquifer recharge by localized percolation through the terrain		
	5.1 Aquifer recharge by localized direct injection		
	5.3 Forestry	■	■
	5.4 Other environmental uses*	?	?

* detailed case by case.

The diverse challenges surrounding GW treatment and reuse underscore the complex interplay between technical, economic, social and regulatory factors. While advancements in diverse technological solutions offer promising results, practical implementation demands substantial financial resources and skilled management. Joint efforts to address these challenges, coupled with education and awareness actions are thus required. The ongoing research into emerging contaminants and risk assessment methodologies are essential for realizing the full potential of GW reuse in fostering water security and environmental sustainability.

5. Conclusions

This thesis contributed to the growing body of knowledge on decentralized water treatment and reuse, shedding light on the potential of forward osmosis and hydroponic systems in addressing water scarcity challenges while promoting circularity in water management practices with a focus on tourism.

The findings of Article 1 underscore the need for improved water management practices in Euro-Mediterranean hotels, where despite widespread use of water-saving devices, limited adoption of water reuse practices was implemented. Given the substantial volumes of GW generated by hotels, coupled with the imperative to minimize freshwater demand in water-scarce regions like the Mediterranean, the adoption of decentralized GW treatment and reuse systems is essential. These systems, when coupled with water-saving measures and comprehensive monitoring practices, can alleviate the burden on municipal wastewater treatment facilities and contribute significantly to water scarcity mitigation.

The FDFO approach, meticulously explored in Articles 2, 3 and 4, emerges as particularly advantageous due to its simplicity and cost-effectiveness stemming from the absence of DS recovery. Proper dilution of the draw solution to be directly applied for hydroponics was achieved in Articles 2 and 3, representing an important novelty. However, challenges such as high reverse solute fluxes observed in osmotic equilibrium conditions in Articles 2 and 3, led to decreased osmotic potential and water flux, underscoring the need for further optimization. Meanwhile, the efficiency of FO for GW treatment was demonstrated in Article 4, producing DS with minimal contamination from the feed GW, making it an excellent candidate for reuse. Nevertheless, decreased rejection of OMP with recirculation time between feed and draw solution highlights the importance of considering this phenomenon for safe GW reuse applications. Additionally, the use of magnesium-phosphate (MgP) salts, as explored in Article 3 in both FO and hydroponics, showcases their competitiveness with traditional fertilizers, suggesting their potential for enhancing circularity and sustainability in agricultural practices.

The growing importance of NBS for water management and treatment lies in the fact that such systems bring co-benefits, in addition to their satisfactory performance in water treatment and simplicity of maintenance, underscoring their suitability for decentralized systems in both urban and isolated areas. In this line, the integration of hydroponic systems for GW treatment and crop production, as explored in Article 5, yields promising results, with effluent complying with European reuse legislation and proper plant development once supplemented with commercial nutrient solution. However, the detection of OMP in edible plants emphasizes the need for further optimization to enhance pollutant removal, especially concerning OMP and their transformation products.

As both membrane technologies and NBS offer versatility in configuration and adaptability to various GW volumes and characteristics, but present different challenges, the integration of FO and hydroponics, as proposed in this thesis, presents a promising avenue to maximize efficiency and results.

By repurposing treated GW for crop irrigation, hotels, and other buildings with high GW generation capability, can enhance circularity, resilience, and resource efficiency, while reducing their environmental footprint. However, the implementation of decentralized systems for GW treatment and reuse faces several barriers, including technical, financial, social, and regulatory challenges, necessitating comprehensive education and awareness campaigns, along with legislative updates to promote safer water reuse practices and address emerging contaminants like OMP. Hence, ongoing research into emerging contaminants and risk assessment methodologies is crucial for realizing the full potential of GW reuse in fostering water security and environmental sustainability.

To sum up, while decentralized GW treatment and reuse systems, and particularly FO and hydroponics, offer promising solutions to address water scarcity and quality challenges, their successful implementation requires concerted efforts across various sectors to overcome technical, economic, social and regulatory barriers. Efforts should be directed towards a paradigm shift to circular economy, considering GW as a resource, promoting the inclusion of edible gardens irrigated with reclaimed water to reduce pressure on freshwater resources and advance sustainable development.

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ANNEXES

Annex I. Supplementary materials of Article 1.

Water management practices in Euro-Mediterranean hotels and resorts

SUPPLEMENTARY INFORMATION TABLES

Table S1 List of questions

Q1: Full name of the establishment
Q2: Year of construction
Q3: Category
Q4: Location (City, Country)
Q5: Capacities (Number of rooms, Number of beds)
Q6: Establishment open to guests (All year/seasonal)
Q7: Average number of guests per year
Q8: Is there seasonal variation in occupancy of the establishment?
Q9: Certificates awarded to the establishment.
Q10: Does your establishment have pools (indoors, outdoors, or both)?
Q11: Does your establishment have spa?
Q12: Does your establishment have spa?
Q13: Excluding spa, how many pools does your establishment have and how big are they? Number of pools and total capacity (m^3)
Q14: How much water does the spa require? Please specify volume in m^3 and the period (per day / per week / *etc*.).
Q15: When necessary, how much water do you replace in your pools? Please specify total amount for all the pools and the unit (m^3 or %).
Q16: How frequently do you replace water in the pools? Please specify per day, week, *etc*., and the periods when the frequency applies, *e.g.*, 'once per week in July and August, once per month in June and September'.
Q18: What treatment do you apply for your pools and spa?
Q19: Do you measure free chlorine (Cl_2)?
Q20: How many pools does your establishment have and how big are they?
Q21: When necessary, how much water do you replace in your pools? Please specify total amount for all the pools and the unit (m^3 or %).
Q22: How frequently do you replace water in the pools? Please specify per day, week, *etc*., and the periods when the frequency applies, *e.g.*, 'once per week in July and August, once per month in June and September'.
Q23: If there is variation in amount and frequency of water replaced per pool, please specify.
Q24: What treatment do you apply for your pools?
Q25: Do you measure free chlorine (Cl_2)?
Q26: How much water does the spa require?
Q27: What treatment do you apply for your spa?
Q28: Do you measure free chlorine (Cl_2)?
Q29: Do you wash used textiles yourself inside your establishment?

Q30: Do you have other facilities on your premises that consume water, *e.g.*, hairdresser, Laundromat for guests, or similar?
Q31: Does your establishment have a golf course?
Q32: How big is the golf course of your establishment?
Q33: Excluding golf course, how big are the green areas in your establishment?
Q34: How big are the green areas in your establishment?
Q35: Since the construction of the establishment, were there any significant changes made to the water infrastructure?
Q36: Which were the changes made to the water infrastructure?
Q37: Which sources of water supply does your establishment use and what are they used for?
Q38: On which water distribution lines do you monitor consumption of water?
Q39: Do you have any water saving devices installed in your establishment?
Q40: Select the saving device(s) present in your establishment: double flush toilet, flow reducer, flow regulators, dispersers, low consumption showers, water saving showers, tap aerator, tappet ventilator, others (specify).
Q41: Water consumption and related annual cost
Q42: Do you separate grey- and blackwater in your establishment?
Q43: Do you analyse the quality of greywater?
Q44: Do you have analysis report on the quality of greywater, and would you be willing to share it with us?
Q45: Do you treat greywater?
Q46: How do you treat greywater?
Q47: What do you reuse treated greywater for?
Q48: You marked you do not treat greywater. Please specify what you do with it.
Q49: Do you analyse the quality of blackwater?
Q50: Do you have analysis report on the quality of blackwater and would you be willing to share it with us?
Q51: Do you treat blackwater?
Q52: How do you treat blackwater?
Q53: What do you reuse treated blackwater for?
Q54: You marked you do not treat blackwater. Please specify what you do with it.
Q55: Do you analyse the quality of wastewater?
Q56: Do you have analysis report on the quality of wastewater, and would you be willing to share it with us?
Q57: Do you treat wastewater?
Q58: How do you treat wastewater?
Q59: What do you reuse treated wastewater for?
Q60: You marked you do not treat wastewater. Please specify what you do with it.
Q61: Are environmental awareness, preservation of natural resources and eco-tourism part of your (future) business strategy?
Q62: To reduce the water consumption of your establishment, are you considering installation of technologies that would enable you the use of alternative water sources and/or (further) treatment of wastewater, in the future?
Q63: Would you participate in other surveys dedicated to the promotion of innovative water treatment technologies aimed at reducing water consumption?

Table S2. Results of the Kruskal-Wallis Test applied to hotel characteristics shown in Table 1.

Hypothesis Test Summary				
	Null Hypothesis	**Test**	**Sig.**	**Decision**
1	The distribution of ***rooms*** is the same across categories of country.	Independent-Samples Kruskal-Wallis Test	0.126	Retain the null hypothesis.
2	The distribution of ***beds*** is the same across categories of country.	Independent-Samples Kruskal-Wallis Test	0.208	Retain the null hypothesis.
3	The distribution of ***number of guests*** is the same across categories of country.	Independent-Samples Kruskal-Wallis Test	0.359	Retain the null hypothesis.
4	The distribution of ***certifications*** is the same across categories of country.	Independent-Samples Kruskal-Wallis Test	0.358	Retain the null hypothesis.
5	The distribution of ***indoors/outdoors pools*** is the same across categories of country.	Independent-Samples Kruskal-Wallis Test	0.271	Retain the null hypothesis.
6	The distribution of ***SPA presence*** is the same across categories of country.	Independent-Samples Kruskal-Wallis Test	0.903	Retain the null hypothesis.
7	The distribution of ***Year of construction*** is the same across categories of country.	Independent-Samples Kruskal-Wallis Test	0.737	Retain the null hypothesis.

Asymptotic significances are displayed. The significance level is 0.050.

Table S3. Results of the chi-square test to evaluate the hotel category distribution among countries. The test reveals the absence of significant differences.

Chi-Square Tests			
	Value	**df**	**Asymptotic Significance**
Pearson Chi-Square	56.061[a]	55	0.435
N of Valid Cases	82		

[a] 69 cells (95.8%) have expected count less than 5. The minimum expected count is 0.01.

Table S4. List of surveyed hotels with information (when available) regarding the country, the stars, the year of construction, the number of rooms and beds (n.a. stand for not available).

Country	Hotel Stars	Year of construction	Number of rooms	Number of beds
Albania	3*	2001	31	97
Albania	3*	2011	16	40
Albania	3*	2011	24	50
Albania	3*	2011	16	40
Croatia	4*	2009	n.a.	1200
Croatia	4*	1924	28	56
Croatia	4*	2012	289	480
Croatia	3*	2011	n.a.	22
Cyprus	5*	1992	239	500
Cyprus	4*	1922	n.a.	515
Cyprus	4*	1985	250	n.a.
Cyprus	5*	1983	193	400
Cyprus	2*	1985	n.a.	200
France	4*	1878	172	362
France	3*	1989	30	36
France	4*	2008	29	33
France	4*	1992	120	180
France	3*	2009	10	22
Gibraltar	4*	1964	127	270
Greece	2*	1967	43	83
Greece	5*	2010	314	950
Greece	4*	2005	n.a.	150
Greece	5*	1991	420	840
Greece	3*	1986	68	160
Greece	2*	1970	39	72
Greece	4*	1999	40	90
Greece	3*	1971	n.a.	269
Greece	3*	1981	n.a.	55
Greece	5*	2000	243	600
Greece	3*	2000	36	110
Greece	2*	1992	7	13
Greece	4*	2004	7	25
Greece	3*	1982	17	45
Greece	1*	1995	32	88
Greece	3*	1972	24	48
Greece	5*	2007	6	6
Greece	4*	1974	96	192
Greece	3*	1980	75	145
Greece	5*	2008	327	782
Greece	5*	2004	56	119
Greece	3*	1981	195	450
Greece	2*	1994	10	30
Greece	5*	2010	213	426
Greece	2*	1998	28	76

Country	Hotel Stars	Year of construction	Number of rooms	Number of beds
Italy	3*	1976	25	60
Italy	4*	3321	150	300
Malta	4*	1963	n.a.	176
Malta	4*	1997	n.a.	280
Malta	4*	1996	202	550
Malta	3*	1986	326	861
Malta	4*	1998	n.a.	110
Malta	4*	1982	90	250
Malta	2*	1981	47	116
Malta	4*	1900	n.a.	200
Malta	4*	2002	175	360
Monaco	4*	1990	403	n.a.
Monaco	4*	1975	n.a.	900
Slovenia	4*	n.a.	n.a.	500
Slovenia	3*	2002	n.a.	52
Slovenia	4*	1995	20	45
Slovenia	3*	1978	30	60
Slovenia	3*	1903	n.a.	89
Spain	3*	1971	195	375
Spain	4*	2014	77	116
Spain	4*	2014	150	300
Spain	5*	2004	180	332
Spain	4*	1997	n.a.	750
Spain	4*	1970	n.a.	260
Turkey	n.a.	1904	16	32
Turkey	5*	2000	286	572
Turkey	5*	2000	300	600
Turkey	3*	2001	n.a.	76
Turkey	4*	2008	n.a.	400
Turkey	5*	1991	187	360
Turkey	n.a.	1997	25	50
Turkey	3*	2000	n.a.	108
Turkey	3*	2001	50	120
Turkey	4*	1962	n.a.	125
Turkey	4*	1991	24	28
Turkey	4*	2012	88	180

Table S5. Water sources for every use in the hotels, by cluster. MN, OW, SW, WW, and RW stand for municipal network, own well, seawater, wastewater, and rainwater, respectively. The following table was elaborated based on the exact answers of each respondent. Some uses (i.e., tap water use from treated wastewater) could be due to respondent misunderstanding of the question.

use/ water sources	cluster	own well	MN	MN, OW	MN, surface	SW, OW, surface	surface water	treated WW	MN, treated WW	SW	RW	other *	n.a.
tap	1	1	16			1							
	2		7				1	1	1				7
	3		7		1								3
	4	2	12					1					8
	5	1	5	1									5
WC	1	15	1										2
	2		7				1	1	1				7
	3	1	6										4
	4	2	11					2					8
	5	1	5					1					5
heating system	1	2	11										5
	2		3				1	1					12
	3		3										8
	4	2	7					1					13
	5		5							1			6
outdoor pool	1												18
	2		5					1	1	2			8
	3		2		1		1						7
	4	2	7							3			11
	5	2	4										6
indoor pool	1		1										17
	2		5				1	1		1			9
	3		1										10
	4	1	2										20
	5	2	2										8
spa	1												18
	2		6				1	1	1	1			7
	3		1										10
	4												23
	5	2	4										6
inside water features	1	1	4										13
	2		4						1				12
	3		3				1						7
	4		1										22
	5	1	2										9
outside water features	1	1	5										12
	2		3										14
	3		2										9
	4	1	2										20
	5	1	2										9
laundry	1	2	8										7
	2		6				1	1					9
	3		3										8
	4	1	7										15
	5	1	5										6

use/ water sources	cluster	own well	MN	MN, OW	MN, surface	SW, OW, surface	surface water	treated WW	MN, treated WW	SW	RW	other *	n.a.
irrigation	**1**	4	6										8
	2		2				1	1			1		12
	3	1	5										5
	4	2	7					1			1		12
	5	1	3										8
golf course	**1**												18
	2		1										16
	3		1										10
	4		1										22
	5	1	1								1		9
cleaning the exterior of the hotel	**1**	3	8										7
	2		5				1	1			1		9
	3		4				1						6
	4	2	10					1					10
	5	1	4										7
others	**1**											1	17
	2											1	16
	3											1	10
	4											1	22
	5											1	11

n.a. stands for not answered.

[*] Other answers from hotels: *air condition collected water is used to water the flowers and cleaning; Provence channel; reverse osmosis water treatment tank; tap water is bought; the installation of air conditioning system is based on the recovery of hot water that produce the air conditioners going through three heat*.

SUPPLEMENTARY INFORMATION FIGURES

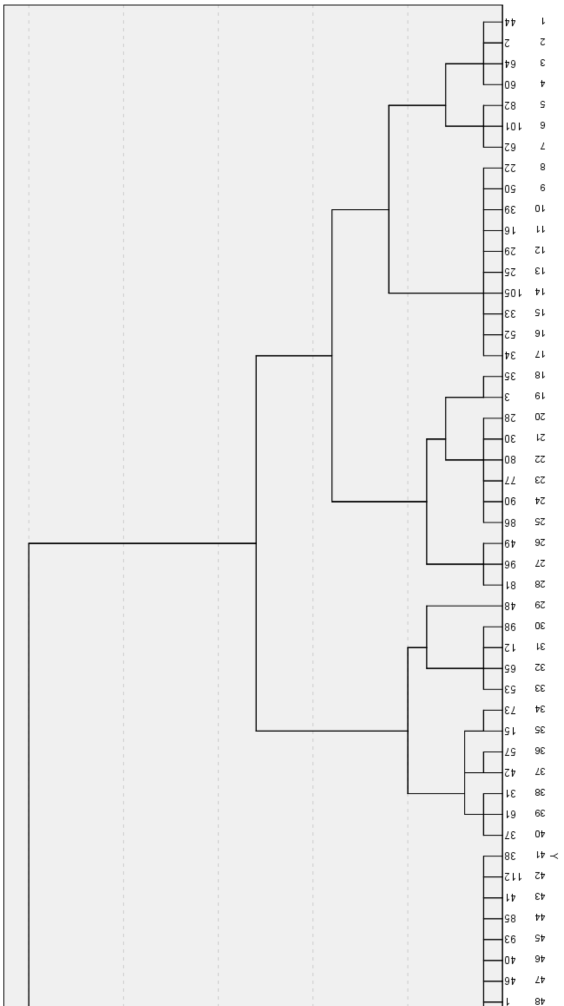
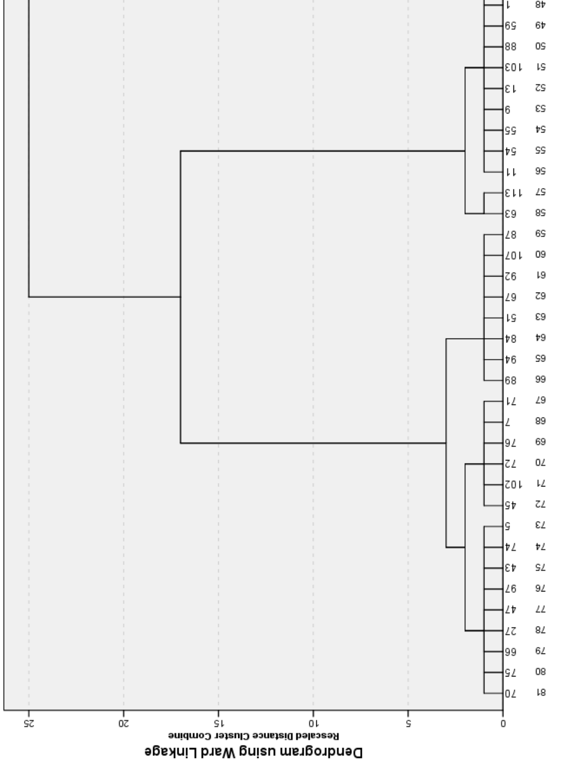



Figure S1. Dendrogram used to determine the number of clusters to retain.

Figure S2. Map of the spatial distribution of hotels and resorts surveyed.

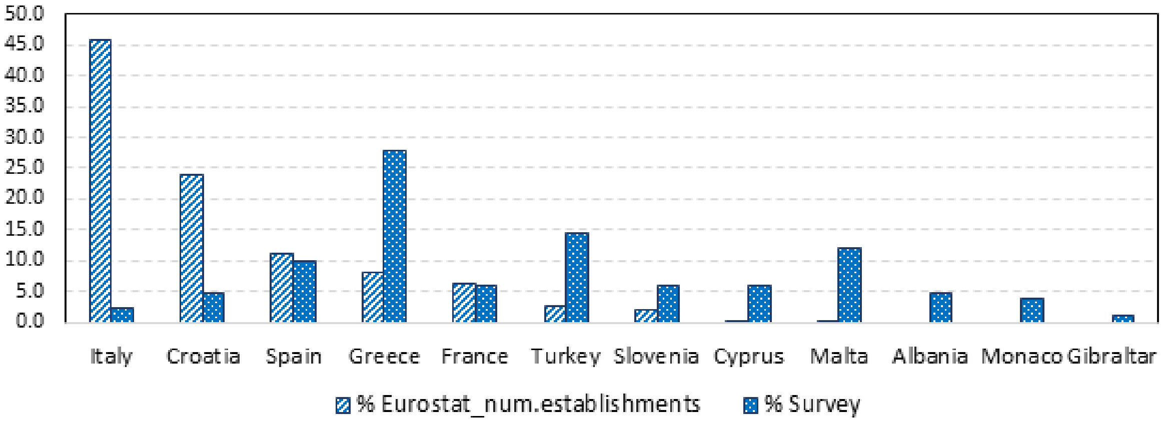


Figure S3. Comparison of the percent representativeness of the Mediterranean countries for the number of establishments according to EUROSTAT data and our survey.

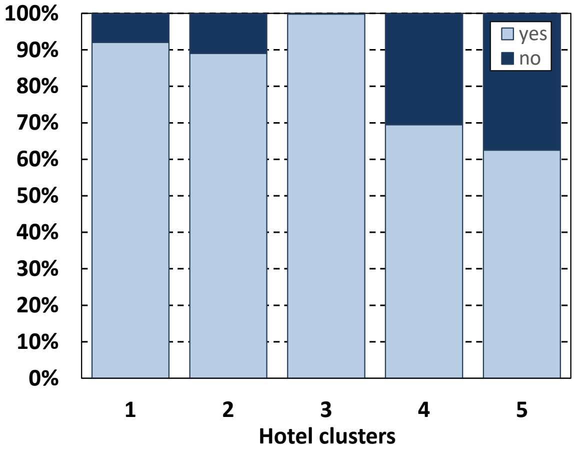


Figure S4. Percentage of hotels with seasonal occupancy by cluster. Answer to the question Q8: is there seasonal variation in occupancy of the establishment?

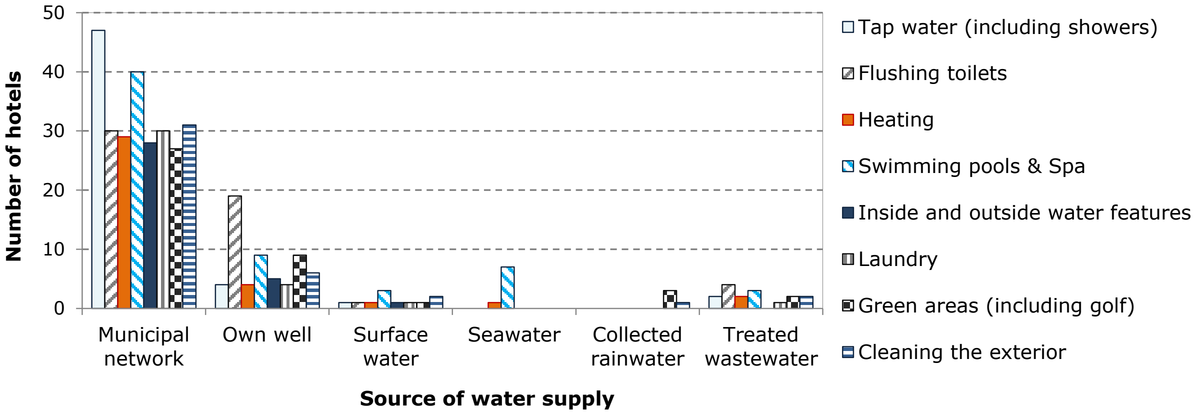


Figure S5. Sources of water for the different uses within the hotels/establishments. More details, divided by clusters, are provided in Table S5.1. The figure was elaborated based on the exact answers of each respondent. Some uses (*i.e.*, tap water use from treated wastewater) could be due to respondent misunderstanding of the question.

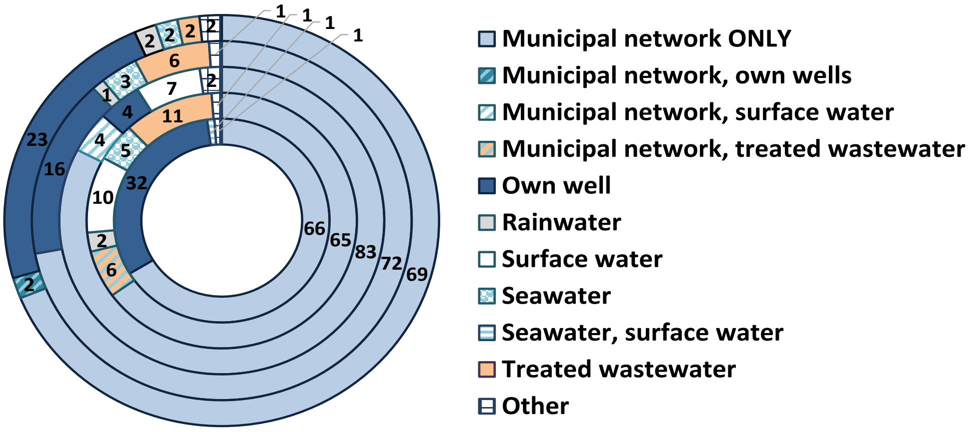


Figure S6. Pie chart of water uses by hotel clusters, Ward method. Clusters from 1 to 5, from inner circle to outer one, values are percentages. Not answered responses (61-68% based on the cluster) are not included in the pie chart. To be highly remarked that all hotels used municipal water supply as their main source. Alternative sources were used only for specific uses within the hotels (and represented in this chart), in addition to municipal network water for all the other uses. The figure was elaborated based on the exact answers of each respondent. Some uses (*i.e.*, tap water use from treated wastewater) could be due to respondent misunderstanding of the question.

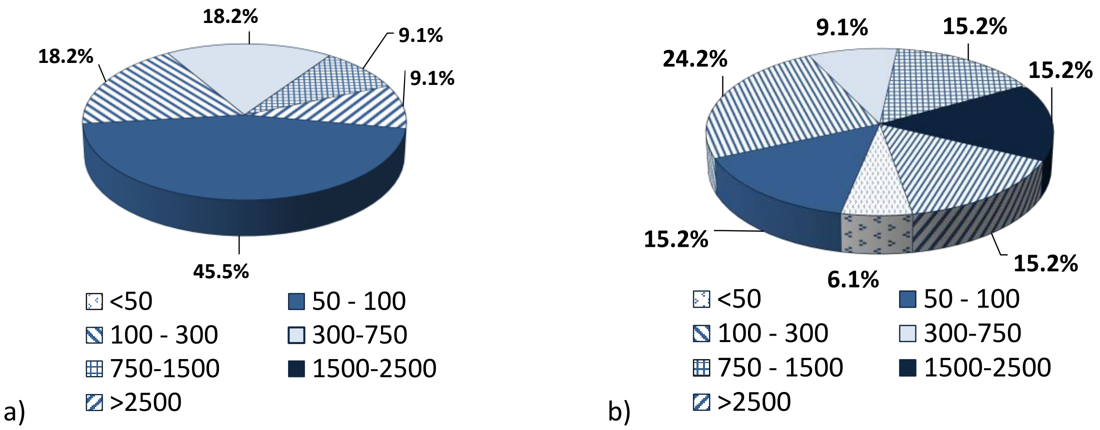


Figure S7. a) size of indoor pools (m^3); b) size of outdoor pools (m^3) in the hotels participating in the survey.

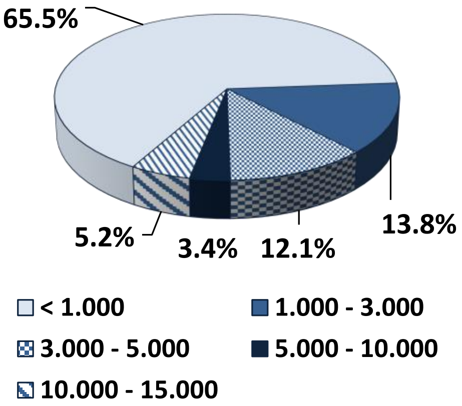


Figure S8. Average size (m^2) of green areas requiring maintenance of the hotels answering Q33 and Q34.

Annex II. Supplementary materials of Article 2.

Exploring the limitations of forward osmosis for direct hydroponic fertigation: impact of ion transfer and fertilizer composition on effective dilution

S1. Relations in molar concentrations between anions and cations along the tests

The relation was calculated as the sum of cation concentrations (mmol/L) divided by the sum of anion concentrations.

Relations in molar concentrations between anions and cations along the tests for tests with DI as FS.

FS/DS	t (min)	DAP	KNO_3	MIX 1	DAP	KNO_3	MIX 0.5	MIX 2	MIX 3	MIX 4	MIX 5
FEED	0	1.4	0.5	0.4	1.1	1.1	2.8	0.2	0.3	0.4	2.0
	30	12.0	1.0	1.0	9.3	1.0	0.7	0.9	0.9	0.9	0.9
	60	12.4	1.0	1.0	9.6	1.0	0.7	0.9	0.9	0.9	0.9
	final*	2.9	1.0	0.8	8.4	0.9	0.7	0.8	0.9	0.8	1.0
DRAW	0	1.0	1.0	1.1	0.9	0.9	1.0	1.0	1.0	1.0	0.9
	30	0.9	1.0	1.0	1.0	1.0	1.2	1.0	1.0	1.0	1.0
	60	0.9	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	0.9
	final*	0.9	1.0	1.0	0.9	1.0	1.0	1.0	1.0	1.0	1.0
Initial DS DAP (M)		0.05		0.05	0.5		0.5	0.050	0.030	0.050	0.025
Initial DS KNO_3 (M)			0.05	0.05		0.5	0.5	0.10	0.08	0.20	0.15

*Final time was 1440 min for tests with 0.05 M and mixes 1-5. Final time was 120, 360 and 105 min for tests with 0.5 M of DAP, KNO_3 and MIX 0.5, respectively.

Relations in molar concentrations between anions and cations along the tests for tests with 6.5 mM of individual salts (NaCl, $MgCl_2$, Na_2SO_4 and $MgSO_4$) as FS and 0.05 M of individual or blended salts as DS

		NaCl			$MgCl_2$			Na_2SO_4			$MgSO_4$		
FS/DS	**t (min)**	**DAP**	**KNO_3**	**MIX 1**	**DAP**	**KNO_3**	**MIX 1**	**DAP**	**KNO_3**	**MIX 1**	**DAP**	**KNO_3**	**MIX 1**
FEED	0	1.0	1.0	1.0	0.9	0.9	0.9	1.0	1.0	1.0	1.0	1.0	1.0
	30	0.9	1.0	1.0	1.0	0.9	1.0	1.0	1.0	1.0	1.0	1.0	1.0
	60	0.9	1.0	0.9	1.0	0.9	0.9	1.0	1.0	1.0	1.0	1.0	1.0
	1440	0.8	1.0	0.9	1.0	0.9	0.9	1.0	1.0	1.0	1.0	1.0	1.0
DRAW	0	1.0	1.0	0.9	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
	30	1.2	1.0	1.0	0.9	1.0	1.0	1.0	0.8	0.9	0.9	1.0	1.0
	60	1.3	1.0	1.1	1.0	1.0	1.0	1.0	0.6	0.9	1.0	1.0	1.0
	1440	1.5	1.0	1.3	0.9	0.8	1.0	1.0	0.8	0.9	0.9	0.8	1.1

S2. Results of tests with 6.5 mM of individual salts (NaCl, $MgCl_2$, Na_2SO_4, $MgSO_4$) in initial FS and 0.05 M of blended or individual fertilizers (DAP and KNO_3) in initial DS

Higher Na^+ passages were observed with the presence of Cl^-, even with higher Na^+ forward fluxes for tests with Na_2SO_4 than with NaCl. Higher Cl^- passages were observed in tests with only KNO_3 due to the high diffusion of NO_3^- ions to FS (exchange NO_3^--Cl^-). However, an order of magnitude lower of Na^+ passage to DS was observed with KNO_3 alone in DS, which can be related with the lower or inexistent mass dilution in the cases with KNO_3 alone.

Content at the beginning		**Initial EC (µS/cm)**		**Final EC (µS/cm)**			**% in mass of feed ion passage to DS**				**Final concentrations in DS (mg/L)***			
FS	**DS**	**FS**	**DS**	**FS**	**DS**	**FS/DS**	**Na^+**	**Mg^{2+}**	**Cl^-**	**S-SO_4^{2-}**	**N**	**P**	**K**	**Na**
NaCl	DAP	730	7970	1042	1139	0.9	30.9		2.1		59.7	190.0		178.6
NaCl	KNO_3	738	6040	915	870	1.0	4.9		3.5		41.1		56.8	130.7
NaCl	MIX 1	781	13200	1240	1345	0.9	35.1		2.5		98.0	156.3	72.7	165.7
$MgCl_2$	DAP	1418	8090	1636	1532	1.1		3.6	0.4		199.2	309.5		
$MgCl_2$	KNO_3	1416	6170	1634	1634	1.0		3.7	2.2		51.6		51.2	
$MgCl_2$	MIX 1	1406	13670	1894	1766	1.1		3.7	0.9		150.3	237.8	193.6	
Na_2SO_4	DAP	1448	8210	1745	1459	1.2	18.5			1.0	50.0	244.1		286.8
Na_2SO_4	KNO_3	1392	6080	1551	1310	1.2	1.7			1.0	64.7		51.8	242.2
Na_2SO_4	MIX 1	1422	13600	1943	1648	1.2	20.8			1.3	91.5	213.1	58.7	275.7
$MgSO_4$	DAP	1057	8070	1348	1120	1.2		5.1		0.1	128.8	199.1		
$MgSO_4$	KNO_3	1057	5930	1348	1120	1.2		0.1		0.1	47.7		36.4	
$MgSO_4$	MIX 1	1055	13520	1595	1277	1.2		5.0		0.3	125.6	175.5	143.9	

***** Colored cells correspond to those cases with proper nutrient concentration for direct hydroponic application (i.e., 100-200, 30-60 and 150-200 mg/L of N, P and K, respectively).

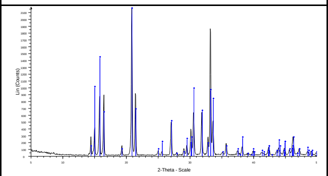
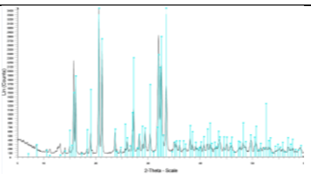
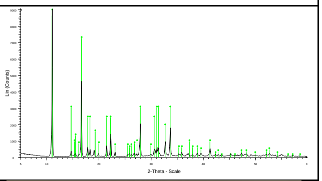
Annex III. Supplementary materials of Article 3.

Second-generation magnesium phosphates as water extractant agents in forward osmosis and subsequent use in hydroponics

2. Materials and Methods

2.1. Magnesium Phosphates Used as Draw Solution in Forward Osmosis

Table S1. View of the magnesium phosphate (MgP) products used as draw solution in forward osmosis (FO).

Ref.	**MgP1**	**MgP2**	**MgP3**
XRD - Dominant mineral phase	Struvite	Hazenite (w/ Newberyite)	Cattiite
XRD diffractograms*			
View of the mineral phase			

3. Results and Discussion

3.1. Acid Dissolution of the Magnesium Phosphates

Table S2. TSS content after acid dissolution of the MgP salts (pH 3.0) if considering 112 g salt per liter of water as the initial dilution ratio.

Reference	**% TSS final vs. initial solids content**
SC	1.8
SN	1.5
HC	1.5
HN	1.2
CC	1.4
CN	2.5

Reference for MgP salts: S, struvite; H, hazenite; C, cattiite.

Reference for acids: C, citric acid; N, nitric acid.

3.2. Water Extraction and Nutrients Dilution through Forward Osmosis

3.2.1. Forward Osmosis Dilution Potential

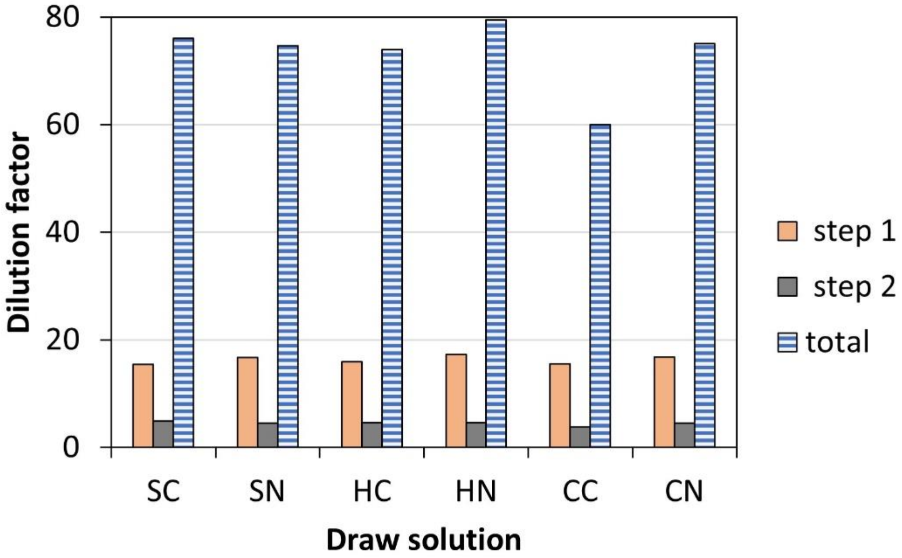


Figure S1. Total dilution factor achieved for the different draw solutions used in the 2-step forward osmosis (FO) process. Reference for MgP salts: S, struvite; H, hazenite; C, cattiite. Reference for acids: C, citric acid; N, nitric acid.

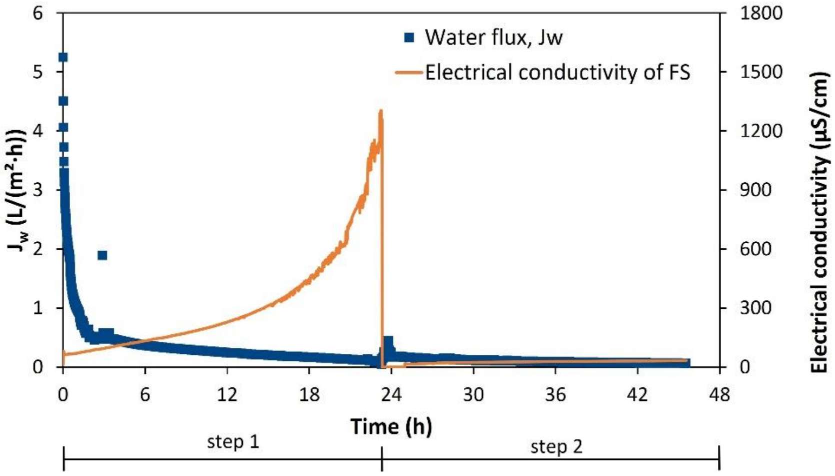


Figure S2. Filtration kinetics example (CC).

3.3. Hydroponic System

3.3.1. Experimental Conditions

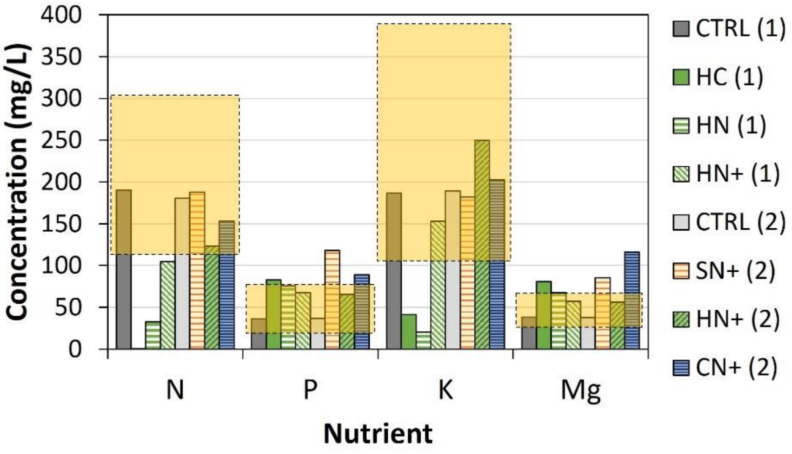


Figure S3. Nutrient concentration in the hydroponic experiments and estimated optimal ranges (±30% values from Table 2). Reference for MgP salts: S, struvite; H, hazenite; C, cattiite. Reference for acids: C, citric acid; N, nitric acid. +, supplemented with KNO_3. In brackets, hydroponic experimental cycle.

3.3.2. Plant Growth Analysis

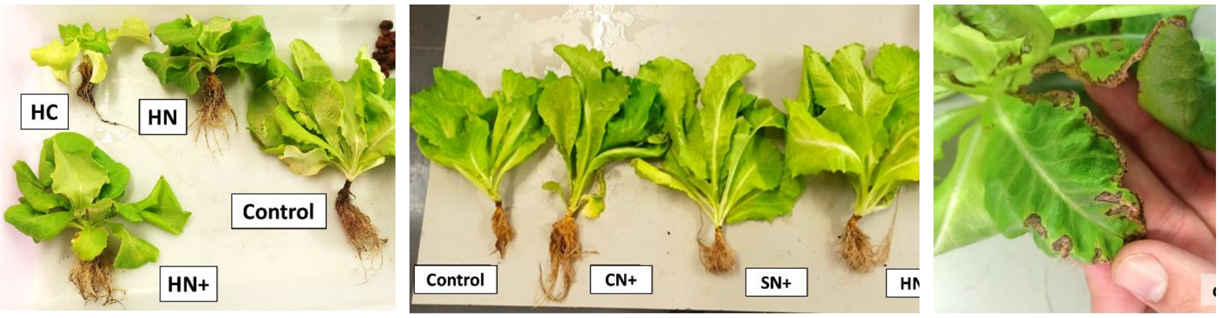
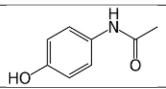
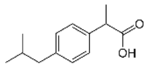
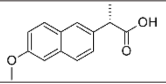
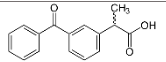
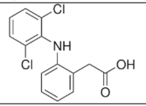
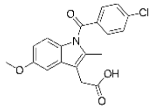
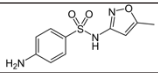
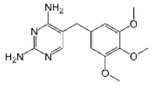
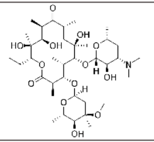
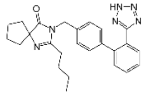
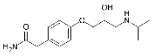
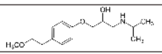
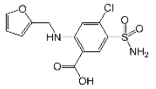
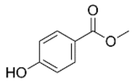
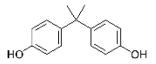
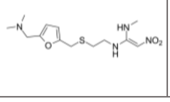


Figure S4. Pictures of the plants after 3 weeks in cycle 1 (**a**) and cycle 2 (**b**), and detail of the tipburn for HN+ condition (**c**).

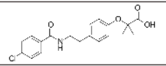
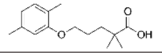
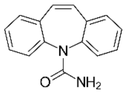
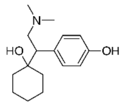
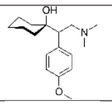
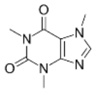
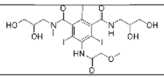
Annex IV. Supplementary materials of Article 4.

Rejection of organic micropollutants from greywater with forward osmosis: a matter of time

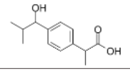
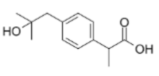
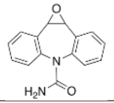
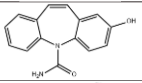
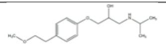
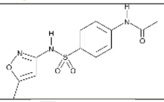
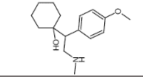
Table S1. Organic micropollutants (OMP) spiked in the feed solution (20 µg/L). Data obtained from Pubchem and Drugbank online databases.

Spiked OMP*										
use	**Compound**		**CAS**	**Charge at feed pH (6)**	**MW[1] (g/mol)**	**pka**	**log Kow**	**structure**	**LOD[2] (µg/L)**	**LOQ[3] (µg/L)**
Analgesics/anti-inflammatory	Acetaminophen	**ACE**	103-90-2	neu.	151.2	9.4	0.5		0.15	0.51
	Ibuprofen	**IBU**	15687-27-1	neg.	206.3	4.9	4.0		0.16	0.53
	Naproxen	**NPX**	22204-53-1	neg.	230.3	4.2	3.2		0.19	0.64
	Ketoprofen	**KTP**	22071-15-4	neg.	254.3	4.5	3.1		1.6	5.4
	Diclofenac[a]	**DCF**	15307-86-5	neg.	296.1	4.2	4.5		0.06	0.20
	Indomethazine	**IND**	53-86-1	neg.	357.8	4.5	0.9		0.04	0.13
Antibiotics	Sulfamethoxazole	**SFX**	723-46-6	neu.	253.3	1.6	0.9		0.04	0.12
	Trimethoprim	**TRI**	738-70-5	pos.	290.3	7.1	0.9		0.01	0.04
	Erythromycin	**ERI**	114-07-8	pos.	733.9	8.9	3.1		0.01	0.02
Antihypertensives	Irbesartan	**IRB**	138402-11-6	neu.	428.5	4.1	5.3		0.01	0.02
B-Blocking agents	Atenolol	**ATE**	29122-68-7	pos.	266.3	9.6	0.2		0.05	0.18
	Metoprolol[b]	**MTP**	51384-51-1	pos.	267.4	9.6	1.9		0.03	0.10
Diuretic	Furosemide	**FUR**	54-31-9	neg.	330.7	3.9	2.0		0.12	0.41
Endocrine disruptors	Methylparaben	**mPar**	99-76-3	neu.	152.2	8.5	2.0		0.02	0.07
	Bisphenol A	**BPA**	80-05-7	neu.	228.3	9.6	3.3		0.24	0.81
Histamine H1 and H2 receptor antagonists	Ranitidine[c]	**RAN**	66357-35-5	pos.	314.4	8.2	0.8		0.03	0.08

Spiked OMP*

use	Compound		CAS	Charge at feed pH (6)	MW[1] (g/mol)	pka	log Kow	structure	LOD[2] (µg/L)	LOQ[3] (µg/L)
Lipid regulators and cholesterol lowering drugs	Bezafibrate	**BZF**	41859-67-0	neg.	361.8	3.3	4.0		0.01	0.05
	Gemfibrozil	**GMF**	25812-30-0	neg.	250.3	4.5	4.8		0.01	0.02
Psychiatric drugs	Carbamazepine	**CBZ**	298-46-4	neu.	263.3	13.9	2.5		0.02	0.06
	Desvenlafaxine	**DVLF**	93413-62-8	pos.	263.4	9.5	2.8		0.06	0.20
	Venlafaxine[d]	**VLF**	93413-69-5	pos.	277.4	10.09	3.2		0.01	0.03
stimulant	Caffeine	**CAF**	58-08-2	neu.	194.2	14.0	-0.1		0.02	0.07
X-ray contrast agent	Iopromide	**IOP**	73334-07-3	neu.	791.1	11.1	-2.1		0.12	0.39

Analyzed transformation products

Parent	Compound		CAS	Charge at feed pH (6)	MW[1] (g/mol)	pka	log Kow	structure	LOD[2] (µg/L)	LOQ[3] (µg/L)
IBU	1-hydroxy-IBU	**IBU-1OH**	53949-53-4	neg.	222.3	4.6	2.4		N.A.	N.A.
IBU	2-hydroxy- IBU	**IBU-2OH**	51146-55-5	neg.	222.3	4.6	2.1		0.54	1.82
CBZ	Epoxy-CBZ	**Ep-CBZ**	36507-30-9	neu.	252.3	16.0	1.3		0.01	0.03
CBZ	2-Hydroxy-CBZ	**OH-CBZ**	68011-66-5	neu.	252.3	9.2	2.1		0.04	0.13
MTP	Metoprolol acid	**MTPA**	56392-14-4	neu.	267.3	3.5	-1.5		0.08	0.25
SFX	N-acetyl-SFX	**N-SFX**	21312-10-7	neg.	295.2	5.7	0.7		0.07	0.23
VLF	N-desmethyl-VLF	**NVLF**	149289-30-5	pos.	263.4	14.4	3		0.02	0.07

* All compounds were purchased from *LGC Standards* except for IOP, VLF and IRB, which were purchased from *Merck;* [1] molecular weight, [2] Limit of detection; for calculation purposes it was considered 0 when a compound was detected<LOD; [3] Limit of quantification; for calculation purposes it was considered 1/2LOQ when a compound was detected <LOQ; Spiked compounds: [a] diclofenac sodium salt, [b] metoprolol tartrate, [c] ranitidine hydrochloride, [d] venlafaxine hydrochloride

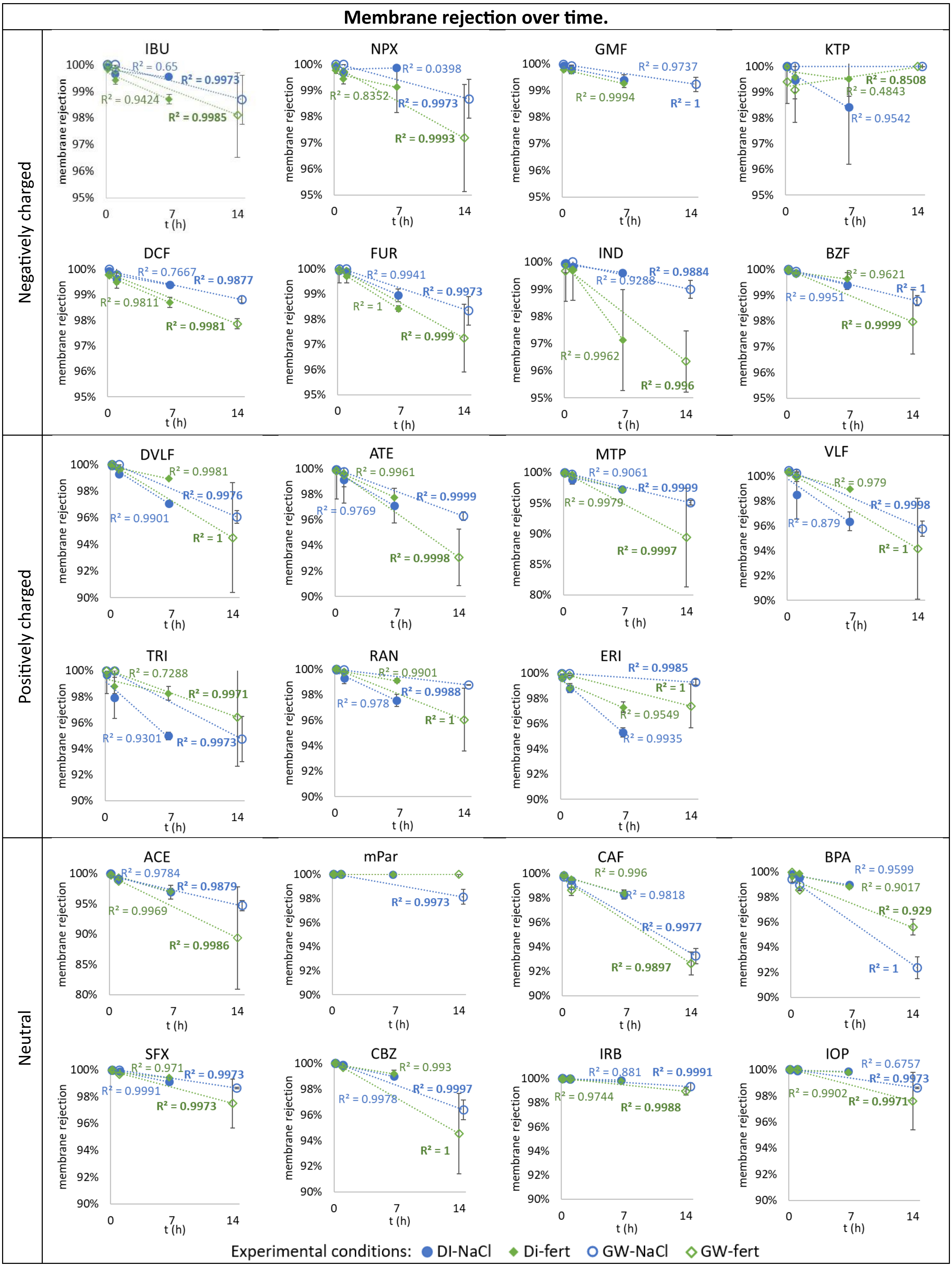


***Figure S1.** Membrane rejection of OMP with time. OMP ordered with ascending molecular weight.*

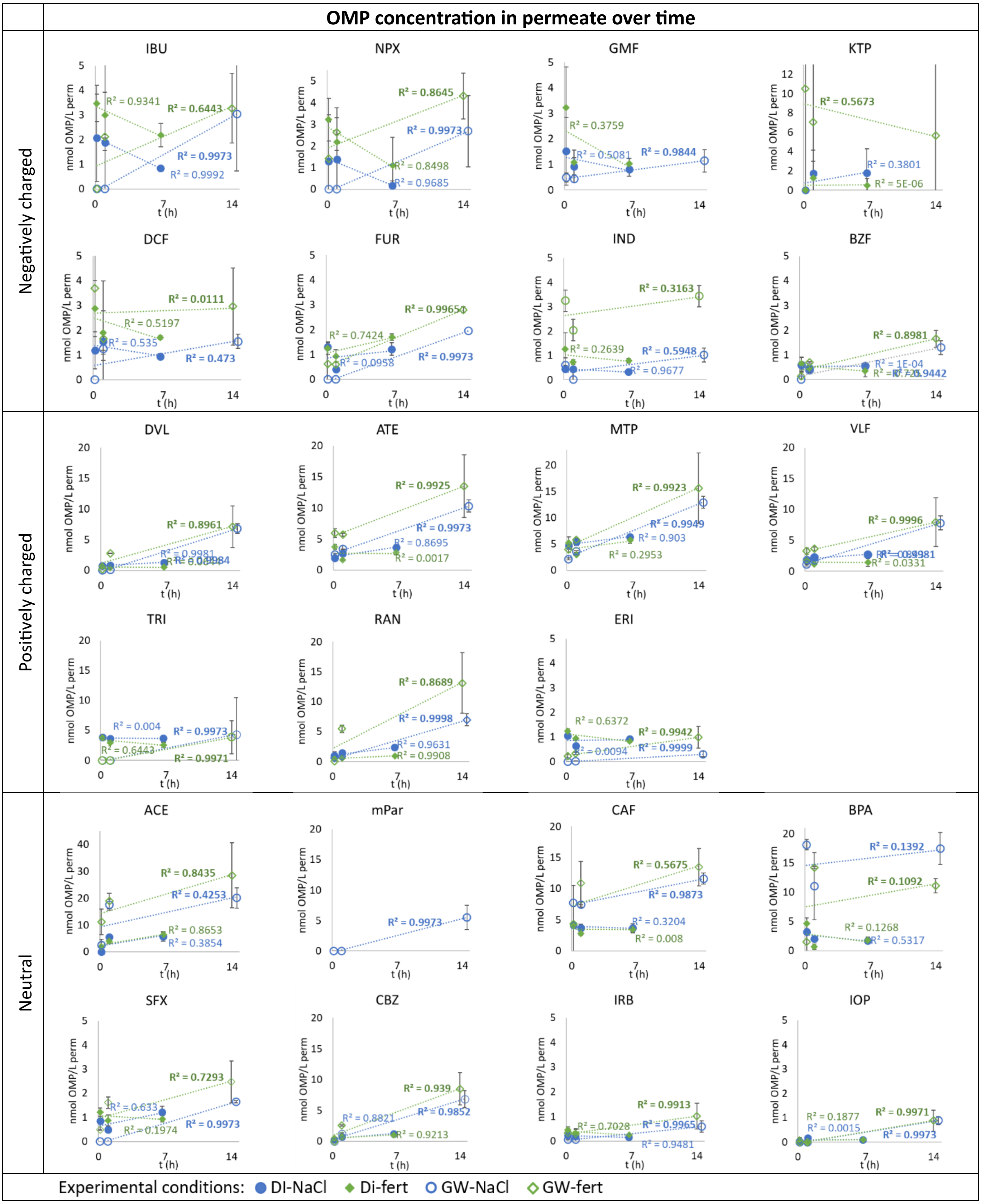


Figure S2. *µmol OMP/L permeate. OMP ordered with ascending molecular weight. Tendences for some of thew conditions and compounds are not shown when the rejection was 100%, and thus the concentration in permeate is 0.*

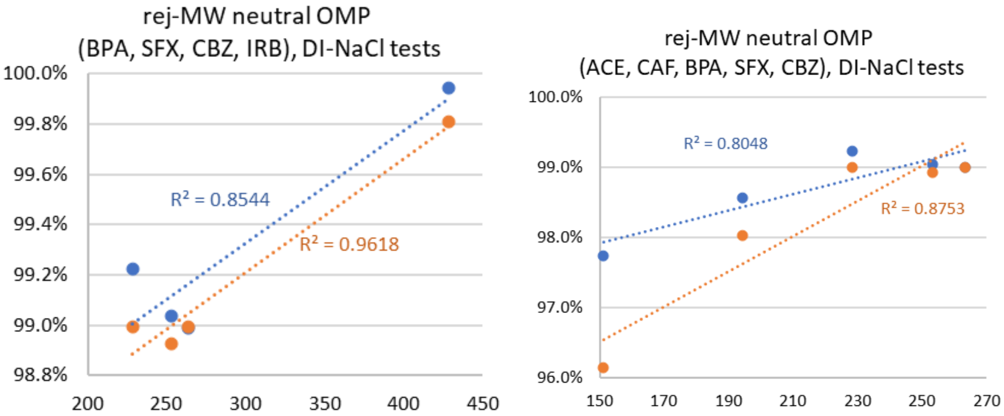


Figure S3. *Relation rejection with time for some neutral OMP in tests with DI water as FS and NaCl as DS.*

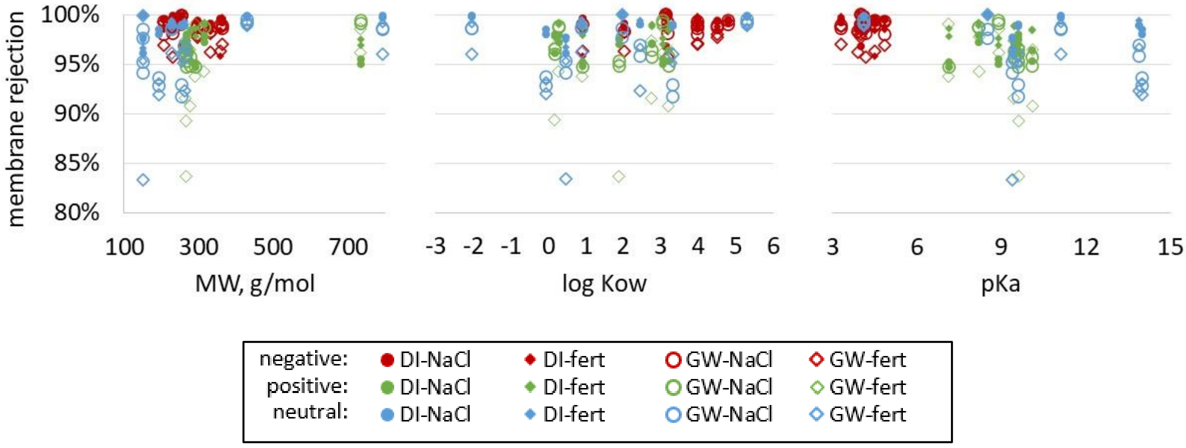


Figure S4. *Rejection at the end of the test in relation with OMP molecular weight, LogK$_{ow}$, and pKa.*

Annex V. Supplementary materials of Article 5.

From shower to table: fate of organic micropollutants in hydroponic systems for greywater treatment and lettuce cultivation

Table S1. Synthetic greywater composition, adapted from Hourlier et al. (2010)

compound	Conc. (mg/L)
$C_3H_8O_3$ (glycerol)	200
$C_3H_6O_3$ (Lactic acid)	100
$(C_6H_{10}O_5)_n$ (α-cellulose)	100
$(NH_4)_2HPO_4$	84
$NaHCO_3$	70
$C_{12}H_{25}OSO_2ONa$	50
Na_2SO_4	50
KNO_3	32
OMP	0.02

Table S2. List of OMP analyzed in the experiments and their properties (obtained from Pubchem and Drugbank online databases), limits of detection (LOD) and quantification (LOQ) for the different matrices and recoveries for lettuce leaves.

	OMP properties and uses								Liquid samples: GW		Solid samples: leaves		
	Compound	**Acronym**	**CAS**	**Charge at pH 7***	**MW, g/mol**	**pka**	**log K_{ow}**	**Use/ parent**	**LOD, µg/L**	**LOQ, µg/L**	**LOD, ng/g d.w.**	**LOQ, ng/g d.w.**	**Avg. recovery (%)**
Spiked OMP	Ibuprofen	**IBU**	15687-27-1	neg.	206.3	4.9	4.0	a	0.86	2.86	8.0	26.6	99
	Naproxen	**NPX**	22204-53-1	neg.	230.3	4.2	3.2		0.21	0.70	40.2	130.4	35
	Indomethacin	**IND**	53-86-1	neg.	357.8	4.5	0.9		0.12	0.40	11.0	36.7	91
	Diclofenac	**DCF**	15307-86-5	neg.	296.1	4.2	4.5		0.21	0.70	40.8	136.1	63
	Acetaminophen	**ACE**	103-90-2	neu.	151.2	9.4	0.5		0.27	0.90	11.0	36.5	73
	Sulfamethoxazole	**SFX**	723-46-6	neg.	253.3	1.6	0.9	b	0.04	0.14	NR	NR	NR
	Ofloxacin	**OFX**	82419-36-1	zwi.	361.4	6.0	-0.4		0.34	1.14	11.9	39.6	45
	Tetracycline	**TET**	60-54-8	zwi.	444.4	3.3	-1.4		0.28	0.93	NR	NR	NR
	Trimethoprim	**TRI**	738-70-5	neg.	290.3	7.1	0.9		0.23	0.77	1.5	5.0	75
	Gemfibrozil	**GMF**	25812-30-0	neg.	250.3	4.5	4.8	c	0.16	0.53	11.0	36.5	34
	Ranitidine	**RAN**	66357-35-5	pos.	314.4	8.2	0.8	d	0.13	0.42	NR	NR	NR
	Atenolol	**ATE**	29122-68-7	pos.	266.3	9.6	0.2	e	0.05	0.17	9.1	30.3	56
	Metoprolol	**MTP**	51384-51-1	pos.	267.4	9.6	1.9		0.1	0.34	21.9	72.9	82
	Venlafaxine	**VLF**	93413-69-5	pos.	277.4	10.1	3.2	f	0.03	0.09	6.5	21.7	91
	Desvenlafaxine	**DVLF**	93413-62-8	pos.	263.4	9.5	2.8		0.05	0.16	3.6	12.1	94
	Carbamazepine	**CBZ**	298-46-4	neu.	263.3	13.9	2.5		0.02	0.05	13.7	45.8	50
	Iopromide	**IOP**	73334-07-3	neu.	791.1	11.1	-2.1	g	0.11	0.37	NA	NA	NA
	Methylparaben	**mPar**	99-76-3	neu.	152.2	8.5	2.0	h	0.02	0.07	NA	NA	NA
	Bisphenol A	**BPA**	80-05-7	neu.	228.3	9.6	3.3	i	0.24	0.81	NA	NA	NA
	Caffeine	**CAF**	58-08-2	neu.	194.2	14.0	-0.1	j	0.02	0.07	NA	NA	NA
Analyzed transformation products (TP)	1-hydroxy-ibuprofen	**IBU-1OH**	53949-53-4	neg.	222.3	4.6	2.4	IBU	1.58	5.28	33.8	112.7	67
	2-hydroxy-ibuprofen	**IBU-2OH**	51146-55-5	neg.	222.3	4.6	2.1		0.54	1.80	51.8	172.6	58
	Epoxy- Carbamazepine	**Ep-CBZ**	36507-30-9	neu.	252.3	16.0	1.3	CBZ	0.12	0.40	2.3	7.7	89
	2OH- Carbamazepine	**2OH-CBZ**	68011-66-5	neu.	252.3	9.2	2.1		0.01	0.03	NA	NA	NA
	Metoprolol acid	**MTPA**	56392-14-4	neu.	267.3	3.5	-1.5	MTP & ATE	0.04	0.13	11.4	38.0	56
	N-acetyl- Sulfamethoxazole	**N-AcSFX**	21312-10-7	neg.	295.2	5.7	0.7	SFX	0.06	0.21	25.6	85.3	34
	N-desmethyl-venlafaxine	**N-VLF**	149289-30-5	pos.	263.4	14.4	3.0	VLF	0.07	0.23	8.4	28.0	100

*Charge: negative (neg.), positive (pos.), zwitterionic (zwi.) and non-ionizable/neutral (neu).

Uses: a: analgesics/anti-inflammatory drugs, b: antibiotics, c: lipid regulators and cholesterol lowering drug, d: histamine H2 receptor antagonist, e: β-blocking agents, f: psychiatric drugs, g: X-ray contrast agent, h: preservative (endocrine disruptor), i: plasticizer (endocrine disruptor), j: stimulant

d.w. stands for “dry weight”, NA stands for “not analyzed”, while NR stands for “not recovered”.

Table S3. Principal Component Analysis: factor loadings of the original variables (plant growth parameters) on the extracted components

	parameter	component		
		1	**2**	**3**
Component matrix	**fresh weight**	0.997		
	root fresh weight	0.901		
	leaf fresh weight	0.980		
	number of leaves			0.910
	average leaf length	0.912		
	average leaf width	0.927		
	leaf area	0.945		
	dry weight	0.969		
	root dry weight leaf dry weight	0.900		
	leaf dry weight	0.825	0.551	
	leaf dry matter content		0.932	
Extraction Sums of Squared Loadings	**Eigenvalues**	8.008	1.727	0.971
	% of variance	72.803	15.702	8.824
	cumulative %	72.803	88.505	97.329

Table S4. Tests of within-subjects effects for plant growth parameters, F statistic results.

source	fresh weight	leaves	LDMC
time	445.882**	3601.500**	44.5882**
time * condition	99.900**	224.167**	99.900**

*significant ($p<0.05$)

**highly significant ($p<0.01$)

Table S5. Removals in the abiotic controls, %

parameter	GWB	GWS	GWN
TSS	90.7	77.2	89.2
TOC	90.0	90.3	90.6
Na	17.8	23.6	18.5
N-NH_4	73.3	66.1	38.5
K	22.0	39.6	20.1
N-NO_3	99.9	98.5	28.0
P-PO_4	26.3	31.7	28.5
S-SO_4		32.4	15.0
IBU	75.2	0	42.5
SFX	68.5	82.4	95.6
NPX	35.2	0	4.6
GMF	32.3	0	26.0
DCF	6.7	0	0
IND	48.6	6.3	38.9
DVLF	0	16.9	20.6
ATE	46.2	34.7	26.7
MTP	47.4	26.2	41.4
VLF	0	0	0
TRI	0	0	4.7
RAN	95.0	54.3	97.2
OFX	90.6	92.6	95.0
TET	92.3	96.1	58.4
ACE	31.7	47.3	100
mPar	100	100	100
CAF	7.5	56.8	47.9
BPA	62.9	100	100
CBZ	44.2	26.5	25.3
IOP	38.9	40.3	22.2
BPA	64.0	100	100
CBZ	46.2	14.8	24.3
IOP	37.7	27.0	0
Avg OMP removal	51.3	45.9	47.3

Table S6. Between subjects-effects of the different OMP removals between conditions: F statistic and pairwise comparisons

OMP	Tests between subjects, F				Pairwise Comparisons***, mean difference (I-J)					
	Corrected Model	Intercept	tweeks	condition	GWB		GWN		GWS	
					GWN	GWS	GWB	GWS	GWB	GWN
IBU	4.568*	220.462**	0.958	6.372**	17.729	76.565**	-17.729	58.836*	-76.565**	-58.836*
SFX	2.049	1728.503**	0.544	2.802						
NPX	5.951**	55.527**	0.256	8.799**	-101.762*	33.368	101.762**	135.130**	-33.368	-135.130**
GMF	17.6802**	27.628**	0.069	26.486**	-80.851	154.443**	80.851	235.294**	-154.443**	-235.294**
DCF	20.520**	21.421**	0.077	30.742**	-127.966**	127.310**	127.966**	255.276**	-127.310**	-255.276**
IND	13.525**	74.668**	0.378	20.099**	-28.327	98.683**	28.327	127.010**	-98.683**	-127.010**
DVLF	0.73	7.292*	0.321	0.935						
ATE	8.384**	158.533**	4.827*	10.162**	87.375**	27.075	-87.375**	-60.300*	-27.075	60.300*
MTP	0.542	230.108**	0.704	0.461						
VLF	0.472	0.081	0.361	0.527						
TRI	2.036	5.142*	0.177	2.965						
RAN	11.637**	2222.893**	22.311**	6.299**	30.944**	24.329*	-30.944**	-6.615	-24.329*	6.615
OFX	7.835**	6336.133**	0.051	11.727*	-5.568	-26.157**	5.568	-20.589**	26.157**	20.589**
TET	5.309**	5740.976**	7.975*	3.976*	-15.583*	-4.744	15.583*	10.839	4.744	-10.839
ACE	0.548	1071.150**	0.302	0.671						
CAF	0.844	50.838**	0.54	0.995						
BPA	9.079**	5601.310**	0.15	13.543**	-6.907	-30.806**	6.907	-23.899**	30.806**	23.899**
CBZ	4.257*	115.715**	0.325	6.223**	20.188	60.901**	-20.188	40.713	-60.901**	-40.713
IOP	1.853	22.129**	2.342	1.609						

*significant (p<0.05)

**highly significant (p<0.01)

***Only performed for those compounds in which p value of condition <0.05

Section S1. Plant growth parameters

Selected parameters were used according to literature on hydroponic cultivation of lettuce: Eregno et al. (2017); Gent (2016); Gent (2017); Sangare et al. (2021); Fraile-Robayo et al. (2017), and as described in theoretical papers : Poorter and Garnier (1996); Hunt et al. (2002); Pandey et al. (2017); van Holsteijn (1980); Dayan et al. (2005) or handbooks (Pérez-Harguindeguy et al., 2013) on the analysis of plant growth.

- Water content of leaves (%, Equation 1): calculated considering dry and wet weight.
- Leaf dry matter content (LDMC; mg/g, Equation 2): calculated as a function of leaf dry and wet mass.
- Relative growth rate (RGR; g/g/day, Equation 3): average daily increase in dry matter per unit dry matter per time.
- Net assimilation rate (NAR; g/cm^2/day, Equation 4): also known as unit leaf rate, shows the increase of plant material per unit of assimilatory material (unit LA) per unit of time.
- Specific leaf area (SLA; cm^2/g, Equation 5): ratio of the leaf area to the dry weight of the leaves. A higher SLA indicates less thick and/or dense leaves.
- Leaf weight ratio (LWR; g/g, Equation 6): ratio of the leaf dry weight to the total plant material dry weight (leaves & roots).

$$water\ (\%) = 100 \times (1 - \frac{LW_{tf}}{LWfresh_{tf}}) \quad (1)$$

$$LDMC = \frac{LW_{tf}}{LWfresh_{tf}} \quad (2)$$

$$RGR = \frac{lnW_{tf} - lnW_{t0}}{t_f - t_0} \quad (3)$$

$$NAR = \frac{\left(W_{tf} - W_{t0}\right) * (lnLA_{tf} - lnLA_{t0})}{\left(t_f - t_0\right) * \left(LA_{tf} - LA_{t0}\right)} \quad (4)$$

$$SLA = \frac{(LA_{tf}/LW_{tf}) - (LA_{t0}/LW_{t0})}{2} \quad (5)$$

$$LWR = \frac{(LW_{tf}/W_{tf}) - (LW_{t0}/W_{t0})}{2} \quad (6)$$

With: W: dry weight of the total plant material (leaves + roots); LW: leaves' dry weight; LW_{fresh}: leaves fresh weight; LA: plants total leaf area. t_0 & t_f refer to the day of planting and harvesting, respectively; lnW: create natural logarithm for W of each plant sampled per treatment, then take the average lnW.

Section S2. Sample preparation for the analyses of OMP in plant tissue (i.e., lettuce leaves)

The methodology for OMP extraction from lettuce leaves was adapted from Montemurro et al. (2020): after grinding the freeze-dried lettuce leaves, 1 g of sample was placed in a 50 mL falcon tube and hydrated with 9 mL HPLC water. The tubes were vortexed for 2 min at 2500 rpm and left to hydrate for 1 h. 10 mL of acetonitrile and 50 µL of formic acid were added in the tubes, vortexed and the extraction salts (1 g NaCl and 4 g $MgSO_4$) were added. The mixture was instantly shaken to prevent crystalline agglomerates formation. Tubes were vortexed and centrifuged at 4000 rpm for 10 min at 4°C . The supernatant, containing the organic phase, was transferred into glass tubes, and left overnight at -20°C for the precipitation of fatty acids and waxes. The following day, the clean-up step involved the transfer of 6 mL of the supernatant into the PSA (primary secondary amine) tubes (150 mg PSA, 150 mg C18, 900 mg $MgSO_4$) and the mixture was vortexed and centrifuged at 4°C for 5 min. The same process was followed for the extraction of roots, replacing the hydration step with EDTA solution instead of water, omitting the formic acid addition and the clean-up step. For all samples, 1 mL of the supernatant was spiked with the internal standard mix at a concentration of 20 µg/L, the sample was evaporated until dryness under nitrogen at room temperature and then reconstituted with 1 mL of water/methanol (80:20, v/v). To remove any possible particles formed from precipitation, a final centrifugation step at 7000 rpm for 10 min was added before UHPLC-MS/MS analysis.

Section S3. Statistical analyses performed with SPSS

a) Plant growth and development: explorative analysis conducted through Principal Component Analysis (PCA) aimed to reduce the number of variables while retaining most of variability in the original data (Afifi et al., 2003). The number of components to be retained was chosen on the basis of the "Scree test" discarding all the components explaining less than half of the variance of one of the original variables. That allowed to select few components able to describe the whole dataset with minimum loss of original information. Before and after treatment growth parameters (fresh weight and leaf-dry matter-LDMC) of each condition (GWB, GWS, GWN, CTRL) were tested through a repeated measures ANOVA design, following Equation 7:

$y_{ijk}=\mu+\alpha_i+\beta_j+(\alpha\beta)_{ij}+\epsilon_{ijk}$ Eq. 7

With: μ: total mean, α_i: effect of the i^{th} level of the within-subject factor (i = 1 before, 2, after); β_j: effect of the j^{th} level of the between-subjects factor (j = 1, GWN, 2, GWS, 3, GWB, and 4, CTRL); $(\alpha\beta)_{ij}$: ij interaction effect, and ϵ_{ijk}: random error assumed $\epsilon_{ijk} \sim N(0,\sigma^2)$.

b) Number of leaves: since these measurements were collected over a span of four weeks, the analysis design for this parameter was univariate with a between subjects' factor and a covariate, following Equation 8:

$yijk=\mu+\alpha_i+\beta_j+(\alpha\beta)_{ij}+X+\epsilon_{ijk}$ Eq. 8

With: X: covariate (time in weeks).

Due to variations in the number of lettuce individuals across the weeks and their associated variability, a Weighted Least Squares method was employed in the Generalized Linear Model.

c) OMP removal: a univariate Generalized Linear Model with a between subjects' factor was used to assess the differences between the OMP removals across treatments (GWB, GWS, GWN), following Equation 9:

$yijk=\mu+\alpha_{ij}+X+\epsilon_{ijk}$ Eq. 9

Section S4. HHRA calculations

Human health risk assessment (HHRA) is commonly assessed through the hazard quotient (HQ; Equation 10), which is the ratio of the estimated daily intake (EDI; Equation 11). The reference values for each OMP were generated for all compounds applying the lowest daily therapeutic dose (LDTD) approach, in the case of pharmaceuticals, or the threshold of toxicological concern (TTC) approach in the case of transformation products. LDTDs were acquired from the public websites (www.reference.medscape.com and drugs.com/dosage/) and normalized for 70 kg body weight, with safety factors either provided in the literature or substituted according to default factors provided by Snyder et al. (2010) to increase homogeneity. TTC values (original source: Kroes et al., 2004) were normalized for 70 kg body weight according to the classification into Cramer Classes when applying "Revised Cramer Decision Tree" and “Extended Cramer rules” in the online version of the Toxtree software (www.apps.ideaconsult.net/data/ui/toxtree). For transformation products, for which no literature TTC value could be found, and neither a Cramer classification in the Toxtree software, the Cramer class of the parent compound was used to generate the TTC value. This was done to generate indictive results only, since the transformation products may have, in some cases, a much higher level of toxicity than their respective parent compound. The potential risk of ingesting the combination of OMP accumulated in the leaves was calculated with the hazard index (HI) (equation (12)).

$$HQ = \frac{EDI}{reference\ value} \qquad (10)$$

$$HI = \sum HQ \qquad (12)$$

$$EDI = \frac{C * IR * \beta_{ww/dw}}{BW} \qquad (11)$$

With: HQ: Hazard quotient; EDI: Estimated daily intake; Reference value, here: LDTD*SF (safety factor to account for uncertainty and extrapolation of the data) or TTC (µg/kg/day); HI: Hazard index for the daily intake; C: concentration of the compound in the edible part of the crop in dry weight (µg/g); C_{fw}: concentration of the compound in the edible part of the crop in fresh weight (µg/g); IR: daily food ingestion rate in units of fresh weight per person in the target group (g/day); $\beta_{ww/dw}$: wet-to-dry conversion factor for plant tissue (unitless); BW: average body weight of the target group (kg), a common default value for European adults is 70 kg.

GWB **GWS** **GWN** **CTRL**

Figure S1. Harvested lettuces at the end of the experiment.

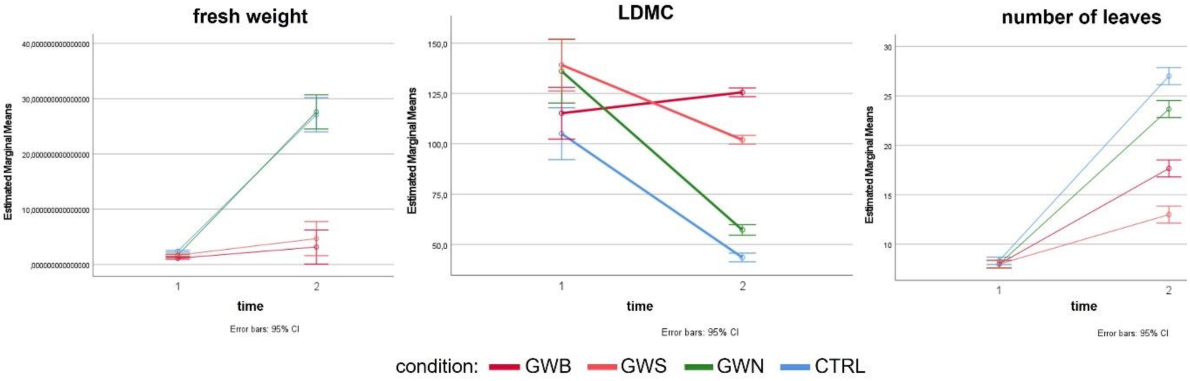


Figure S2. Estimated marginal means of the variable most associated with each of the extracted compounds: fresh weight for component 1, leaf dry matter content for component 2, and number of leaves for component 3.

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Annex VI. Participation in congresses and conferences.

Participation in international congresses and conferences with oral presentation				
conference	**year**	**country**	**title**	**authors**
IWA EcoSTP 2023 - Ecotechnologies for Wastewater Treatment	2023	Spain	Fertilizer drawn forward osmosis for greywater treatment and subsequent reuse in hydroponics	E. Mendoza, J. Vosse, Gaetan Blandin, Joaquim Comas, Gianluigi Buttiglieri
ICWS2022 - 17th International Conference on Wetland Systems for Water Pollution Control	2022	France	Steps towards circularity in touristic accommodations: greywater treatment and edible cultivation in hydroponic systems	E. Mendoza, J. Vosse, M. Castaño, J.A.C. Castellar, L.H.M.L.M. Santos, J. Comas, G. Buttiglieri
The Second International Symposium on Nanomaterials and Membrane Science for Water, Energy and Environment Desalination and reuse face to water scarcity	2022	Morocco	Fertilizer drawn forward osmosis for greywater treatment	E. Mendoza, J. Vosse, M. Castaño, J.A.C. Castellar, J. Comas, G. Buttiglieri
12th Micropol & Ecohazard conference	2022	Spain	Hydroponic systems with edibles for greywater treatment and reuse	E. Mendoza, J. Vosse, M. Castaño, J.A.C. Castellar, J. Comas, G. Buttiglieri
WETPOL2021 - 9th international symposium on wetland pollutant and dynamics and control	2021	Austria (online)	Hydroponic systems with edible plants for greywater treatment and organic micropollutant removal	Mendoza, E., Vosse, J., Castellar, J.A.C., Comas, J., Buttiglieri
IWA EcoSTP 2021 - Ecotechnologies for Wastewater Treatment	2021	Italy (online)	Fertilizer drawn forward osmosis for sustainable greywater reuse in touristic Mediterranean regions	E. Mendoza, G. Blandin, J. Comas, G. Buttiglieri
ETEi2020 - Environmental Technology for Impact	2020	Netherlands (online)	Fertilizer drawn forward osmosis for sustainable greywater reuse in touristic Mediterranean regions	E. Mendoza, G. Blandin, J. Comas, G. Buttiglie

Participation in international congresses and conferences with poster				
conference	**year**	**country**	**title**	**authors**
12th Micropol & Ecohazard conference	2022	Spain	Hydroponic systems with edibles for greywater treatment and reuse	E. Mendoza, J. Vosse, M. Castaño, J.A.C. Castellar, J. Comas, G. Buttiglieri

Participation in national congresses and conferences with oral presentation				
conference	**year**	**country**	**title**	**authors**
Congreso IWA YWP - Young Water Professionals Spain 20	2022	Spain	Dilución osmótica de solución fertilizante mediante ósmosis directa y posterior aplicación en sistemas hidropónicos	E. Mendoza, J. Vosse, G. Blandin, L. Alonso, J. Comas, G. Buttiglieri
JoDoc2020 - IV conference of pre-doctoral researchers of the UdG	2020	Spain	Fertilizer-drawn forward osmosis for sustainable water reuse	E. Mendoza, G. Blandin, J. Comas, G. Buttiglieri
ICRA10y - Water research in perspective: beyond 2020	2019	Spain	CLEaN-TOUR. Circular Economy to facilitate urban water reuse in a touristic city	E. Mendoza, G. Blandin, H. Gattringer, J. Comas, G. Buttiglieri
YWP2019 - Congreso IWA Young water Professionals Spanish Chapter 2019	2019	Spain	Evaluación de la ósmosis directa para el regadío y la reutilización sostenible del agua en regiones turísticas mediterráneas	E. Mendoza, G. Blandin, J. Comas, G. Buttiglieri
BRM2019 - Jornada sobre Biorreactors de membrana	2019	Spain	Evaluación de la ósmosis directa para el regadío y la reutilización sostenible del agua en regiones turísticas mediterráneas	E. Mendoza, G. Blandin, J. Comas, G. Buttiglieri

Participation in congresses and conferences as co-author (J. Vosse was the presenter in all cases)					
conference	**year**	**country**	**title**	**authors**	**type**
IWA EcoSTP 2023 - Ecotechnologies for Wastewater Treatment	2023	Spain	Plant growth potential of hotel greywater reuse in hydroponic system	J. Vosse; Esther Mendoza; Joaquim Comas; Gianluigi Buttiglieri	presentation
WICC2023 - Water Innovation and Circularity Conference	2023	Greece	Hotel greywater reuse in hydroponic system: Plant growth potential	Josephine Vosse; Esther Mendoza; Joaquim Comas; Gianluigi Buttiglieri	presentation
12th Micropol & Ecohazard conference	2022	Spain	Hazard characterization methodology for the human exposure to pharmaceuticals through the ingestion of food crops irrigated with reclaimed water	J. Vosse, L.H.M.L.M. Santos, E. Mendoza, J. Comas, S. Rodriguez-Mozaz, G. Buttiglieri	poster
JoDoc2022 - VI Conference of Pre-doctoral Researchers of University of Girona	2022	Spain	Water reuse for irrigation: How to perform hazard characterization for the human exposure to pharmaceuticals accumulated in food crops.	J. Vosse, L.H.M.L.M. Santos, E. Mendoza, J. Comas, S. Rodriguez-Mozaz, G. Buttiglieri	presentation
WETPOL2021 - 9th international symposium on wetland pollutant and dynamics and control	2021	Austria (online)	Human health risk assessment for the ingestion of food crops irrigated with greywater – Feasibility study for water reuse.	J. Vosse, L.H.M.L.M. Santos, E. Mendoza, J. Comas, S. Rodriguez-Mozaz, G. Buttiglieri	presentation

Annex VII. Agreement documents of the co-authors of the articles included in this thesis.

Dr Arianna Azzellino, as co-author of the following articles:

Mendoza, E., Ferrero, G., Slokar, Y.M., Amores, X., **Azzellino, A.** and Buttiglieri, G., 2023. Water management practices in Euro-Mediterranean hotels and resorts. *International Journal of Water Resources Development*, *39*(3), pp.485-506. https://doi.org/10.1080/07900627.2021.2015683

Mendoza, E., Vosse, J., **Azzellino, A.**, Santos, L. H., Semitsoglou-Tsiapou, S., Comas, J. and Buttiglieri, G., 2024. From shower to table: fate of organic micropollutants in hydroponic systems for greywater treatment and lettuce cultivation. *Blue-Green Systems*, 6(1), p.70 https://doi.org/10.2166/bgs.2024.051

Accepts that Ms. Esther Mendoza presents the cited articles as the principal author and as part of her doctoral thesis and that said articles cannot, therefore, form part of any other doctoral thesis.

And for all intents and purposes, hereby signs this document.

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Mr. Àlex Bayo, as co-author of the following article:

Mendoza, E., Magrí, A., Blandin, G., **Bayo, À.**, Vosse, J., Buttiglieri, G., Colprim, J. and Comas, J., 2023. Second-Generation Magnesium Phosphates as Water Extractant Agents in Forward Osmosis and Subsequent Use in Hydroponics. *Membranes*, *13*(2), p.226. https://doi.org/10.3390/membranes13020226

Accepts that Ms. Esther Mendoza presents the cited article as the principal author and as part of her doctoral thesis and that said article cannot, therefore, form part of any other doctoral thesis.

And for all intents and purposes, hereby signs this document.

Dr Giuliana Ferrero, as co-author of the following article:

Mendoza, E., **Ferrero, G.**, Slokar, Y.M., Amores, X., Azzellino, A. and Buttiglieri, G., 2023. Water management practices in Euro-Mediterranean hotels and resorts. *International Journal of Water Resources Development*, *39*(3), pp.485-506. https://doi.org/10.1080/07900627.2021.2015683

Accepts that Ms. Esther Mendoza presents the cited article as the principal author and as part of her doctoral thesis and that said article cannot, therefore, form part of any other doctoral thesis.

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27/11/2023

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Dr Yness March Slokar, as co-author of the following article:

Mendoza, E., Ferrero, G., **Slokar, Y.M.**, Amores, X., Azzellino, A. and Buttiglieri, G., 2023. Water management practices in Euro-Mediterranean hotels and resorts. *International Journal of Water Resources Development*, *39*(3), pp.485-506. https://doi.org/10.1080/07900627.2021.2015683

Accepts that Ms. Esther Mendoza presents the cited article as the principal author and as part of her doctoral thesis and that said article cannot, therefore, form part of any other doctoral thesis.

And for all intents and purposes, hereby signs this document.