



Universidad de Concepción

Dirección de Postgrado

Facultad de Ciencias Ambientales

Programa de Doctorado en Ciencias Ambientales mención Sistemas Acuáticos Continentales

**EVALUACIÓN TÉCNICA Y AMBIENTAL DE LA ELIMINACIÓN DE FÓSFORO EN
HUMEDALES CONSTRUIDOS PARA EL TRATAMIENTO DE AGUAS
RESIDUALES**

**Tesis para optar al grado de Doctor en Ciencias Ambientales con Mención en Sistemas
Acuáticos Continentales**

VALENTINA PAZ CARRILLO LÍBANO

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Profesor Guía: **Dra. Gladys Vidal Sáez**
Facultad de Ciencias Ambientales,
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Esta Tesis de Doctorado en Ciencias Ambientales con Mención en Sistemas Acuáticos continentales fue realizada en los laboratorios del Grupo de Ingeniería y Biotecnología Ambiental (GIBA-UDEC) de la Facultad de Ciencias Ambientales, de la Universidad de Concepción.

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DEDICATORIA

A mí y todo el esfuerzo que dedicado en este proyecto...

“La prueba final del conocimiento es tu capacidad de transmitirlo a otra persona “

Richard P. Feynman



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2018-2022

GRUPO DE INGENIERIA Y BIOTECNOLOGIA AMBIENTAL (GIBA-UDEC)

FACULTAD DE CIENCIAS AMBIENTALES

UNIVERSIDAD DE CONCEPCION

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Relacionadas con el proyecto

1. **Carrillo, V.,** Fuentes, B., Gómez, G. & Vidal, G. (2020) Characterization and recovery of phosphorus from wastewater by combined technologies. *Reviews in Environmental Science and Bio/Technology* 19, 389–418. DOI 10.1007/s11157-020-09533-1.
2. **Carrillo, V.,** Collins, C., Brisson, J., & Vidal, G. (2021). Evaluation of long-term phosphorus uptake by *Schoenoplectus californicus* and *Phragmites australis* plants in pilot-scale constructed wetlands. *International Journal of Phytoremediation*, 24(6), 610-621. DOI:10.1080/15226514.2021.1960478.
3. **Carrillo, V.,** Gómez, G., & Vidal, G. (2022). Phosphorus uptake by macrophyte plants in monocultures and polycultures in constructed wetlands for wastewater treatment. *Ecological Engineering*, 106690. DOI: 10.1016/j.ecoleng.2022.106690.
4. **Carrillo, V.;** Casas, Y., Neumann, P. and Vidal, G. (2022). Life cycle analysis of a horizontal flow constructed wetland for the treatment of municipal wastewater under cold and warm seasons. (Manuscript terminado).

No relacionadas con el proyecto

5. Segura D., **Carrillo V.**, Remonsellez F., Araya M., Vidal G. 2017 Comparative public perception of the desert and humidities regions for the sewage treated reuse in Chile. Water. DOI:10.3390/w10030334
6. **Carrillo V.**, Espinoza D., Barahona S., Quispe J., Fuentes B., Vidal G. y Remonsellez F. 2022. Effect of salinity on bacterial diversity supported on natural pumice stones using a trickling biofilter for wastewater treatment. (En proceso de envío) a revista ISI. Revista Bioresource Technology o Water research.

4. CAPÍTULOS DE LIBRO Y OTRAS PUBLICACIONES

1. **Carrillo V.**, Leiva, A. M. and Vidal, G. 2019. Constructed wetlands: An emerging green technology for phosphorus treatment in industrial wastewater. In: Emerging Contaminants: Environmental Implications and Management. Editor: Ram Naresh Bharagava. Editorial: Springer Nature Singapore Pte Ltd., Singapore. DOI: 10.1007/978-981-13-7904-8_9. ISBN 978-981-13-7903-1. Publicado.
2. López, D., Leiva, A.M., **Carrillo V.**, Gómez, G. and Vidal, G. 2021. Humedales Construidos. En: Soluciones basadas en la naturaleza para la descontaminación de descargas puntuales y difusas. Editoras: Gladys Vidal, Gloria Gómez y M. Cristina Diez. Editorial RIL, Universidad de Concepción, Chile. ISBN 978-956-227-465-4. Publicado.
3. **Carrillo V.**, Gómez G., Fuentes B., Lagos O. y Vidal G. 2021. El fósforo como nutriente: perspectivas globales, ambientales y su aplicación en la agricultura. Serie comunicacional CHRIAM, Universidad de Concepción. Publicado.

5. PARTICIPACION EN EVENTOS CIENTIFICOS INTERNACIONALES Y NACIONALES

1. **Carrillo V.**, Leiva, A. M. and Vidal, G. (2018) "Humedales construidos: una tecnología verde emergente para el control de la contaminación por fósforo". Presentación Oral: Water Congress 2019-7° International congress on water in mining and industrial processes", en Santiago de Chile realizada de manera presencial el 15 al 17 de mayo de 2019.
2. **Carrillo V.** and Vidal G. (2020). "Long-term phosphorus uptake by *Phragmites australis* and *Schoenoplectus californicus* in constructed wetlands". Presentación oral: 2° Congreso de Jóvenes Profesionales del Agua, IWA 2020, organizado por la Universidad Católica de Manizales, Colombia. Fue realizado de manera online desde el 9 al 12 de noviembre del 2020.
3. **Carrillo V.**, Collins C. and Vidal G. (2021). "Phosphorus mass balance in a wetland constructed on a pilot scale in 8 years of operation". Presentación oral: Conferencia Panamericana sobre Sistemas de Humedales para el Tratamiento y Mejoramiento de la Calidad del Agua, realizado de manera online en Florianópolis, Brasil el 28-29 de abril de 2021.
4. **Carrillo V.**, Urrutia N. and Vidal G. (2021). "Eliminación de fósforo de aguas servidas mediante tecnologías convencional y no convencional". Presentación oral: Water Congress 2021-9° International congress on water management in mining and industrial processes, que se realizó online en la ciudad Santiago, Chile desde el 7 al 9 de julio del 2021.
5. **Carrillo V.** and Vidal G. (2021). "Influence of operational parameters on long-term phosphorus removal in pilot-scale constructed wetlands". Presentación oral: 9th International Symposium on Wetland Pollutant Dynamics and Control (WETPOL 2021) que se realizó online

por University of Natural Resources and Life Sciences en Viena, Austria desde el 13 al 17 de septiembre del 2021.

6. Carrillo, V., Casas Y. and Vidal G. (2022). “Análisis de ciclo de vida de humedales construidos”. Presentación oral: 10° Congreso Internacional en Gestión del Agua en Minería y Procesos Industriales. Aceptado a realizar desde el 7-9 de septiembre del 2022.

6. LINEAS E INTERESES DE INVESTIGACION

Los intereses se centran en encontrar nuevas soluciones tecnológicas para resolver problemáticas relacionadas con el recurso hídrico dándole una perspectiva en el ámbito innovador, económico y sustentable cuidando tanto los recursos naturales como los ecosistemas acuáticos. En los últimos años, las aguas servidas no sólo constituyen una fuente alternativa de agua dulce, sino que se han considerado un recurso desaprovechado, debido a que contiene muchos componentes valiosos, como energía química, nutrientes, como el fósforo y nitrógeno, y otros como metales pesados. La línea principal de investigación se centra en desarrollar tecnologías de recuperación con la finalidad de cerrar el ciclo. Estos desarrollos se centran en gran medida en consideraciones ambientales como la tecnología sostenible y lograr eficiencias en la recuperación. Tecnologías no convencionales y descentralizadas como los humedales construidos se han considerado tanto para tratamientos de aguas como para la obtención de materias primas.

7. EXPERENCIA EN DOCENCIAS

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2. Año 2017, **Profesor responsable** para la Carrera Ingeniería Civil Ambiental, Departamento de Ingeniería química, Facultad de Ingeniería y Ciencias geológicas, Universidad católica Del Norte, Antofagasta, Chile. **ASIGNATURA:** Herramientas Ambientales II, Curso de 5° año de carrera.
3. Año 2017, **Profesor responsable** para la Carrera Ingeniería Civil Ambiental, Universidad católica Del Norte, Antofagasta, Chile. **ASIGNATURA:** metodología y orientación para la medición de variables ambientales, Curso 6° año de carrera.
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Co-guia de tesis de pregrado

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2. Año 2020, **Alumno Nancy Urrutia** de la Carrera de Ingeniería Ambiental, de la facultad de Ciencias Ambientales de la Universidad de Concepción. El cual trabaja en la tesis titulada: “Eliminación de fósforo de aguas servidas mediante tecnologías convencional y no convencional: Una aproximación desde balances de materia”.

Ayudantías

1. Primer semestre, año 2018, **Introducción a la Ingeniería Ambiental (Código 99023)**, dictada por la Dra. Gladys Vidal.
2. Segundo semestre, año 2018, **Aspectos ambientales de procesos productivos y alternativas de prevención de la contaminación (Código 999019)**, dictada por la Dra. Gladys Vidal.
3. Primer semestre, año 2019, **Introducción a la Ingeniería Ambiental (Código 99023)**, dictada por la Dra. Patricia Gonzales.
4. Segundo semestre, año 2019, **Gestión integral de residuos sólidos (Código 999055)**, dictada por la Dra. Patricia Gonzales.
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2. Año 2020, **Gastos de Operación y Pasantía** para Estudiantes de Doctorado en Chile de CONICYT.
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9. OTRAS ACTIVIDADES ACADEMICAS

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2. Asistencia a **charlas académicas** realizadas en el Centro de Ciencias Ambientales EULA, facultad de Ciencias Ambientales y Centro CRHIAM Centro de Recursos Hídricos para la Agricultura y la Minería de la Universidad de Concepción.
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4. Charla en **1000 Cientific@s 1000 Aulas del Programa Explora de CONICYT**, en este caso en el Proyecto asociativo regional (PAR), Explora Nuble de la universidad de Concepción. Debido a la contingencia social, no pudo realizarse, por lo que fue suspendida desde el establecimiento educacional.
5. **Workshop** Web of Science –Journal Citation Reports - Essential Science Indicators – EndNote, dictado en la biblioteca central de la Universidad de Concepción el **03/04/2019**.
6. **Divulgación científica participando de un video promocional** para la prevención del covid-19 realizado por el Centro CRHIAM (Centro de Recursos Hídricos para la Agricultura y la Minería de la Universidad de Concepción) en **conjunto con la SEREMI** de Ciencia, Tecnología, Conocimiento e Innovación de la Macrozona Centro Sur, **septiembre 2020**. (<https://www.facebook.com/watch/?v=323860945702749&ref=sharing>)
7. Participación en el **Segundo Encuentro de Estudiantes e Investigadores Postdoctorales CRHIAM** presentación oral: "*Evaluación de la eficiencia de retención de un humedal construido de flujo horizontal subsuperficial escala piloto a largo plazo*" **realizado el 15/09/2020**. Obteniendo el premio a mejor presentación oral.
8. **Expositora en el ciclo de charlas CRHIAM** exponiendo como título "*Fósforo en aguas servidas: principios y tecnologías de recuperación*", realiza el **jueves 01/07/2021**. <https://www.youtube.com/watch?v=fAay4BgyDgE>.
9. **Participación en responder preguntas** sobre el agua a estudiantes de la escuela El Rincón de Puchuncaví en el marco del **Congreso Nacional e Interregional del programa de Indagación Científica (ICEC) 2021**, formando parte del CRHIAM, **en agosto 2021**.
10. **Expositora de la charla** "*El fosforo en aguas servidas y su perspectiva ambiental*" en el cierre del primer semestre académico del Departamento de Química, Universidad Católica del Norte. **Realizada el 08/07/2021**.

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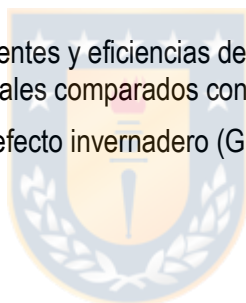
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RESUMEN

El crecimiento acelerado urbano, pronostica aumentos dramáticos en la generación de aguas residuales, donde el fósforo es el principal nutriente responsable de la eutrofización de los cuerpos de agua, generando uno de los problemas más grandes y futura amenaza a los ecosistemas acuáticos. Los humedales construidos han sido una tecnología ampliamente utilizada para el tratamiento de aguas residuales en zonas descentralizadas siendo una alternativa ambientalmente atractiva. En general, la tecnología de humedales construidos se diseña y se construye con monocultivos que consiste en solo una especie de planta seleccionada para el tratamiento de las aguas residuales. Se ha visto que la selección de la planta y el tipo de cultivo como los mono o policultivos (dos o más especies de plantas) mejora la eliminación de fósforo desde las aguas residuales.

Sin embargo, los estudios de humedales construidos se enfocan desde el punto de vista técnico, aumentando las eficiencias, o rendimientos del tratamiento sin investigar la evaluación o beneficios ambientales que realmente ofrecen. En este sentido, la investigación de análisis de ciclo de vida en humedales construidos que permita comparar sistemas de monocultivos con policultivos es limitada. Por lo tanto, se hace necesario evaluar si el desempeño técnico de los mecanismos de eliminación de fósforo en los humedales construidos con distintos sistemas de cultivos influye en el desempeño ambiental.

Debido a lo antes indicado, el objetivo de esta tesis de doctorado fue evaluar técnica y ambientalmente la eliminación de fósforo en sistemas de monocultivo y policultivos en un humedal construido para el tratamiento de aguas residuales, con la finalidad de evaluar el desempeño ambiental. Primero se identificaron los mecanismos de eliminación de fósforo en humedales construidos (Capítulo III, IV). Seguido por la evaluación de la asimilación de fósforo por plantas en sistemas de monocultivo y policultivo (Capítulo V). Finalmente se realizó la evaluación del desempeño ambiental de estas a través de la herramienta de análisis de ciclo de vida (Capítulo VI).

Durante este trabajo de investigación se estudió un humedal construido de flujo subterráneo horizontal (HSSF) a escala piloto con monocultivos y policultivos. Se implementaron cuatro celdas

de cultivo con un área de 4,5 m², tres se sembraron con monocultivos de *Phragmites australis* (Phr) planta comúnmente utilizada, *Schoenoplectus californicus* (Sch) especie nativa y *Cyperus papyrus* (Cyp) planta ornamental, y un policultivo se sembró con *Cyperus papyrus* y *Zantedeschia aethiopica* (Cyp/Zant) especies ornamentales. Se evaluaron parámetros fisicoquímicos e *insitu*, eficiencia de eliminación de fósforo, características de crecimiento, producción de biomasa, contenido y asimilación de fósforo y emisiones de gases de efecto invernadero (GEI), que fueron agrupadas dependiendo de la estación del año en estación cálida (primavera/verano) y estación fría (otoño/invierno).

Los resultados mostraron que la eliminación de fósforo tuvo un mejor desempeño en el sistema de policultivo plantado con especies ornamentales Cyp/Zant con una eficiencia de eliminación de 30-33%. Seguido por el monocultivo ornamental Cyp con un 22-27% y finalmente los monocultivos Phr y Sch entre un 9-18%. No se observó un efecto significativo en el rendimiento entre las estaciones cálida y fría. Sin embargo, la eliminación de fósforo fue entre 3-9% mayor en la estación fría dependiendo de la especie. La mayor parte del fósforo ingresado fue retenido por el medio de soporte (adsorción/precipitación) y microorganismos (asimilación/transformación) en el HSSF con 13-31%. Las plantas (asimilación) representaron entre un 4-26%, mientras que el fósforo en los efluentes estuvo entre 57-79%. Los principales factores que se correlacionaron con la eficiencia de eliminación de fósforo fueron la carga de fósforo, la carga hidráulica y el oxígeno disuelto.

La producción y la densidad de la biomasa vegetal varió de 1,5 a 5,4 kg de peso seco (PS)/m² y de 435 a 1298 individuos/m². La especie Sch se adaptó mejor al HSSF con una cobertura de 89% y una biomasa de 4,9 kgPS/m², esto se debió a que es una especie nativa. De manera contraria las plantas ornamentales mostraron una biomasa en el monocultivo Cyp de 1,8 kgPS/m² y el policultivo Cyp/Zant de 2,5 kgPS/m² mostrando una baja adaptabilidad, sobre todo la especie Zant. La asimilación de fósforo promedio por las plantas fue 3 gP/m² y 6 gP/m² para los monocultivos Phr y Sch y de 30 gP/m² para el monocultivo Cyp y el policultivo Cyp/Zant. Además, la asimilación de fósforo en la estación cálida fue hasta 6 veces mayor en los tallos debido a su etapa de crecimiento. Mientras que en la estación fría fue hasta 7,5 veces mayor en las raíces durante la etapa de senescencia.

El desempeño ambiental del sistema del policultivo (Cyp/Zant) presentó un impacto ambiental 14% menor que los monocultivos para la categoría eutrofización de agua dulce, reduciendo la eutrofización de aguas continentales. En cambio, en la categoría de cambio climático el policultivo Cyp/Zant mostró el mayor potencial de impacto ambiental con 8,05 kgCO₂eq/m³, principalmente debido al efecto directo de las emisiones de GEI. Dependiendo del escenario seleccionado, el impacto ambiental de la eutrofización del agua dulce llegó a ser cerca de 328 y 277 veces mayor que el impacto ambiental estimado para la categoría de cambio climático para Phr y Sch respectivamente. Mientras que fue 60 y 38 veces más para los escenarios Cyp y Cyp/Zant. Por lo tanto, una disminución sustancial de las concentraciones de fósforo (20-30%) en el efluente conllevaría a una compensación ambiental en términos de emisiones de GEI, los cuales fueron hasta 3 veces más en los sistemas de policultivos.



ABSTRACT

Accelerated urban growth forecasts dramatic increases in wastewater generation, where phosphorus is the main nutrient responsible for the eutrophication of water bodies, generating one of the biggest problems and future threats to aquatic ecosystems. Constructed wetlands have been a widely used technology for wastewater treatment in decentralized areas as an environmentally attractive alternative. In general, constructed wetland technology is designed and constructed with monocultures consisting of only one plant species selected for wastewater treatment. Plant selection and type of culture such as mono or polycultures (two or more plant species) have been found to improve phosphorus removal from wastewater.

However, studies of constructed wetlands focus on the technical point of view, increasing treatment efficiencies or yields without investigating the evaluation or environmental benefits they actually provide. In this sense, life cycle analysis research on constructed wetlands that allows comparing monoculture with polyculture systems is limited. Therefore, it is necessary to evaluate whether the technical performance of phosphorus removal mechanisms in constructed wetlands with different culture systems influences environmental performance.

Due to the above, the goal of this PhD thesis was to evaluate phosphorus removal technically and environmentally in monoculture and polyculture systems in a constructed wetland for wastewater treatment, in order to assess the environmental performance. First, the mechanisms of phosphorus removal in constructed wetlands were identified (Chapter III, IV). This was followed by the evaluation of phosphorus assimilation by plants in monoculture and polyculture systems (Chapter V). Finally, the environmental performance of these systems was evaluated using the life cycle analysis tool (Chapter VI).

During this research work, a pilot scale horizontal subsurface flow constructed wetland (HSSF) with monocultures and polycultures was studied. Four culture cells with an area of 4,5 m² were implemented, three were planted with monocultures of *Phragmites australis* (Phr) commonly used plant, *Schoenoplectus californicus* (Sch) native species and *Cyperus papyrus* (Cyp) ornamental plant, and one polyculture was planted with *Cyperus papyrus* and *Zantedeschia aethiopica* (Cyp/Zant) ornamental species. Physicochemical and insitu parameters, phosphorus removal efficiency, growth characteristics, biomass production, phosphorus content and assimilation, and

greenhouse gas (GHG) emissions were evaluated, which were grouped depending on the season of the year into warm season (spring/summer) and cold season (fall/winter).

The results showed that phosphorus removal performed best in the polyculture system planted with Cyp/Zant ornamental species with a removal efficiency of 30-33%. Followed by the Cyp ornamental monoculture with 22-27% and finally the Phr and Sch monocultures between 9-18%. No significant effect on yield was observed between warm and cold seasons. However, phosphorus removal was between 3-9% higher in the cold season depending on the species. Most of the incoming phosphorus was retained by the supporting medium (adsorption/precipitation) and microorganisms (assimilation/transformation) in the HSSF with 13-31%. Plants (assimilation) accounted for 4-26%, while phosphorus in effluent was between 57-79%. The main factors that correlated with phosphorus removal efficiency were phosphorus loading, hydraulic loading and dissolved oxygen. Plant biomass production and density ranged from 1.5 to 5.4 kg dry weight (DW)/m² and from 435 to 1298 individuals/m². The Sch species was best adapted to the HSSF with a cover of 89% and a biomass of 4.9 kgPS/m², this was because it is a native species. On the contrary, the ornamental plants showed a biomass in the Cyp monoculture of 1.8 kgPS/m² and the Cyp/Zant polyculture of 2.5 kgPS/m² showing a low adaptability, especially the Zant species. The average phosphorus assimilation by the plants was 3 gP/m² and 6 gP/m² for the Phr and Sch monocultures and 30 gP/m² for the Cyp monoculture and the Cyp/Zant polyculture. Moreover, phosphorus assimilation in the warm season was up to 6 times higher in the stems due to their growth stage. While in the cold season it was up to 7.5 times higher in roots during the senescence stage.

The environmental performance of the polyculture system (Cyp/Zant) showed a 14% lower environmental impact than monocultures for the freshwater eutrophication category, reducing the eutrophication of inland waters. In contrast, in the climate change category, the Cyp/Zant polyculture showed the highest potential environmental impact with 8.05 kgCO₂eq/m³, mainly due to the direct effect of GHG emissions. Depending on the selected scenario, the environmental impact of freshwater eutrophication became about 328 and 277 times higher than the environmental impact estimated for the climate change category for Phr and Sch respectively. While it was 60 and 38 times higher for the Cyp and Cyp/Zant scenarios. Therefore, a substantial decrease in phosphorus concentrations (20-30%) in the effluent would lead to an environmental offset in terms of GHG emissions, which were up to 3 times higher in the polyculture systems.

CAPÍTULO I

INTRODUCCIÓN



1. AGUAS RESIDUALES

Las aguas residuales son un componente crítico del ciclo del agua. Generalmente, reciben menos atención en comparación con los retos de abastecimiento y agua potable, especialmente en un contexto de escasez hídrica (WWAP, 2017). La cantidad de agua residual generada por una población es proporcional al consumo de agua potable. Además, el crecimiento acelerado urbano, pronostica aumentos dramáticos en la generación de aguas residuales. El aumento de la población y de los ritmos de consumo significan a su vez un aumento de la producción de aguas residuales. Por lo tanto, se hace necesario su gestión, siendo fundamental en la agenda 2030, para los objetivos de desarrollo sostenible (ODS) (NU, 2018). Las aguas residuales se consideran como *“una combinación de uno o más de los siguientes elementos: efluentes domésticos que consisten en aguas negras (excremento, orina y lodos fecales) y aguas grises (aguas residuales de lavado y baño); agua de establecimientos comerciales e instituciones, incluidos hospitales; efluentes industriales, aguas pluviales y otras escorrentías urbanas; y escorrentías agrícola, hortícola y acuícola”* (Raschid-Sally y Jayakody, 2008).

Las aguas residuales se pueden clasificar de acuerdo con su origen demográfico o su composición. Según su origen estas pueden ser de tipo urbano o rural ya sea por la cantidad producida o por la densidad poblacional. Sin embargo, esta clasificación es variada según la demografía; en USA el consumo por asentamiento rural se considera $< 3800 \text{ m}^3/\text{L}$, en UE $< 2000 \text{ hab-Eq}$, mientras que en Chile menor a 1.000 habitantes (USEPA, 2000; Unión Europea en la directiva EU 91/271; Araya et al., 2014). En cuanto a las estimaciones de las producciones de aguas residuales en Chile, la generación de tipo urbano varía entre $150\text{-}170 \text{ L}/(\text{hab}\cdot\text{d})$, y para las aguas residuales de tipo rural se estima un valor de $130\text{-}160 \text{ L}/(\text{hab}\cdot\text{d})$ (Vera, 2012). Por otro lado, de acuerdo a la composición química puede variar entre aguas concentrada, media o diluida según las características.

1.1. Características de las aguas residuales

Las aguas residuales están compuestas por un 99% de agua y por un 1% de sólidos suspendidos, coloidales y disueltos. Normalmente los componentes de las aguas residuales tienden a ser una compleja mezcla de compuestos orgánicos e inorgánicos lo que permite caracterizarlas de distintas formas. Por lo tanto, para realizar una adecuada gestión de dichas aguas, es imprescindible

conocer en forma más detallada su naturaleza. La calidad de las aguas residuales puede definirse por sus características físicas, químicas y biológicas (Liu y Lipták, 2020).

Los parámetros físicos incluyen el olor, la temperatura, los sólidos, temperatura, la turbidez el color y olor; **a)** Los sólidos de las aguas residuales pueden ser sedimentables, suspendidos o disueltos. Aproximadamente, el 60% de los sólidos son sedimentables y un 75% de los sólidos son de naturaleza orgánica (Vidal y Araya, 2014). Los sólidos suspendidos totales (SST) son aquellos que son visibles y por lo general flotan en las aguas residuales entre la superficie y el fondo, estos pueden ser removidos utilizando procesos de sedimentación o filtración. Por otro lado, los sólidos suspendidos volátiles (SSV) representan la fracción de sólidos suspendidos que se volatilizan a 600° C convirtiendo la materia orgánica en CO₂ y H₂O (Liu y Lipták, 2020); **b)** La temperatura puede determinar la solubilidad de diversos gases como el oxígeno y también puede ejercer efecto en las reacciones químicas y biológicas que pueden ocurrir en las aguas (Vidal y Araya, 2014); **c)** La turbiedad y el color, son características relacionadas con la materia en suspensión, organismos microscópicos y partículas que afectan el traspaso de la luz a través del agua (Liu y Lipták, 2020); **d)** El olor causado por los gases liberados durante el proceso de descomposición de la materia orgánica en las aguas residuales (Liu y Lipták, 2020).

Los parámetros químicos están asociados al contenido orgánico e inorgánico de las aguas residuales; **a)** El pH, que expresa una tendencia de acidez o alcalinidad de una solución y generalmente se encuentra en un rango neutro (6,5-8,5) en las aguas residuales; **b)** Los nutrientes, compuestos principalmente por nitrógeno (orgánico, amoníaco, nitrito y nitrato) y fósforo (fosforo orgánico e inorgánico) en sus diferentes formas; **c)** Los metales pesados como arsénico (As), cadmio (Cd), cromo (Cr), plomo (Pb), mercurio (Hg) y plata (Ag), como también los cloruros, sulfuros y sulfatos; **d)** La demanda química de oxígeno (DQO), que es definida como la masa de oxígeno necesaria para la completa oxidación de los componentes orgánicos del agua, **e)** La demanda biológica de oxígeno a los cinco días (DBO₅) que se relaciona con la medición del oxígeno disuelto que consumen los microorganismos durante el proceso de oxidación bioquímica de la materia orgánica durante 5 días, cuyos valores típicos en las aguas residuales varían de 400 a 100 mg/L de DBO₅ (Liu y Lipták, 2020).

Las características biológicas de las aguas residuales son de gran importancia, ya que se asocian principalmente con la presencia de microorganismos tales como bacterias, protozoos, helmintos, rotíferos, algas, entre otros, siendo las bacterias, las que se encuentran en mayor abundancia. Los parámetros bacteriológicos incluyen coliformes, coliformes fecales, patógenos específicos y virus. En la Tabla 1.1 se muestran los rangos de los parámetros fisicoquímicos típicos medidos en las aguas residuales de tipo urbano o rural.

Tabla 1.1. Parámetros fisicoquímicos típicos encontrados en las aguas residuales (sin tratar) en zonas urbanas y rurales.

Parámetro	Unidad	Asentamiento urbano	Asentamiento rural
Demanda biológica de oxígeno (DBO ₅)	mg/L	110-800	200-500
Demanda química de oxígeno (DQO)	mg/L	210-1600	200-1600
Sólidos suspendidos totales (SST)	mg/L	120-450	100-500
Nitrógeno total (NT)	mg/L	20-85	35-10
Amonio (NH ₄ ⁺)	mg/L	12-50	6-60
Nitrógeno total Kjeldahl (NTK)	mg/L	20-80	-
Nitrato (NO ₃ ⁻)	mg/L	<1	<1
Fósforo total (PT)	mg/L	2-23	6-30
Fosfato (PO ₄ ⁻³)	mg/L	3-14	6-25
Coliformes fecales (CF)	NMP/100 ml	1,0E3–2,0E8	1,0E6–1,0E10

NMP: Numero Más Probable

Fuente: (Vidal y Araya, 2014).

2. FÓSFORO EN LAS AGUAS RESIDUALES

El fósforo (P) es un elemento esencial para la vida, cumpliendo un rol fundamental en los procesos de la bioenergía celular formando parte de las moléculas de ATP y ADP. Por lo tanto, el fósforo no tiene sustituto y es un recurso no renovable necesario para el desarrollo de la vida y el funcionamiento de los ecosistemas terrestres, acuáticos, la productividad agrícola, entre otros. Dada esta relación (P/crecimiento) el fósforo biológicamente es un nutriente limitante, es decir el nutriente que alcanza su mínimo o consumo total antes que otros nutrientes (Blank, 2012). Sin

embargo, dada esta relación estequiométrica su escasez y abundancia genera una paradoja pasando de nutriente a contaminante (Cordell y White, 2014).

El fósforo en las aguas residuales se mide a través del fósforo total, que es un indicador ambiental para aguas, donde aproximadamente el 70% se encuentra como fósforo inorgánico y el 30% como fósforo orgánico en aguas residuales (Valsami-Jones et al., 2004). Los valores de fósforo total en las descargas de aguas residuales van desde 2-30 mg P/L variando entre zonas urbanas y rurales (Vidal y Araya, 2014). Se prevé que el flujo de fósforo en el ecosistema podría aumentar en un 150% de 1,3 a 3,3 millones de toneladas anuales entre el año 2000 al 2050. Esto se debe principalmente al crecimiento de la población, la rápida urbanización, el aumento del número de hogares con saneamiento y conexiones a los sistemas de alcantarillado, y a la falta de eliminación de nutrientes en los sistemas de tratamiento de aguas residuales (OCDE, 2012).

Debido a este constante aumento de la población mundial, lo que a su vez significa un aumento de los requerimientos alimenticios, el uso de fertilizantes ricos en nutrientes se ha intensificado aumentando significativamente los flujos naturales de fósforo hacia la atmósfera, suelos, aguas continentales y finalmente los océanos. Rockström et al. (2009), asegura que estamos próximos a superar el umbral del ciclo de fósforo, donde los niveles actuales (1,5 Mt P/año) ya superan los umbrales críticos para muchos estuarios y sistemas de agua dulce, y asegura que el límite del flujo hacia los océanos no debe aumentar diez veces el flujo natural de fósforo. Esto se debe al aumento del consumo de fertilizantes, la mala gestión de los desechos animales, el cambio de uso de suelo y las descargas de fuentes puntuales domésticas o industriales y fuentes difusas (Liu et al., 2008). Los flujos que conllevan pérdidas de fósforo incluyen la erosión del suelo, la escorrentía superficial (fuentes difusas) y descargas de fuentes puntuales (Rittmann et al., 2011). Alrededor del 62% de la carga de fósforo es de fuentes puntuales (aguas residuales (54%) e industriales (8%)), mientras que las fuentes difusas (agricultura (38%)) contribuyen con el resto (Mekonnen y Hoekstra, 2018). Dichas fuentes pueden generar serios problemas ambientales, tales como: acumulación de sedimentos, contaminación de aguas subterráneas y principalmente la eutrofización de las aguas continentales (Smith y Schindler, 2009).





2.1. Impactos ambientales del fósforo en aguas residuales

Los problemas ambientales que se asocian a las descargas de fósforo tienen un fuerte impacto sobre los ecosistemas tanto terrestres como acuáticos. En el caso del fósforo presente en las aguas residuales, se ve un efecto directo en los ecosistemas acuáticos, reduciendo su calidad y alterando los sistemas ecológicos, los cuáles se pueden intensificar por el volumen de descarga, composición de las descargas o por las características de los cuerpos receptores (OCDE, 1982; Mekonnen y Hoekstra, 2018). Uno de los principales impactos del fósforo es la eutrofización de las aguas continentales. La eutrofización es uno de los problemas más grandes y una amenaza real de los ecosistemas acuáticos, 5 de los 4 continentes presentan problemas de eutrofización en lagos, entre un 41 y 54% de sus lagos eutrofizados (Dokulil y Teubner, 2010). Este fenómeno consiste en el enriquecimiento principalmente de nitrógeno (N) y fósforo, que, asociados a buenas condiciones de luz, provoca floraciones de cianobacterias que son tóxicas para los seres humanos y el ganado, su excesivo crecimiento agota el oxígeno disuelto en el agua, causando la muerte de peces, y muchos problemas relacionados con los suministros de agua, pérdida de la biodiversidad y otros servicios ecosistémicos (Smith y Schindler, 2009). Este aumento de las algas cianobacterias es responsable del color verde de las masas de agua como lagos, embalses, ríos. Un experimento en Canadá realizado por Schindler et al. (1973), pudo comprobar que el fósforo es el nutriente limitante, por lo tanto, es el principal factor de la eutrofización.

Finalmente, la eutrofización de en las aguas dulces y en los océanos costeros, con la posible escasez de fósforo en las próximas décadas, pueden tener un impacto cada vez mayor debido al cambio climático. Se prevé que el cambio climático afectará el destino fósforo de forma directa con cambios temporales y espaciales debido a los cambios de temperaturas y el patrón de precipitaciones (Schoumans et al., 2015). La Tabla 1.2 muestra la clasificación trófica de los cuerpos de agua señala por Smith et al. (1999). Según esto, la eutrofización se desata en ríos y lagos con concentraciones de 0,03 a 1 mgP/L (OCDE, 2012; Smith et al. (1999). Un caso de estudio es el lago Lanalhue en el sur de Chile, donde se encontraron concentraciones promedio de fósforo total de 0,08 mg/L, por lo que presenta una condición trófica de un cuerpo de agua eutrófico (EULA, 2018).

Por otra parte, se calcula que el deterioro de la calidad del agua ya ha reducido la biodiversidad de los ríos, lagos y humedales en aproximadamente un tercio a nivel mundial, con las mayores pérdidas en China, Europa, Japón, el sur de Asia y el sur de África. En países en desarrollo según la OCDE, (2012) se espera que aumenten este tipo de condiciones por dos razones, descargas directas de las aguas residuales y el aumento de la producción agrícola. Alrededor de 2500 millones de personas aún carecen de servicios de saneamiento, lo que, combinado con la rápida urbanización, el crecimiento de la población y la infraestructura deficiente promueve la propagación de enfermedades y la liberación desenfrenada de nutrientes como el fósforo, lo que genera importantes preocupaciones ambientales y de salud (Gallego-Schmid y Tarpani, 2019).

Tabla 1.2. Rango de condición trófica.

Condición trófica	Fósforo total (mg/L)	Nitrógeno total (mg/L)	Clorofila a (µg/L)	Color
Oligotrófica	< 0,01	< 0,35	< 3,5	
Mesotrófica	0,01-0,03	0,35 – 0,65	3,5 - 9	
Eutrófica	0,03 – 1,0	0,65- 1,2	9 - 25	
Hipereutrófica	> 1,0	> 1,2	> 25	

Fuente: (Smith et al., 1999).

3. TRATAMIENTOS DE AGUAS RESIDUALES

La gestión de las aguas residuales ha sido una parte importante de las civilizaciones a lo largo de los milenios, evidenciando en consecuencia muchos aspectos sociológicos y avances tecnológicos a lo largo de los años (Gallego-Schmid y Tarpani, 2019). Con el pasar de los años, nacieron las plantas de tratamiento de aguas residuales (PTAR), que han sido diseñadas y operadas para reducir la contaminación de las aguas residuales producidas por las actividades humanas con el fin de minimizar las influencias negativas sobre la calidad ambiental y la salud humana (Zang et al., 2015). Convenientemente el diseño de las PTAR se va modificando según las necesidades de calidad ambiental regionales y globales, marcos regulatorios, crecimiento económico, ubicación geográfica y desarrollo social (Gallego-Schmid y Tarpani, 2019). Por lo tanto, la tecnología seleccionada estará fuertemente relacionada con estas necesidades.

En Chile existe un porcentaje de cobertura sanitaria del 99,9% de tratamiento de aguas residuales y un 97,3% de alcantarillado para las zonas urbanas. Lo cual ubica a nuestro país como uno de los países con mejor cobertura sanitaria a nivel latinoamericano y a nivel de países desarrollados miembros de la OCDE. En la actualidad, Chile cuenta con 301 PTAR. La tecnología más utilizada en el país es el sistema de lodos activados, representando el 57,8% del total de plantas existentes; seguida de las lagunas aireadas (18,3%), los emisarios submarinos (11,0%) y otras tecnologías (12,9%) (SISS, 2020). Sin embargo, la población rural (conformada por un 13%), solo un 18-20% cuenta con servicio de alcantarillado y la cobertura de los sistemas de tratamiento solo alcanza un 10% para la población rural (SISS, 2020).

El proceso de tratamiento de las aguas residuales posee tres partes, recolección, tratamiento y descarga. Donde el sistema de tratamiento de aguas consta de 3 etapas: **a) Tratamiento Primario;** **b) Tratamiento Secundario;** y **c) Tratamiento Terciario.** El tratamiento primario reduce los sólidos en suspensión del agua residual haciendo sedimentar los materiales suspendidos usando tratamientos físicos y químicos. El proceso químico consiste en la adición de reactivos químicos o bien por las propiedades químicas de diversos compuestos. El tratamiento secundario elimina la materia orgánica biodegradable presente en forma disuelta o coloidal, mediante procesos biológicos en que microorganismos, fundamentalmente bacterias, realizan reacciones metabólicas, produciendo la degradación y posterior mineralización de la materia orgánica. Por último, el tratamiento terciario consiste en obtener mejores rendimientos de eliminación de DBO₅ y materia orgánica en suspensión y en forma disuelta, así como también reducir otros contaminantes como nutrientes, patógenos y metales. En esta etapa se pueden aplicar tratamientos físicos, químicos y biológicos (Metcalf and Eddy, 2003; Vera, 2012; Vidal y Araya, 2014). Dicho esto, los tratamientos secundarios o terciarios implican el uso de tecnologías que se pueden clasificar como sistemas convencionales o no convencionales de tratamiento.

3.1. Sistemas convencionales para el tratamiento de aguas residuales

Las tecnologías para el tratamiento de aguas residuales que se engloban bajo la denominación de sistemas convencionales se emplean en asentamientos urbanos de los países desarrollados, y se caracterizan por ser tecnologías mecanizadas, con altos consumos energéticos, bajo valor estético, y necesidad de personal especializado para su mantenimiento (García y Corzo, 2008). Algunos

mecanismos que destacan son sedimentación, filtración, adsorción, precipitación química, intercambio iónico, degradación biológica, entre otras. Estos procesos ocurren de forma secuencial en tanques y reactores, y a velocidades aceleradas gracias al aporte de energía. Por tanto, son consideradas como una solución intensiva desde el punto de vista de la energía, y de la poca área superficial necesaria para su implementación. La Figura 1.1 resume el tratamiento de aguas residuales según las tecnologías para las PTAR (Vera, 2012; García y Corzo, 2008). Las tecnologías convencionales más utilizadas en Chile son lodos activados, lagunas aireadas, reactores anaerobios y flujo continuo, tratamiento primario + desinfección, biodisco entre otros (Vera, 2012; Vidal y Araya, 2014).

3.2. Sistemas no convencionales para el tratamiento de aguas residuales

Las tecnologías para el tratamiento de aguas residuales denominadas como sistemas no convencionales o soluciones basadas en la naturaleza se emplean para los asentamientos rurales o de baja población. Este tipo de tecnologías se basa en el uso de procesos naturales, de baja manipulación y operación. Estas tecnologías se emplean para la eliminación de DBO₅, nitrógeno y fósforo, sin emplear en el proceso algún tipo de aditivo químico. Además, las tecnologías basadas en la naturaleza están caracterizadas por la escasa necesidad de personal de mantenimiento, un consumo energético reducido, una baja o nula producción de lodos, y pueden generar un realce estético al emplear componentes del medio natural. Se ubican cerca del origen con gran adaptabilidad debido al bajo o nulo uso de energía, bajo costo económico o personal capacitado.

Las tecnologías no convencionales que destacan son sistemas de lombrifiltro, fosa séptica, biofiltro, zanjón de infiltración y los humedales construidos. Sin embargo, una de sus principales desventajas incluye bajos porcentajes de remoción de materia orgánica (30-90%) nutrientes (10-60%). En comparación los sistemas convencionales como lodos activados y reactores anaerobios que alcanzas remoción de materia orgánica de 90-98% y nutrientes 15-90% (Vera, 2012).

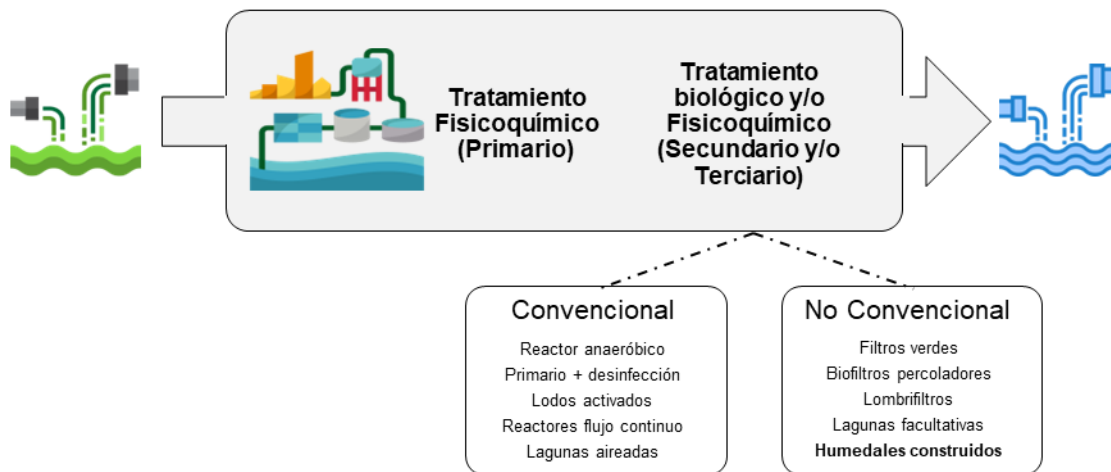


Figura 1.1. Cuadro resumen de tecnologías convencionales o no convencionales para el tratamiento de aguas residuales. *Fuente: Elaboración propia.*

4. SISTEMAS NO CONVENCIONALES: HUMEDALES CONSTRUIDOS PARA EL TRATAMIENTO DE AGUAS RESIDUALES

Dentro de las tecnologías basadas en la naturaleza están los humedales construidos, los cuáles han resultado ser una solución atractiva para el tratamiento de aguas residuales, de aguas pluviales, de aguas residuales industriales y provenientes de la escorrentía agrícola (Kadlec y Wallace, 2009; Vyzamal, 2010). Los humedales construidos se han desarrollado como un tratamiento biológico de tecnología natural, sostenible y de bajo impacto ambiental que produce beneficios más allá del tratamiento convencional de las aguas residuales; dichos beneficios incluyen espacios verdes, filtración del aire, hábitat de la fauna, conservación de la biodiversidad, disminución de los costes energéticos, reciclaje de nutrientes, reutilización de los efluentes para la agricultura o el riego, y fuente potencial de alimentación animal o cultivo de biocombustibles (Ingrao et al., 2020).

Durante los últimos años los humedales construidos han ganado terreno para tratar las aguas residuales tanto municipales como industriales en muchas regiones con diferentes climas como tropical, árido o boreal (Ingrao et al., 2020). Esta tecnología destaca por su bajo costo, con diseños de fácil operación y mantención, presentan un bajo consumo energético y poseen una buena integración al medio ambiente (Vyzamal, 2007; Wu et al., 2015). En este sentido los humedales

construidos están enfocados para su uso en sectores rurales dado que dependiendo del humedal estos requieren una superficie específica por persona equivalente (PE), los valores de superficie pueden ir desde 1 a 20 m²/PE (Kadlec y Wallace, 2009). Por lo tanto, para sectores urbanos con una densidad poblacional elevada no sería factible el uso de esta tecnología por la falta de espacio.

Los humedales construidos involucran distintos componentes como la vegetación, el medio de soporte, suelo, agua y microorganismos, lo que permite que por mecanismos físicos, químicos y biológicos se logre depurar los efluentes líquidos (Vymazal, 2010). Por lo tanto, estos componentes son factores cruciales que influyen en el desempeño de los humedales construidos los cuales cambian directa o indirectamente los procesos primarios de eliminación de contaminantes. La principal función de estos sistemas es la eliminación de la carga orgánica, nutrientes, organismos patógenos y contaminantes emergentes (Wu et al., 2015).

La biodegradabilidad de los efluentes residuales y las cargas de entrada son factores críticos para lograr mayores tasas de eliminación utilizando sistemas de humedal construido (Saeed y Sun, 2017). Los humedales construidos han demostrado tener una alta eficiencia de remoción de materia orgánica y nutrientes como nitrógeno y fósforo con rendimientos de 30-95%, 20-75% y 10-78% respectivamente (López et al., 2015; Vymazal, 2007; Vymazal, 2010). En el caso de los nutrientes, Vymazal (2007) demostró que el nitrógeno y el fósforo tenían eficiencias de remoción de 40-55% y 40-60% respectivamente. En el caso del fósforo, la carga eliminada varió entre 45 y 75 gP/m²año según el tipo de humedal construido y la carga de entrada.

La variabilidad en la eficiencia del tratamiento de las aguas residuales en un humedal construido se ve influenciada por distintos factores como la hidráulica, la dirección de flujo y el tipo de vegetación. La Figura 1.2 muestra la clasificación de los tipos de humedales construidos (Kadlec y Wallace 2009). Según la hidráulica, el tipo de circulación del agua, los humedales se clasifican en flujo superficial, o también llamado flujo de agua libre (FWS), y en flujo subsuperficial, a su vez los humedales construidos de flujo subsuperficial se pueden clasificar según la dirección de flujo del agua en horizontales (HSSF) o verticales (VSSF). Otra clasificación es el tipo de vegetación a utilizar, pueden ser macrófitas flotantes, macrófitas enraizadas emergentes o sumergidas (Kadlec y Wallace 2009). Además, se pueden combinar varios tipos de configuraciones de humedal construido para lograr un mayor efecto de tratamiento, estos se llaman sistemas híbridos.

Generalmente se realiza la combinación para lograr una mayor eficiencia en un tratamiento más complejo o específico (Kadlec y Wallace 2009; Vymazal 2010).

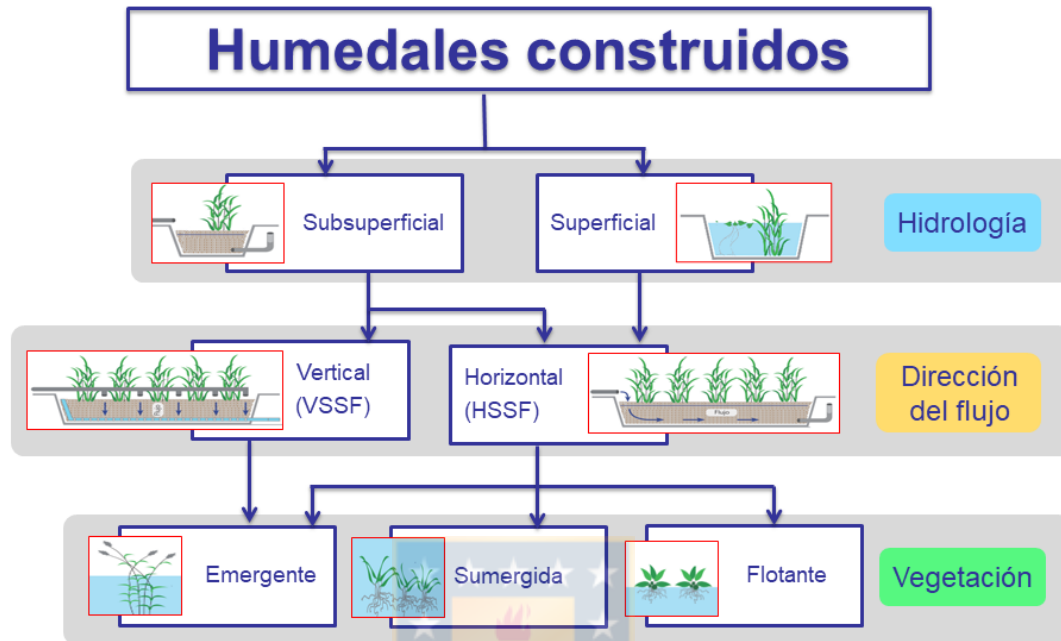


Figura 1.2. Clasificación de los humedales construidos para el tratamiento de efluentes líquidos. Fuente: Adaptado de Vymazal, (2007); Kadlec y Wallace, (2009).

4.1. Humedales construidos de flujo horizontal subsuperficial (HSSF en inglés)

Los HSSF, consisten en un lecho rectangular plantado con vegetación emergente, donde el agua es alimentada por un extremo del sistema y fluye lentamente, siguiendo una trayectoria horizontal por debajo de la superficie fluyendo de manera uniforme a través del medio poroso para ser recolectada finalmente a la salida del sistema (López et al., 2015). Tienen una pendiente de fondo entre 0,5 a 1% que está cubierta por una lámina impermeable con profundidades que no exceden los 0,6 m (Kadlec y Wallace, 2009). En comparación con otros tipos de humedales construidos presentan una serie de ventajas como la disminución de malos olores y la menor presencia de vectores, permite protección a variaciones de temperaturas y poseen una mayor área superficial disponible para el tratamiento y crecimiento de biopelículas sobre el medio de soporte y asociadas a las raíces de las macrófitas (Wu et al., 2015).

En estos sistemas, los contaminantes se eliminan por degradación microbiana, procesos químicos y físicos, poseen zonas aeróbicas restringidas a las áreas adyacentes a las raíces de las plantas y zonas anaeróbicas y anóxicas en la zona del medio filtrante (Vymazal, 2010). Los compuestos orgánicos se degradan eficazmente principalmente por degradación microbiana en condiciones anóxicas/anaeróbicas, ya que la concentración de oxígeno disuelto en el medio de soporte es muy limitada. La Tabla 1.3 muestra las características de diseño, operación y depurativas de este tipo de humedales. En los HSSF las eficiencias de eliminación varían entre 65-95% con cargas de entrada de 3-15 gDBO₅/m²d (López et al., 2015); los sólidos en suspensión se retienen predominantemente por filtración y sedimentación y la eficiencia de eliminación suele ser muy alta (> 80%). El principal mecanismo de eliminación de nitrógeno en los HSSF es la desnitrificación con eficiencias del 20-75% con cargas de entrada de 1-10 gNT/m²d. Mientras que la eliminación de fósforo muestra eficiencias de 15-78% con cargas de 0,04-0,6 gPT/m²d.

Varios estudios se han centrado en el diseño, operación, desarrollo y rendimiento de los humedales construidos (Stefanakis y Tsihrintzis 2012; Wu et al., 2015), y en la capacidad de estos sistemas diseñados para eliminar contaminantes. Varma et al. (2021) estudiaron los factores que pueden afectar el rendimiento de los humedales construidos, los cuales incluyen: la tasa de carga hidráulica (HLR), el tiempo de retención hidráulica (HRT), el pH, la temperatura y el oxígeno disuelto (DO). Asimismo, Gorgoglione y Torretta (2018) determinaron que para un buen desempeño del humedal construido está influenciado por varios factores que incluyen la vegetación, los tipos de medio de soporte y la hidráulica/hidrología, niveles de agua y el tiempo de residencia. Sin embargo, hay menos estudios que se centran en la operación sostenible y el efecto ambiental que hay en la aplicación y operación de estos sistemas. El control de algunos parámetros podría disminuir el impacto ambiental. Por lo tanto, este tema sigue siendo un desafío. En particular, las especies de plantas y medio de soporte son factores críticos que influyen en la capacidad de eliminación de contaminantes sobre todo en la actividad de eliminación de fósforo.

Tabla 1.3. Características de operación, diseño y depurativas de los humedales construidos.

Tipo de humedal construido	Características de diseño		Características de operación		Características depurativas					
	Profundidad [m]	Área unitaria [m ² /P.E.]	HRT [d]	HLR [mm/d]	Materia orgánica		Nitrógeno		Fósforo	
					Cargas aplicadas [gDBO ₅ /m ² d]	Eficiencias eliminación [%]	Cargas aplicadas [gNT/m ² d]	Eficiencias eliminación [%]	Cargas aplicadas [gPT/m ² d]	Eficiencias eliminación [%]
Flujo superficial (FWS)	0,06-1,2	5,0-20	5,0-15	12-50	1,0-11	54-88	0,02-4,2	20-52	0,1	10-66
Flujo subsuperficial horizontal (HSSF)	0,3-1,0	1,2-12	2,0-10	20-50	3,0-15	65-95	1,0-10	20-75	0,04-0,6	15-78
Flujo subsuperficial vertical (VSSF)	0,5-1,4	0,85-5,5	1,0-2,0	27-110	10-60	30-95	2,8-30	35-55	0,06	23-60

P.E.: Personas equivalentes; HRT: Tiempo de retención hidráulico; HLR: Tasa de carga hidráulica.

Adaptado de López et al., (2016a).

4.2. Mecanismos de eliminación de fósforo en HSSF

La eliminación de fósforo en los HSSF se genera a través de procesos que se basan en principios biológicos y ciclos biogeoquímicos, donde el grado de participación de estos procesos dependen del tipo de humedales construidos y sus componentes bióticos y abióticos (Vymazal 2007). La Figura 1.3 muestra las distintas transformaciones de fósforo en el suelo y en la columna de agua, la cual incluye procesos como adsorción, desorción, precipitación, descomposición, fragmentación, lixiviación, mineralización, sedimentación y asimilación de plantas y microorganismos (Vymazal y Kröpfelová 2008).

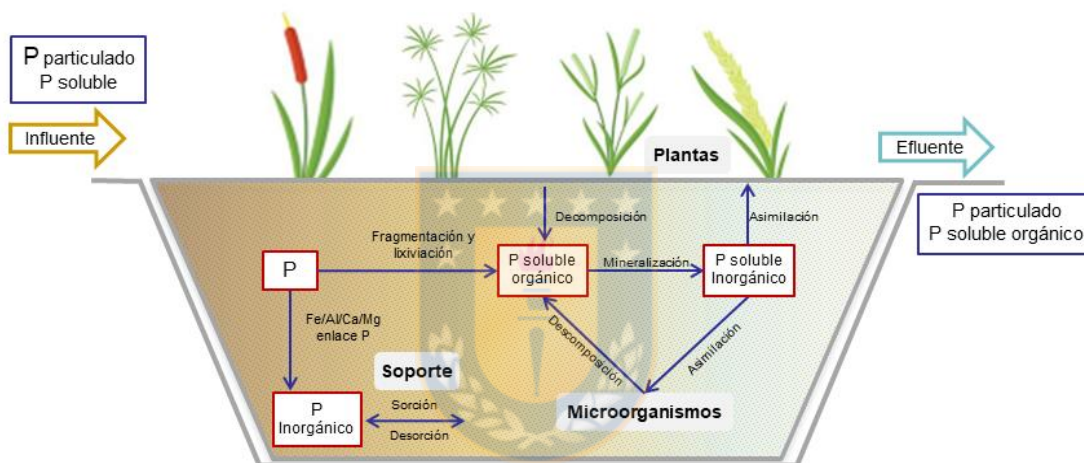


Figura 1.3. Transformaciones de fósforo en humedales construidos de flujo horizontal subsuperficial (HSSF). Fuente: elaboración propia.

El fósforo entra como partícula o soluble a la columna de agua del HSSF que es rápidamente absorbido por la biopelícula que crece adherida al medio de soporte, a las raíces y a los rizomas de las plantas (Kadlec y Wallace, 2009). En la biopelícula ocurre la eliminación biológica de fósforo en forma de fosfato a través de la asimilación de plantas y microorganismos; y la mineralización de los restos de vegetación y del fósforo orgánico soluble (Vymazal y Kröpfelová, 2008). Parte del fósforo particulado no es absorbido por las plantas o microorganismos y tiende a precipitar generando acumulación. Esta precipitación y posterior sorción de fósforo está estrechamente relacionada con las propiedades fisicoquímicas e hidrológicas del material del medio de soporte (Vohla et al., 2011). La sorción de fósforo en los HSSF está controlada por la interacción del

potencial de óxido-reducción (ORP), valores de pH y minerales de Fe, Mg, Al y Ca (DeLaune y Reddy, 2008).

La eficiencia de remoción de fósforo por lo tanto se puede generar a través de la asimilación por planta (25-30%), asimilación por microorganismos (12-13%), precipitación con cationes (Ca, Mg, Fe, Al) adsorción en el medio de soporte (38-46%) (López et al., 2016). La selección del medio de soporte es el proceso de mayor relevancia en un humedal construido para la eliminación de fósforo (Vohla et al., 2011). Algunos materiales son naturales como la grava, zeolita, arena, y otros corresponden a productos artificiales como la bentonita o subproductos industriales (escorias de hornos) (Arias et al., 2001; Vohla et al., 2011; Saeed et al., 2017). La participación de los microorganismos en los humedales es fundamental depende de los microorganismos acumuladores de polifosfato (PAO siglas en ingles) para absorber el fósforo de las aguas residuales, en exceso más allá de sus requerimientos de crecimiento, en condiciones anaeróbicas y aerobias/anóxicas, por lo que concentran el fósforo en la biomasa (Yuan et al. 2012). El fósforo de los influentes en un humedal construido es asimilado por las plantas a través de las hojas y las raíces (Vymazal, 2007). En particular, las especies de plantas es un factor crítico que influyen en la capacidad de eliminación de fósforo.

4.2.1. Plantas Tipo de planta

La literatura sobre el área es amplia, pero la mayoría de los estudios tienden a dar mayor peso a los aspectos de ingeniería de un sistema de humedales y una importancia limitada a las especies de plantas. Las funciones de las plantas en los humedales construidos son la provisión de sustrato (raíces y rizomas) para el crecimiento de bacterias adheridas, pérdida radial de oxígeno (difusión de oxígeno desde las raíces a la rizosfera) y asimilación de nutrientes. El fósforo es un requerimiento principal para el crecimiento y reproducción de las plantas, las macrófitas enraizadas absorben los nutrientes principalmente a través de sus sistemas de raíces. El fosfato soluble (ortofosfato) es la única forma de fósforo que se cree que es utilizada directamente por algas y macrófitas. Este es asimilado a través de las células epidérmicas y lo utilizan para sintetizar materiales orgánicos para su propio crecimiento (Wang et al., 2008b). Por lo tanto, representa un vínculo importante entre el ciclo de fósforo orgánico e inorgánico en los humedales construidos (Vymazal, 2007).

La acumulación de nutrientes en las plantas es limitada, es decir, representa sólo una pequeña proporción (2-9%) de las tasas de cargas debido a la capacidad de saturación de la planta (Luo et al., 2018; Vohla et al., 2005; López et al., 2015). Este almacenamiento de fósforo en la biomasa aérea de las macrófitas emergentes suele ser a corto plazo, debido a que la absorción de la planta representa sólo el almacenamiento temporal porque los nutrientes se liberan al agua después de la descomposición de la planta. Por lo tanto, las porciones de macrófitas sobre el suelo devuelven el fósforo al agua, en el caso de FWS mientras que en los HSSF y VSSF, devuelve el fósforo bajo tierra (Kadlec y Wallace, 2009; Vyzamal, 2007).

La eficiencia de la planta en un humedal construido depende de varios factores: tipo del humedal, (por ejemplo, flujo vertical, horizontal, superficial o subsuperficial, con o sin recirculación), calidad y cantidad de las cargas de los efluentes residuales, sus combinaciones como sistemas de cultivos, estaciones y clima, el tipo de medio de soporte y la gestión de la planta, como el régimen de cosecha (Shelef et al., 2013). Sobre todo, la elección de las especies de plantas es un aspecto particularmente importante en el diseño y hay varios factores que afectan, como la distribución geográfica, el clima y las condiciones del hábitat, la disponibilidad de las plantas en los viveros, el mantenimiento a largo plazo y los objetivos del proyecto, deben ser tomados en consideración (Leto et al., 2013). Las plantas más comunes utilizadas en los humedales construidos son *P. australis* (35,29 %), *T. latifolia* (17,65 %), *J. effusus* (8,82 %), *P. arundinacea* (7,84%) y *Z. latifolia* (5,88%) (Xu et al., 2019). Las especies como *Phragmites* y *Typha* spp. han sido más utilizadas debido a su tolerancia a cambios sustanciales en pH (4-10), salinidad (20-45 mgCl/L), temperatura (10-32 °C) y asimilación de nutrientes (López et al., 2016).

Una especie de las más utilizadas es *P. australis* que ha mostrado sus beneficios, como su gran capacidad de propagación a largo plazo, su desarrollo radicular vertical aumentando la conductividad hidráulica en un humedal construido, sus rizomas y la gran variedad de vida que alberga, lo que potencia el tratamiento del humedal construido (Uddin y Robinson, 2018; Zheng et al., 2020). Por el contrario, una especie poco común y menos conocida es *S. californicus*, que se distribuye a lo largo de las costas del Atlántico y del Pacífico de América, desde California hasta Chile siendo una especie nativa en Chile (Macía y Balslev, 2000). Similar a *S. californicus* es *S. validus*, que se distribuye en el norte de América y ha sido menos utilizada en los humedales

construidos (Greenaway y Woolley, 2001; Zhang et al., 2007b). En general hay poca información sobre esta especie.

La eliminación por parte de las plantas ha mostrado concentraciones varían entre 0.15% y 0.25% de peso seco de la planta, eliminando entre 5 y 10% de fósforo las aguas residuales (Vera et al., 2014; Maucieri et al., 2020). Sin embargo, se ha visto que la retención de fósforo por las plantas puede alcanzar mayores valores aproximados a 20% dependiendo del tipo de planta, carga de fósforo en el influente, escala de humedales construidos y parámetros operacionales como tiempo de retención hidráulica y temperatura (Wu et al., 2013). En cuanto a la asimilación de fósforo por la planta varía entre 1 y 40 gP/m² dependiendo de la especie, sitios (raíz, rizomas, tallo, hoja, flor) y también varía durante la estación del año. Sobre suelos como tallos, hojas y flor se han informado rangos que varían entre 0,1 a 19 gP/m² (Vymazal, 2007). Mientras que bajo suelo (raíz y rizomas) puede contener alrededor del 50% en especies como el jacinto de agua (*E. crassipes*) 45 gP/m² (Vymazal, 2007), y la lenteja de agua (*L. minor*) eliminando un 13 gTP/m². Sin embargo, son especies flotantes (Adhikari et al., 2015). Además, se ha reportado que la asimilación de fósforo generalmente es más alta durante el comienzo de la temporada de crecimiento (comienzo de la primavera), antes de que se alcanza la tasa de crecimiento máxima (Vymazal, 2007). Sin embargo, estos incrementos de biomasa no deben ser considerados como parte de la capacidad de eliminación de fósforo sostenible a largo plazo de los humedales (Kadlec y Wallace, 2009).

4.2.1.1. Plantas ornamentales

Las plantas ornamentales surgen como una alternativa que promete mejorar la infraestructura dando una apariencia estética en los sistemas de tratamiento. En un humedal construido con alta producción de plantas ornamentales, la recolección puede ser una actividad económica, brindando beneficios sociales y económicos, como la mejora de los paisajes y una mejor calidad del hábitat entregando un servicio ecosistémico (Sandoval et al., 2019). Además del valor estético que pueden tener las plantas ornamentales, tienen un gran sistema de raíces y lo suficientemente fuerte como para absorber materia orgánica. Por lo tanto, puede absorber más nutrientes como el fósforo para el crecimiento y almacenar el exceso de nutrientes en su tejido que otras plantas acuáticas como *T. latifolia*, *P. australis* entre otras (Haritash et al., 2017; Sandoval-Herazo et al., 2018; Hidayah et al., 2021).

Las plantas ornamentales son típicas de regiones subtropicales o tropicales. Sin embargo, también se han desarrollado en climas mediterráneos (Leiva et al., 2018; Leto et al., 2013). Algunas de las especies utilizadas en humedales construidos son; *Canna* spp, *Iris* spp, *Heliconia* spp, *Zantedeschia* spp, *Eichornia* ssp, y *Anthurium* ssp. (Abou-Elela et al., 2017; Sandoval et al., 2019; Marín-Muñiz et al., 2020). Las especies del género *C. indica* se utilizan en todos los continentes, siendo Asia el que las utiliza con mayor frecuencia. El género *Iris* y *Heliconia* se ha usado en Asia, junto con Europa y América del Norte. Mientras que *Z. aethiopica* se usa con mayor frecuencia en México, y con menor frecuencia en Europa, África y América Central y del Sur (Sandoval et al., 2019).

Especies como *C. papyrus*, comúnmente llamada papiro es una especie de planta herbácea perenne, provista de un grueso rizoma y tallos que rondan los 3-5 m de altura. En el ápice sostiene una umbela de hojas alargadas y cartilaginosas. Flores reunidas en pequeñas espigas que dan origen a una umbela 10-45 cm de largo. Se multiplica principalmente a través de sus rizomas. Esta especie se encuentra en la mayoría de las zonas de humedales tropicales de África oriental y central. La vegetación se caracteriza por poseer una alta productividad bajo temperaturas favorables (20 a 33 °C), generalmente en ambientes húmedos e iluminados. Tolera un pH entre 6 y 8,5. Su tasa de crecimiento es muy rápida (0,4 a 1,5 cm/d) (Abou-Elela et al., 2017; Leiva et al., 2018) y posee un gran potencial en la captación de nutrientes debido a la permeabilidad de sus raíces delgadas que permiten una gran interacción raíz-agua. Las estructuras de raíces de *C. Papyrus* proporcionaron más sitios de fijación microbiana, suficiente tiempo de residencia de aguas residuales, atrapamiento y asentamiento de partículas suspendidas, área de superficie para adsorción de contaminantes, absorción, asimilación en tejidos vegetales y oxígeno para la oxidación de materia orgánica e inorgánica en la rizosfera, lo que explica su alta eficiencia en el tratamiento (García-avila et al., 2019).

Asimismo, *Z. aethiopica* o mejor llamada cala blanca pertenece a la familia de las Aráceas y es una de las plantas estudiadas en sistemas subsuperficiales (Morales et al., 2013; Sandoval-Herazo et al., 2018). La cala blanca es una planta perenne originaria de África meridional. Sin embargo, se ha desarrollado en América, crece en áreas húmedas, sombreadas y con abundante agua. Se distribuye en regiones subtropicales, con temperaturas que varían entre los 12- 25 ° C (aunque

soporta heladas). Puede alcanzar alturas de 1,5 m y produce entre 2 a 3 flores de color blanco por bulbo (Sacoto, 2010). Posee como órgano basal subterráneo un rizoma, presenta dormancia estival y su floración es a finales de invierno a primavera (Morales et al., 2013).

Se ha visto que las plantas ornamentales tienen efectos positivos en la eliminación de contaminantes. De hecho, estos sistemas logran eficiencias de remoción de SST, DQO y DBO₅ superiores al 60%. Además, se han documentado eficiencias de eliminación de NH₄⁺ N y PT en los rangos de 48–55% y 24–50% respectivamente (Leiva et al., 2018). En pruebas experimentales en humedales construidos con dos especies de plantas, indicaron que el *C. Papyrus* presentó mayor capacidad de remoción de contaminantes como DQO (80,69%), DBO₅ (69,87%), NH₄ (69,69%), PT (50%), CT (98,08%) y CF (95,61%) que el caso de *P. Australis* (García-avila et al., 2019). Además, Abou-Elela et al. (2017) informaron una absorción de fósforo de 70,2 gP/m² por *C. Papyrus* en un HSSF a escala real (área de superficie 185,5 m²). La especie *Z. aethiopica* ha sido menor estudiada en cuanto a su asimilación de fósforo. Sin embargo, Zurita et al. (2009) en un HSSF plantado con *Z. aethiopica* mostraron eficiencias de eliminación de fósforo total de 44%.

4.2.1.2. Tipo de cultivo (monocultivo y policultivo)

Generalmente los humedales construidos se diseñan y se construyen con monocultivos que es solo una especie seleccionada para el tratamiento de aguas residuales. Se ha visto una mejora en la selección de la planta y el tipo de cultivo para la eliminación de contaminantes en humedales construidos. Los monocultivos tienen poca diversidad de plantas lo que lo hace menos resiliente frente a eventos inoportunos como efectos climáticos o plagas y enfermedades (Liang et al., 2011). Por lo tanto, se planteó la idea de combinar especies entregando mayor diversidad de plantas para el tratamiento de humedales construidos (Rodríguez y Brisson, 2016).

Se ha visto que los policultivos han mejorado los rendimientos en humedales construidos. Un estudio comparativo entre un sistema de monocultivo sembrado con *C. indica* y un sistema de policultivo sembrado con *C. indica* y *L. salicaria* mostró que las eficiencias de eliminación de DQO fueron 1,2 veces mayores en el sistema de policultivo (Zhou et al., 2017). También se ha demostrado que el policultivo de plantas de humedales puede mejorar la liberación de exudados de raíces que podrían estimular la absorción de compuestos de nitrógeno y fósforo (Marín-Muñiz

et al., 2020). Fue así como los policultivos al aumentar la diversidad mejoran el rendimiento y funcionamiento para la eliminación de nutrientes en los humedales construidos. Dell'Osbel et al. (2020) evaluaron el desempeño técnico de un sistema híbrido que combina humedal construido de HSSF y VSSF con policultivo y plantas ornamentales. Estos sistemas mostraron una capacidad de remoción de materia orgánica de un 84% y nutrientes como el fósforo de 94%. Calheiros et al. (2015) en un HSSF plantado con flores ornamentales (*C. flaccida*, *Z. aethiopica*, *C.indica*, *A. africanus* y *W. borbónica*) mostraron una eficiencia de eliminación de fósforo de 72%. Donde la especie *Z. aethiopica* se adaptó fácilmente en los primeros 3 meses de estabilización aumentando 3 veces su número de siembra y creciendo hasta 1,43 m en 10 meses. Por lo tanto, esto indica que puede ser una buena especie para la eliminación de fósforo en humedales construidos con sistemas de policultivo.

De modo contrario, Liang et al. (2011) observaron que el humedal de monocultivo tuvo tasas de remoción de DQO y $\text{NH}_4^+\text{-N}$ significativamente más altas que el humedal de policultivo durante el primer año de operación. Asimismo, Zhang et al. (2007), consideraron que la competencia entre las plantas que lo componen en un humedal mixto resultó en una menor remoción de nutrientes, indicando que la competencia entre especies puede afectar la remoción de nutrientes y la estabilidad de la vegetación en humedales construidos. Sin embargo, se ha comprobado que este rendimiento no solo depende del cultivo, sino que, del tipo de plantas a utilizar, por ejemplo, *C. papyrus* es más invasiva que *P. australis* (García-avila et al., 2019). Por otro lado, el híbrido de *C. indica*, planta ornamental creció mejor en un sistema monocultivo que en policultivo (Marín-Muñoz et al., 2020).

Otros factores son el tipo de raíz con la cual compiten, la estacionalidad y las temporadas de crecimiento; la temporada de crecimiento de *P. arundinacea* comienza temprano en la primavera, mientras que *P. australis* comienza a crecer más tarde, pero continúa hasta el otoño (Vymazal y Kröpfelová, 2008). También se debe considerar los rendimientos a corto plazo y a largo plazo, Liang et al. (2011) encontraron que un humedal con policultivo tuvo una densidad entre 85,6 y 123,8 individuos/m², mientras que el monocultivo presentó una densidad entre 56 y 86,3 individuos/m². Sin embargo, durante el primer año, el humedal de monocultivo tuvo una mayor biomasa (2,0 kg de peso seco (PS)/m²) en comparación con el sistema de policultivo (1,7 kgPS/m²).

De este modo, no se tiene con claridad cual cultivo es más eficiente. El efecto del uso de monocultivos o policultivos tienen comportamientos multifactoriales, dependientes de condiciones climáticas, etapas y tipos de plantas y variables operativas. Lo cual limita la predicción de los mecanismos y comportamiento de eliminación de fósforo. Sobre todo, la comparación con humedales construidos en otras regiones con distintas condiciones climáticas como heladas, áridas o zonas tropicales. Por eso se hace necesario investigaciones locales con las características propias del clima y la biodiversidad de la zona como especies nativas, datos de monitoreo *insitu* y a escala.

5. HERRAMIENTAS DE EVALUACIÓN AMBIENTAL

A pesar de ser muchos estudios que abordan el análisis de los tratamientos de aguas, en general se centran únicamente en aspectos técnicos y/o operativos (Wu et al., 2015), sin considerar la evaluación ambiental la cual podría interferir o sobrevalorar los resultados obtenidos. Sin embargo, frente a los nuevos paradigmas de la sustentabilidad, se ha motivado la búsqueda de nuevas herramientas adecuadas que permitan un certero diagnóstico del ciclo de vida y problemas ambientales (contaminación, eutrofización, ocupación de suelo entre otros), que ayuden a la correcta toma de decisiones sobre las acciones, procesos, y finalmente consecuencias derivadas de la puesta en marcha. Algunas herramientas de evaluación son la huella hídrica, huella de carbono, huella ecológica, eco-eficiencia o análisis de ciclo de vida (ACV) entre otras (Riquelme y Neumann, 2021). El análisis de ciclo de vida (ACV) se erige como una herramienta competitiva, sistemática y objetiva para evaluar los potenciales impactos ambientales a lo largo de todo su ciclo de vida de un producto o proceso (Corominas et al., 2013). Es así como el ACV se ha convertido en la mejor herramienta de evaluación medioambiental para exponer de forma transparente los impactos ambientales.

5.1. Análisis de ciclo de vida

El ACV es una metodología de gestión ambiental que permite la evaluación de los impactos ambientales de las entradas y salidas de materiales y energía durante cada etapa de la vida (adquisición de materiales, construcción, operación, desmantelamiento) de un producto o proceso de estudio. Se pueden considerar materias primas, necesidades energéticas, emisiones,

transporte, generación de residuos y subproductos, disposición final, hasta recuperación de energía o subproductos con la finalidad de obtener información cuantificable que puede ser útil para reducir los impactos por diseños u operación de procesos. El principal interés de esta metodología es comparar ambientalmente distintos productos, comprendiendo que en muchos casos los impactos ambientales no ocurren durante la etapa de uso, sino durante la producción, transporte o disposición de residuos.

Esta metodología está normalizada mediante la Organización Internacional de Normalización (ISO, siglas en inglés), quien desarrollo la norma ISO 14.040:2006 y 14.044:2006 (ISO, 2006a, 2006b). El ACV conta de cuatro fases las cuáles se muestran en la Figura 1.4.

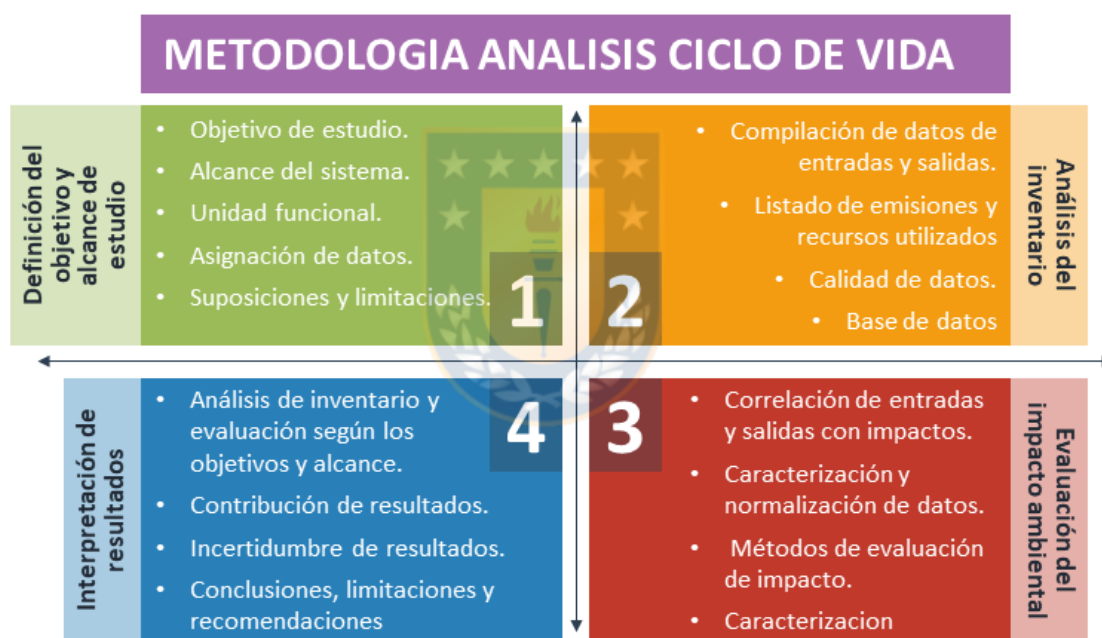


Figura 1.4. Fases de un análisis de ciclo de vida. *Fuente: Adaptado ISO, 2006.*

La primera parte de un ACV es **definir el objetivo y alcance del sistema**, el cual se debe justificar para llevar a cabo el proceso, así como la aplicación prevista. Además, el alcance revela el nivel de detalle del estudio. Por ejemplo, el ACV puede incluir la adquisición de materiales/energía, infraestructura/construcción, operación/uso, desmantelamiento y remediación/restauración como etapas del ciclo de vida según el objetivo planteado. También se elige la unidad funcional (UF) para permitir una comparación justa de los elementos de interés. La UF debe incluir el período de tiempo

consideración en el ACV y las líneas de base para el tamaño y la función específica del producto o proceso.

En la segunda fase se realiza un **análisis del inventario (ICV)** para definir y contabilizar las entradas y salidas de materiales y energía para cada etapa de vida y proceso dentro del límite del sistema definido. Dentro de las emisiones se consideran tanto al aire, agua y suelo, mientras que los recursos utilizados provienen de la naturaleza y/o tecnosfera. Esta etapa se considera la más exigente del estudio en términos de tiempo y precisión de los datos con la finalidad de determinar la validez del estudio (Corominas et al., 2013). Se distinguen dos tipos de datos; los primarios cuando se trata de medidas directas del sistema de estudio como monitoreos, muestreos, entrevista entre otros siendo de mayor calidad. Mientras que los datos secundarios, se obtienen cuando los datos son proporcionados por bases de datos como estadísticas, documentos, reporte, literatura etc. Una de las bases más utilizadas es la Ecoinvent Database siendo la más completa y general (Weidema et al., 2013).

En la tercera fase se realiza la **evaluación del impacto del ciclo de vida (EICV)** la cual consiste en calcular los impactos ambientales asociados a las emisiones y los recursos clasificándolo según su potencial de impacto. En primer lugar, los impactos se clasifican en categorías de impacto de punto medio y luego se normalizan con respecto a las entradas/salidas totales de un sistema de referencia para comparar los potenciales impactos. El impacto potencial de una sustancia se da en relación con un factor de caracterización dominante para cada categoría. Por ejemplo, 1 g de NH_3 tiene el mismo efecto de acidificación que 1,88 g de SO_2 en la categoría acidificación terrestres. Con la finalidad de ordenar las principales alteraciones que pueden tener las emisiones y recursos sobre el medio ambiente es que se define una serie de categorías de impacto ambiental las cuáles miden en unidades físicas diferentes que corresponden al principal compuesto responsable del impacto (Corominas et al., 2013). La Tabla 1.4 muestra las categorías de impacto en punto medio con la unidad correspondiente. Este procedimiento se realiza y difiere según el método a utilizar. Algunos de los métodos de evaluación de impacto más desarrollados son: Eco-Indicator 99, Método EPD, CML, IMPACT 2002+, ReCiPe, TRACI I, BEES. Los cuáles han sido incluidos en diferentes softwares de ACV (SimaPro, Umberto, OpenLCA, GaBi entre otros (Casas-Ledón, 2021; Corominas et al., 2013).

Finalmente, está la **interpretación de los datos**, donde los resultados de del ICV y el EICV son considerados y analizados en conjunto. Esta fase tiene como objetivo presentar los resultados de forma clara y comprensible, identificando los puntos conflictivos más significativos. Además, la verificación de los resultados en cuanto a su integridad, sensibilidad, consistencia e incertidumbre. Por último, establecer conclusiones, limitaciones y recomendaciones para los procesos de la toma de decisiones. Los cuáles deben reflejar el objetivo y alcance propuesto definido en el estudio (Corominas et al., 2013; Casas-Ledón, 2021).

Tabla 1.4. Categorías de impacto para la evaluación de potenciales impactos ambientales.

Categoría de impacto	Unidad
<i>Punto medio</i>	
Recursos minerales	kg Sb eq
Agotamientos fósiles	kg oil eq
Calentamiento global	kg CO ₂ eq
Agotamiento de ozono	kg CFC-11 eq
Acidificación	kg SO ₂ eq
Eutrofización	kg P eq; kg N eq
Ecotoxicidad	kg 1,4-DB eq
Cambio uso de suelo	m ²
Agotamiento de agua	m ³
Toxicidad humana	kg 1,4-DB eq

Fuente: *Elaboración propia.*

Tal como muestra la Figura 1.4, la relación entre todas las fases del ACV es un proceso iterativo en el que se deben revisar los resultados de cada etapa una y otra vez si es necesario. El volver a etapas anteriores releva un nivel creciente de detalle en el análisis, es decir, partir desde un ACV conceptual a uno detallado; o redefinir los aspectos metodológicos que fueron definidos en las primeras fases los cuáles son impulsados por los resultados obtenidos.

5.2. Análisis de ciclo de vida en humedales construidos

El ACV permite abordar de manera comprehensiva las distintas etapas involucradas en la generación, uso y disposición de bienes y servicios, cuantificando su impacto potencial. En general los estudios de ACV sobre los tratamientos de aguas residuales pueden utilizarse como una

herramienta para la fase de diseño, operación, tipo de tecnología y planificación (Corominas et al., 2020). Además, por ejemplo, elegir una tecnología que pueda proporcionar las características de rendimientos deseadas para las cargas iniciales necesarias, teniendo en cuenta los impactos totales generados a lo largo de su ciclo de vida. En los últimos tres años, un número creciente de investigadores han aplicado el ACV para evaluar el desempeño ambiental de las PTAR (310 publicaciones en Web of Science en comparación de las 29 publicaciones el año 2013).

La mayoría de las investigaciones han estudiado el impacto ambiental de las tecnologías convencionales, como los tratamientos aeróbicos, frente a las soluciones basadas en la naturaleza (no convencionales o descentralizadas) (Kalbar et al., 2013; Lopsik, 2013; Garfi et al., 2017; Gongora et al., 2021). Machado et al. (2007) también compararon tratamientos para aguas residuales con un humedal construido, una infiltración de velocidad lenta y un proceso de lodo activado. Descubrieron que los impactos del ciclo de vida del humedal construido y de la infiltración eran mucho menores que los de la planta de lodos activados, especialmente en lo que respecta al potencial de calentamiento global ($4,01E4$ kg $CO_2eq/P.E.$), la acidificación (434 $SO_2eq/P.E.$) y la eutrofización ($3,43E3$ kg $PO_4^{3-}eq/P.E.$). Además, la fase de operación reveló que presentaron mayor impacto debido a la energía necesaria para la aireación. Fuchs et al. (2011) demostró que las plantas convencionales requieren un gran consumo de energía que a su vez supone un 50% en operación y mantenimiento.

Kalbar et al. (2013) compararon cuatro PTAR mediante un ACV; lodos activados; reactor por lotes de secuenciación, reactores anaeróbicos + laguna facultativa y humedales construidos. Los resultados mostraron que los reactores por lotes de secuenciación ocuparon los primeros lugares en consumo de energía y potencial de cambio climático ($31,97$ kg $CO_2eq/P.E.$), pero también produjeron un efluente $0,10$ kg $PO_4^{3-}eq/P.E.$, con respecto a los compuestos orgánicos y los nutrientes. Mientras que los humedales construidos mostraron un consumo de energía insignificante y un cambio climático negativo ($-3,86$ kg $CO_2eq/P.E.$), pero un mayor impacto en la categoría de eutrofización con 3.40 kg $PO_4^{3-}eq/P.E.$

Teniendo en cuenta lo anterior, se destaca que las alternativas no convencionales presentan bajo consumo de energía en comparación de las tecnologías convencionales. Específicamente, el impacto ambiental potencial de la PTAR convencional puede ser entre 2 y 5 veces mayor que la

generada por los sistemas basados en la naturaleza como humedales construidos híbridos y sistemas de estanques de algas de alta tasa atendiendo a 1500 P.E. (Grafi et al. 2017). Sin embargo, una de las desventajas es la ocupación de suelo, debido a que los humedales construidos requieren mayores superficies de terreno para su implementación. Aun así, son apropiados para zonas rurales debido a los bajos requerimientos de energía y eficiencias según lo requerido (Corominas et al., 2013). Algunos estudios han demostrado que la fase de construcción en tecnologías no convencionales puede contribuir entre un 60-80% al impacto total (Fuchs et al. 2011; Garfí et al., 2017; Resende et al. 2019). Cuanto más pequeño sea el tamaño de la planta de tratamiento y menos uso en la energía el tratamiento, más influyente se vuelve la construcción con respecto a los impactos ambientales del ciclo de vida.

Hasta la fecha solo existe un número limitado de estudios sobre ACV en humedales construidos (87 en total). Corbella et al. (2017) evaluaron las celdas microbianas en humedales construidos basadas en materiales de grava y grafito. Observaron hasta un 20% menos de impacto ambiental en los humedales construidos con grava que con la gravilla. Otros estudios compararon la diferencia entre los HSSF frente a los de VSSF, siendo los de VSSF significativamente menores (50%) a largo plazo (Fuchs et al., 2011). Debido a una menor superficie y materiales de construcción. Flores et al. (2019), estudiaron humedales construidos para el tratamiento de aguas residuales de viñedos, donde en la época de vendimia los caudales eran 10 veces mayores que el resto del año, obteniendo impactos ambientales 4 veces mayores en la época de vendimia.

En general los impactos de los humedales construidos se centran en la categoría eutrofización, debido a las descargas de aguas residuales tratadas, donde son el principal responsable alcanzando entre 80-100% (Flores et al., 2019; Resende et al., 2019; Gongora et al., 2021). Cabe considerar las limitaciones, donde el impacto puede ser variable según el área de descarga la cual puede ser un ecosistema sensible o los límites de descargas asociados a las normas que impone cada región (Gallego-Schmid y Tarpani, 2019). A pesar de que los humedales construidos son diseñados para reducir los contaminantes y por consiguiente la eutrofización. Sin embargo, cada tecnología trae otros impactos ambientales adversos relacionados con la infraestructura asociada, emisiones, consumo de recursos naturales y energía, llamados impactos inducidos (Godin et al., 2012) Asimismo se ha reportado que, para requerir una eliminación eficiente de fósforo de las

aguas residuales, se requiere una mayor mecanización o tecnologías avanzadas lo cual conlleva un aumento del impacto ambiental, en categorías como cambio climático, agotamiento del ozono, a la formación de oxidantes fotoquímicos (Fuchs et al., 2011; Zang et al., 2015).

Por lo tanto, la categoría cambio climático es la segunda categoría que más se estudia, en el caso de los humedales construidos ya que tiene un efecto positivo debido al bajo consumo de energía. La energía llega a representar entre un 20-50% la categoría de cambio climático (Fuchs et al., 2011; Resende et al., 2017; Flores et al., 2019). Sin embargo, el uso de energía son emisiones indirectas, y los humedales construidos pueden tener emisiones directas en su operación lo cual puede corresponder 45-55% (Corbella et al., 2017). En general las emisiones directas de CO₂ se consideran biogénicas y en humedales construidos no se consideran. No obstante, no todas estas emisiones deben considerarse biogénicas porque hasta un 10% del carbono orgánico total presente en las aguas residuales puede ser de origen fósil (Gallego-Schmid y Tarpani, 2019). Rodríguez-García et al. (2012) concluyeron que estas emisiones de CO₂ no biogénicas pueden tener una importancia similar al potencial de cambio climático que las asociadas a la electricidad.

Se ha visto que los humedales construidos son fuentes de gases de efecto invernadero (GEI) (Mander et al., 2014; Maucieri et al., 2017). Durante los procesos de eliminación de contaminantes de las aguas residuales en humedales construidos liberan compuestos gaseosos directos a la atmosfera. Entre los gases GEI, el dióxido de carbono (CO₂), el metano (CH₄) y el óxido nitroso (N₂O) son los más peligrosos para el medio ambiente que contribuyen al calentamiento global. Se ha visto que la presencia de vegetación y el tipo de especies de plantas tienen un efecto significativo en las emisiones de CO₂, con flujos casi el doble en humedales construidos plantados. Esto se debe principalmente a la liberación de oxígeno en la rizosfera por macrófitos, mayor disponibilidad de carbono lábil (por ejemplo, exudado de plantas) para la actividad de microorganismos y la respiración de las raíces de las plantas (Maucieri et al., 2017). Un trabajo sobre un HSSF a gran escala estimó que el promedio diario de CO₂ que se liberó a la atmosfera era entre 17-33% del C que se eliminó de las aguas residuales en primavera. Las condiciones ambientales, como la temperatura, tienen una correlación positiva con la liberación de carbono (Maucieri et al., 2017). Por lo tanto, la estacionalidad fue influyente en si el humedal construido es sumidero o fuente de carbono (Barbera et al., 2014).

El CH₄ es el GEI más importante emitido por los humedales construidos. Esto se debe a la acumulación intensiva de materia orgánica que es degradada principalmente por procesos microbiológicos anaeróbicos en condiciones anóxicas-anaeróbicas en los HSSF demostradas por un potencial redox negativo y concentraciones de DO < 2 mg/L (Vymaza y Kröpfelová, 2008). Algunos factores como la oxigenación pueden inhibir la emisión de CH₄ creando una condición aeróbica. Asimismo, las plantas pueden influir en los procesos microbianos del suelo de los humedales construidos (Wang et al., 2013). El crecimiento de la raíz altera el estado del potencial de oxidación-reducción (ORP) del suelo, lo que resulta en un mayor consumo de CH₄ debido a la renovación del material de la raíz y la liberación de oxígeno. Algunas plantas como el cómo *J. effusus*, *T. latifolia*, *Z. latifolia* y *P. australis* pueden emitir CH₄, por lo que su elección se hace importante (Mander et al., 2014).

La investigación también ha indicado que la producción de biomasa vegetal, el carbono y el nitrógeno de la biomasa microbiana están fuertemente correlacionados con la riqueza de especies de plantas en humedales construidos. Por lo tanto, el tipo de cultivo a utilizar puede ser un parámetro para influir en las emisiones GEI. En policultivos pudieron comprobar un aumento del flujo de CH₄, aumentando la riqueza de especies de plantas. Wang et al. (2013) encontraron mayor CH₄ emisión de policultivo (*Z. latifolia* y *P. australis*; 780 mg/m²d) que monocultivo (*P. australis*; 567 mg/m²d). Asimismo, Xu et al. (2019) en una revisión observaron que el sistema de policultivo, con un valor máximo de emisión de CH₄ alcanzó 5,9 g/m²d, que es aproximadamente 2,3 veces mayor que el del sistema de monocultivo (2,6 g/m²d). En el caso de N₂O tiene la misma tendencia, pero no observaron un aumento de N₂O por unidad de eliminación de nitrógeno en el humedal construido. También se ha encontrado que la riqueza de especies no tiene un efecto significativo sobre las emisiones y que estas pueden ser variadas por los tipos de plantas a utilizar.

A pesar de que estos estudios destacaron las emisiones GEI, hay escasos estudios de ACV que evalúen el desempeño ambiental de diferentes tipos de plantas, plantas ornamentales o sistemas de cultivos en humedales construidos. Como se mencionó anteriormente las emisiones GEI pueden ser variables debido a la especie de plantas, como la estacionalidad que influyen en estos sistemas naturales. De las investigaciones reportados sobre ACV en humedales construidos todos utilizan como planta la especie *P. australis* (Machado et al., 2007; Kalbar et al. 2013; Garfí et al. 2017;

Resende et al., 2019). Además, Corbella et al. (2017), Garfí et al. (2017), Flores et al. (2019) entre otros estimaron las emisiones directas de los humedales o consideran emisiones propuestas por estudios previos de Mander et al. (2014), o Fuchs et al. (2011). Gallego-Schmid et al. (2019) en una revisión de ACV para tratamientos de aguas observaron que solo un 40% de los estudios consideran las emisiones indirectas GEI y el 60% tanto las indirectas como las directas. Por lo tanto, la investigación sobre las emisiones y el impacto ambiental del sistema de tratamiento puede estar sobreestimado.

6. FORMULACIÓN DE LA PROPUESTA DE INVESTIGACIÓN

En este sentido, la investigación de ACV en humedales construidos que compare sistemas de monocultivos con policultivos es limitada. Según los antecedentes mostrados las plantas ornamentales y el policultivo cumplen un rol importante en mejorar el desempeño de la eliminación de fósforo. La planta ornamental *C. papyrus* se destaca por sobre las demás debido a una de las especies ornamentales más conocida, estabilidad de la vegetación y alta asimilación de fósforo. Mientras que la especie *Z. aethiopica* llama la atención por su falta de conocimiento en la asimilación de nutrientes y desarrollo en regiones distintas a las tropicales. Hasta donde sabemos no existen antecedentes de humedales construidos plantados con sistemas de policultivos con esta combinación de especies *C. papyrus* y *Z. aethiopica* y se espera que sean más eficientes en eliminación de fósforo siendo así un tratamiento de mejor desempeño ambiental que los sistemas plantados con monocultivos con plantas como *P. australis* (más utilizada en humedales construidos) y *S. californicus* (especie nativa).

Sin embargo, a pesar de que los humedales construidos son sistemas no convencionales y amigables con el medio ambiente. Se ha visto que los humedales construidos son fuentes de gases de efecto invernadero (GEI). Por lo tanto, su tratamiento puede estar asociados a una serie de impactos ambientales, lo que genera la necesidad de una evaluación integral con el fin cuantificar los supuestos. La Figura 1.5 muestra un esquema resumen de la investigación realizada. Primero, es necesario identificar los mecanismos de eliminación de fósforo en un HSSF y los factores operacionales que pueden influir en el rendimiento de la eliminación de fósforo en humedales. Además, evaluar la importancia de la planta a través de la asimilación de fósforo en un humedal construido plantado con sistemas de monocultivo y policultivo. Finalmente, para evaluar el

desempeño ambiental se utiliza la herramienta basada en el ACV para cuantificar los impactos ambientales. De esta manera, considerar tanto sus dimensiones técnicas como ambientales entregan una evaluación integral del tratamiento con humedales construidos. Por lo tanto, esta tesis busca contribuir al desarrollo de este conocimiento, evaluando y cuantificando los impactos ambientales de los humedales construidos con sistemas de monocultivo y policultivo, enfocándose principalmente en la eliminación de fósforo. Lo cual permite establecer la base de diseño, construcción, estudio y evaluación (técnica y ambiental) de nuevos sistemas a escala piloto o industrial.



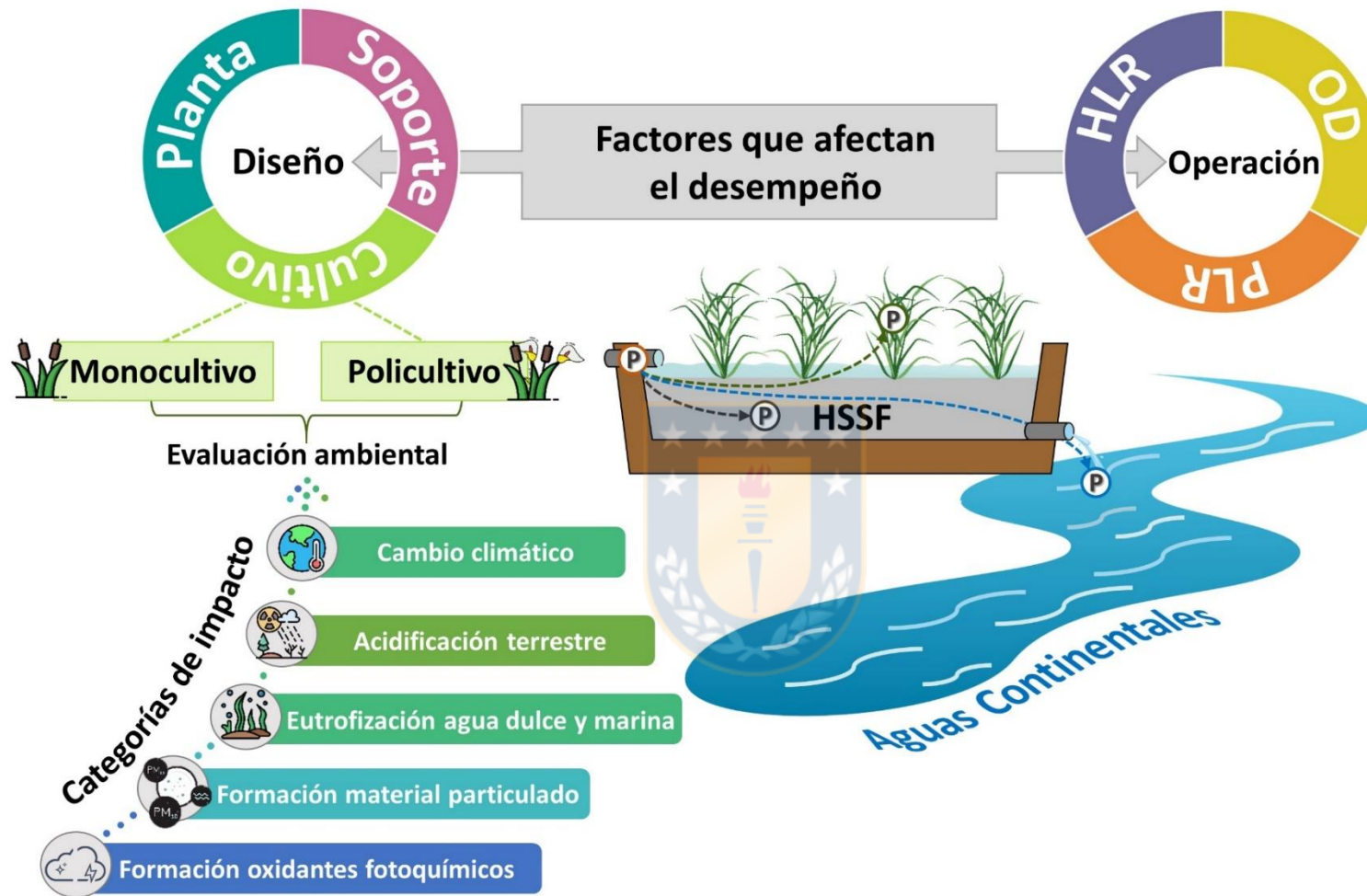


Figura 1.5. Esquema general del proceso evaluado en esta investigación. PLR: carga de entrada de fósforo; HLR: tasa de carga hidráulica; DO: oxígeno disuelto; HSSF: Flujo Horizontal subsuperficial.

CAPÍTULO II

HIPOTESIS Y OBJETIVOS



1. HIPÓTESIS

Debido a que los humedales construidos con sistemas de policultivos aumentan la eficiencia de eliminación de fósforo en comparación con los sistemas de monocultivos, los impactos ambientales se verán disminuidos, mejorando su desempeño ambiental.

2. OBJETIVOS

2.1. Objetivo general


Evaluar técnica y ambientalmente la eliminación de fósforo en sistemas de monocultivo y policultivos en un humedal construido para el tratamiento de aguas residuales.

2.2. Objetivos específicos

1. Identificar los mecanismos de eliminación de fósforo en un humedal construido para el tratamiento de aguas residuales.
2. Evaluar la asimilación de fósforo en sistemas de monocultivo y policultivo en humedales construidos para el tratamiento de aguas residuales.
3. Evaluar el desempeño ambiental para la eliminación de fósforo por plantas en sistemas de monocultivo y policultivos en un humedal construido para el tratamiento de aguas residuales.

CAPÍTULO III

CHARACTERIZATION AND RECOVERY OF PHOSPHORUS FROM WASTEWATER BY COMBINED TECHNOLOGIES



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Characterization and recovery of phosphorus from wastewater by combined technologies

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Abstract

Phosphorus is a critical element in agriculture because of its role in fertilizing fields. Thus, and due to sewage discharges, phosphorus is also present in aquatic ecosystems, causing eutrophication. Phosphorus can be found in inorganic and organic forms. One solution to phosphorus-related conflicts is the application of technologies for the recovery of phosphorus from wastewater and its possible reuse. However, existing technologies are focused on the elimination/recovery of inorganic phosphorus, while technologies based on combined mechanisms have demonstrated greater efficiency in the treatment of different forms of phosphorus and its recovery. This article reviews the operational factors of the different technologies based on the physical, chemical and biological mechanisms of phosphorus recovery. Emerging combined technologies that have been able to maximize the recovery of organic and inorganic phosphorus from different wastewater streams are also reviewed. Thus, the forms of phosphorus must be understood for the appropriate technology for the recovery different forms of P in wastewater discharges to be chosen, providing environmental protection to aquatic ecosystems.

Keywords. Phosphorus recovery; combined technologies; wastewater; organic phosphorus; inorganic phosphorus

1. INTRODUCTION

Phosphorus (P) is an essential chemical element for living beings that has no substitute and is a non-renewable resource (Tarayre et al. 2016). It is naturally found in geological deposits of phosphate rock or phosphorite, which are unevenly distributed throughout the world (Desmidt et al. 2015). In recent years, P has taken on great importance due to the depletion of this mineral, with approximately 95% extracted P used in agriculture, mainly as fertilizer (Jasinski 2018). Globally, apart from the mineral reservoir of phosphorite rock, P is found in surface water and oceans. The greatest P flows to aquatic ecosystems are from soil erosion, runoff and point source discharges. The discharge of high concentrations of P into wastewater encourages excessive proliferation of algae and floating plants, resulting in eutrophication of aquatic systems (Mekonnen and Hoekstra 2018).

A long-term sustainable solution to address the dual problems of P mineral shortages and P-based eutrophication is to remove P from wastewater and implement P recovery technologies in water treatment (Tarayre et al. 2016; Venkiteshwaran et al. 2018). However, there is currently a large knowledge gap in the understanding of the various forms of P and their bioavailability potential, including with respect to their susceptibility to different P treatment processes and the fraction of P that can cause eutrophication of water bodies. In a recent meta-analysis, Venkiteshwaran et al. (2018) found that P in water is not always present in the most recoverable form for direct reuse. Gu et al. (2011) showed that the fractional composition of P and its removal efficiency varied according to different physical, chemical and biological treatment technologies. Therefore, the lack of understanding of its distribution and structures in the environment limits the design of effective P mitigation and recovery approaches (Venkatesan et al. 2018).

A prerequisite for the development of technologies for P recovery is the knowledge of P characteristics, technical principles of treatment and a good database for a complete analysis. Therefore, this examination provides P recovery technologies based on physical, chemical and biological principles. Generally, many reviews discuss these issues, however this review is based on data in data giving it an added value. In addition, this review aims to give a view on technologies based on combined mechanisms taking advantage of mechanisms to improve the efficiency of recovery of total P fractions in wastewater. The design of appropriate new technologies for the

effective recovery of P from wastewater will contribute significantly to meeting future P demand. At the same time, P concentrations in wastewater effluents will be reduced, providing environmental protection to aquatic ecosystems.

2. PHOSPHORUS CHARACTERIZATION

P is an essential element for all life: plants, animals, microorganisms and bacteria. P is a non-metallic element of the periodic table, which can be found bound to O, C, N or various metals. In nature, P is found almost exclusively as phosphate, in both organic and inorganic forms (Fuentes et al. 2006). Organic P is presented as organic phosphate esters, while inorganic P is presented as minerals (apatite, Brushite, Monetite, Variscite) (Desmidt et al. 2015). Organic P is poorly characterized and is considered diverse in size and structure, ranging from simple organic P compounds such as sugar phosphates, phospholipids, nucleus acids and phosphate inositol to phosphoric acid esters (Fuentes et al. 2006). Organic phosphates are esters that are subclassified according to the number of ester groups attached to each phosphate. Therefore, phosphate monoesters have one carbon per P, while phosphate diesters have two (Turner et al. 2005).

For phosphate to be available, organic P must be hydrolyzed and mineralized by phosphatase enzymes that catalyze chemical reactions by releasing inorganic P, as illustrated in Figure 3.1 (Monbet et al. 2007). Phosphate diesters must then be hydrolyzed by the enzyme phosphodiesterase while phosphate monoesters must be hydrolyzed by the enzyme phosphomonoesterase prior to phosphate release (Turner et al. 2005). In the case of phosphate inositol, the phosphate must be released by the enzyme phytase, but evidence of hydrolysis and biological utilization of inositol phosphates is poorly known (Turner et al. 2002). This process is fundamental for the biological absorption of phosphate ions, which are easily assimilated (immobilized) by plants and microorganisms. It also plays a vital role in the growth, development, and maintenance of the P cycle in ecosystems (Fuentes et al. 2006; Turner et al. 2002).

Inorganic P is presented by phosphate ions such as polyphosphates formed by tetrahedral structural units of phosphate joined together that share oxygen atoms and vary according to pH. At pH under acidic conditions, the dominant phosphate species is orthophosphoric acid (H_3PO_4), which has a pK_a of 2.14 and is a weak, colorless acid that is soluble in water. In contrast, in alkaline conditions

orthophosphate (PO_4^{3-}) predominates; it has a pK_a of 12.35 and is considered the most readily available form of phosphate for biological absorption. Between a pH range of 5 and 9 at a pK_a of 7.19, the dominant species are dihydrogen phosphate (H_2PO_4^-) and hydrogen phosphate (HPO_4^{2-}). Another group of inorganic P compounds includes linearly condensed and cyclic polyphosphates (Vymazal and Kröpfelová 2008).

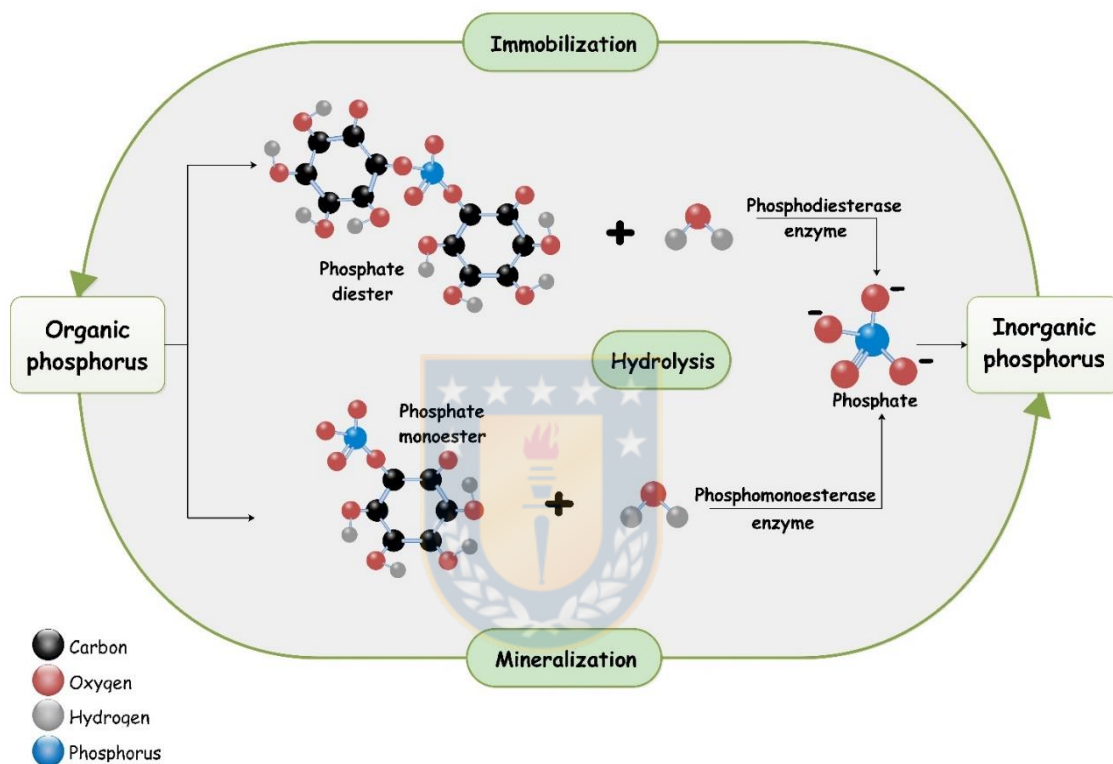


Figure 3.1. Process of transformation of organic P into inorganic P through extracellular enzymes of vegetable and microbial origin.

2.1. Analysis of phosphorus in wastewater

Understanding of the different forms, fractions and analyses of P in water is necessary for the application of P treatment technologies. P concentrations can be expressed in two different ways, as phosphate or orthophosphate (PO_4^{3-}) or as phosphate phosphorus ($\text{PO}_4^{3-}\text{-P}$). PO_4^{3-} is a measure of the amount of orthophosphate molecules in a sample, while $\text{PO}_4^{3-}\text{-P}$ is a measure of the amount of phosphorus ions in a sample (APHA 2012). P analyses include two general process steps: conversion of the form of P of interest into orthophosphate through chemical digestion and

colorimetric determination of orthophosphate. For the determination of P in water the ascorbic acid method, which consists of the reaction of the phosphate ion with the molybdate ion (MoO_4^{2-}), resulting in phosphomolybdate ($[\text{PO}_4\text{Mo}_{12}\text{O}_{33}]^{3-}$), is generally used. This compound, when reduced by ascorbic acid, forms a blue complex that is measured in the spectrophotometer (APHA 2012). However, it is important to note that of all the P compounds present in water, only the phosphate ion can form the blue molybdenum complex. Therefore, the phosphate ion (PO_4^{3-} , HPO_4^{2-} , H_2PO_4^- , H_3PO_4), which may be free ion or chemically interchangeable (labile) form, is considered P-reactive (RP). Meanwhile, all other compounds of both organic and inorganic P are considered non-reactive (NRP).

To separate P analytically, a membrane filtration process with a pore size of 0.45 μm is required. This process results in dissolved or soluble P and particulate P (APHA 2012). Figure 3.2 summarizes the organic and inorganic forms of P in water, including analytical separation in dissolved or soluble and particulate forms. In addition, P fractions that may be recalcitrant, bioavailable, or labile are considered. The recalcitrant fraction is related to P particles, which are often formed when organic or inorganic P is precipitated or associated with particles, either a precipitate, a soil matrix, or a sludge (Gu et al. 2011). When inorganic P is precipitated with metals such as Al and Fe, it is barely bioavailable and therefore considered non-reactive phosphorus (NRP). The NRP fraction, in addition to the P particulate, includes organic P and inorganic polyphosphates. The NRP typically constitutes only a small fraction of TP in the influent wastewater (1-10 %) (Venkiteshwaran et al. 2018).

Meanwhile, the bioavailable fraction includes P that is easily assimilable and supports the primary production of aquatic microorganisms (Monbet et al. 2007). Analytically, bioavailable P can be interpreted as dissolved reactive phosphorus (DRP) or dissolved inorganic phosphorus (DIP) (Gu et al. 2011); however, this hypothesis is not entirely correct (Li and Brett 2012), as studies have indicated the importance of dissolved organic phosphorus (DOP) as an important source of nutrients for eutrophication (Monbet et al. 2007; Qin et al. 2015). DOP is considered a labile component, susceptible to hydrolysis, prone to being bioavailable and is used as a supplementary source of P in the absence of inorganic P for aquatic microorganisms (Monbet et al. 2007). Qin et al. (2015) indicated that approximately 75.4 % (0.043 mg/L) of effluent DOP was bioavailable for algae growth.

It should be noted that the measurement of bioavailable DOP does not have standardized methods or adequate techniques with respect to measuring the bioavailability of P from wastewater effluent, so its value is not entirely accurate (Li and Brett 2013).

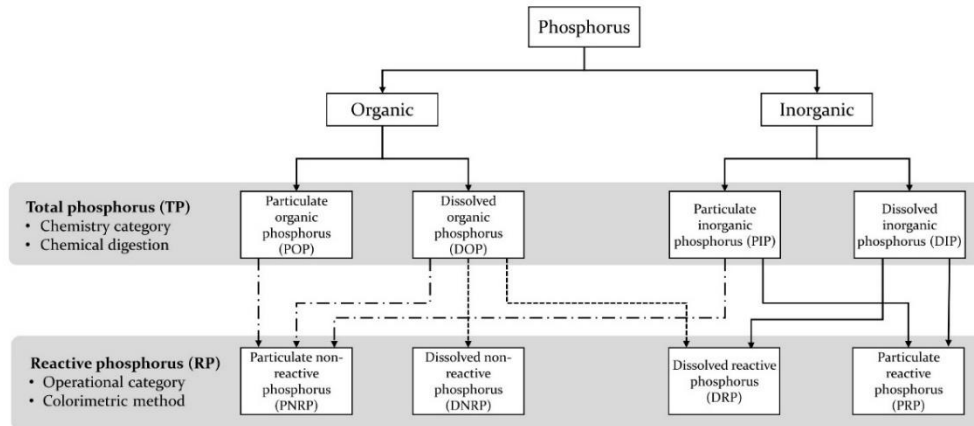


Figure 3.2. Scheme of the operational mobility of P based on analytical methods. The dotted-point-dotted line (— · — · —) is classified as the recalcitrant fraction of P, the continuous line (—) as the bioavailable fraction of P and the dotted line (— · —) is classified as the labile fraction of P.

Some researchers such as Monbet et al. (2007) and Li and Brett (2013) have demonstrated the mobility that P has in transforming itself and the potential for bioavailability compared to chemical analyses. Li and Brett (2013) determined that 81% of cases did not conform to the assumption that DRP is approximately equal to bioavailable P; for example, apatite or hydroxyapatite is considered a reactive inorganic category, but it presented low availability (Li and Brett 2013). Biological assays have been shown to be an alternative for quantifying biologically available phosphorus (BAP). Monbet et al. (2007) demonstrated through a bioassay that recalcitrant fractions (NRP and P particles) can also result in the growth of cyanobacteria and algae. Li and Brett (2012) compared the methodology for measuring TP, total reactive phosphorus (TRP) and BAP in a treatment in wastewater treatment plants (WWTPs), where the influent corresponded to 2.75 mgTP/L, 2.48 mgTRP/L and 2.18 mgBAP/L. They concluded that the BAP corresponded to 79% for TP and 88% for TRP. It is therefore possible to approximate BAP with other chemical analyses of P, such as

TRP analysis, which is a more conventional and less time-intensive analysis than BAP bioassays (Li and Brett 2012; Monbet et al. 2007).

2.2. Phosphorus concentrations in wastewater

Table 3.1 shows concentrations of organic matter and nutrients (N and P) in different types of wastewaters. Industrial wastewater of animal and plant origin has high TP concentrations of 12-780 and 35-350 mg/L. The lowest TP concentrations (0.3-2.3 mg/L) are observed in aquaculture industries, as effluents with a volume of 10,000 m³/d play a fundamental role in the dilution of P concentrations (Comeau et al. 2001; Schulz et al. 2003). In addition, the cellulose and tannery industries have TP concentrations <1 mg/L (Ekholm et al. 2007; Chamorro et al. 2010). By contrast, swine industries present high P concentrations, reaching 780 mgTP/L, with only 15% found as dissolved P (Ichihashi and Hirooka 2012). Kim et al. (2016) characterized an effluent of anaerobically digested porcine wastewater and obtained a TP concentration of 612 mg/L, with 36% corresponding to dissolved PO₄³⁻-P (221 mg/L).

Only few studies determined by DRP analysis the phosphate ion values in different types of wastewaters. The values showed phosphate concentrations of 0.12-350 mg/L, accounting for 34-100% of TP (Ekholm et al. 2007; Gu et al. 2011; Markou et al. 2012; Wood et al. 2008; Schulz et al. 2003). In wastewater from the olive and pulp and paper mill industries phosphate accounts for 95 and 100%, respectively (Markou et al. 2012; Leiviskä et al. 2008). In industrial wastewater from sources such as tannery, aquaculture and swine operations, phosphate accounts for 33%, 35% and 36% of TP, respectively (Kim et al. 2016; Lefebvre et al. 2005; Schulz et al. 2003). PO₄³⁻-P concentrations are similar (0.01-221 mg/L), and the phosphate fraction ranges from 33 to 94% of TP. The abattoir industry presented the highest ratio, with PO₄³⁻-P accounting for 84 and 94% of TP, with concentrations of 23 and 33 mg/L, respectively (Ge et al. 2015; Lemaire et al. 2009).

Table 3.1. Physicochemical characteristics of different types of wastewaters.

Type of water	COD (g/L)	pH	TN (mg/L)	NH ₄ ⁺ -N (mg/L)	NO ₃ ⁻ -N (mg/L)	TP (mg/L)	PO ₄ ³⁻ -P (mg/L)	Reference
Domestic	0.2-1	7.0-8.5	28-100	6.0-85	1.0-36	5.0-30	4.0-20	Li et al. (2018), Andrés et al. (2018), Pronk et al. (2015), Luo et al. (2016), Dueñas et al. (2003), Markou et al. (2012), Coskun et al. (2010), Yalcuk et al. (2010), Ammary (2004), Del Bubba et al. (2004)
Olive mill	40-153	4.6-7.4	131-2900 ^a	2.3-25	99-194	64-350	60-114	Mosse et al. (2011), Bustamante et al. (2005), Petruccioli et al. (2002)
Winery	12.8-50	5.0-5.5	35-110 ^a	2.0 ^b	0.9	35-77	35	Ge et al. (2015), Lemaire et al. (2009), Gannoun et al. (2009), Gutiérrez-Sarabia et al. (2004)
Abattoir	2.9-68	6.8-7.3	294-670 ^a	56-150	1.6	28-49	23-40	Yetilmezsoy and Sapci-Zengin (2009), Yetilmezsoy and Sakar (2008), Finlayson and Chick (1983)
Poultry	1.8-12	6.9-7.9	98-1825 ^a	34-987	0.08	15-446	7.0-28	Kim et al. (2016), Villamar et al. (2015), Ichihashi and Hirooka (2012), Neubauer et al. (2012)
Swine	25-60	6.8-7.8	2350-3570	1775-2540	0.5-1.5	194-780	45-221	Falahati et al. (2018), Passero et al. (2015), Villamar et al. (2013), Wang et al. (2010), Wood et al. (2008), Harris et al. (2008), Mantovi et al. (2003)
Dairy manure	1.2-38	7.0-8.3	65-3305 ^a	22-200	0.3-10	12-266	8.5-13	Arivoli et al. (2015), Jarpa et al. (2012), Chandra and Singh (2012), Chamorro et al. (2010), Leiviskä et al. (2008), Ekholm et al. (2007)
Pulp and paper	0.13-22	6.8-7.8	0.53-24	0.4	-	0.5-2.4	0.01-2.3	Oladoja et al. (2017), Schulz et al. (2003), Comeau et al. (2001)
Aquaculture	0.03-0.13	6.6-7.5	2.4-19	0.6-1.3	0.7-19	0.15-0.35	0.12	Bering et al. (2018), Zita et al. (2015), Šostar-Turk et al. (2005)
Laundry	0.28-0.83	6.8-9.5	290-670 ^a	2.2-2.5	0.2-0.6	10.0-12	1.7-4	da Fontoura et al. (2017), Calheiros et al. (2009), Lefebvre et al. (2005), Cooman et al. (2003)
Tannery	2-4	7.5-8.4	160 ^a -390	98-343 ^b	0.3-59	0.4-21	0.06-7	Punzi et al. (2015), Lim et al. (2010), Ong et al. (2009)
Textile	0.3-1.7	7.5-10	62	1.7-34	3.4-30	-	2.0-17	

The particulate fraction is not always mentioned in studies, since in general only the dissolved fractions are determined analytically. Ekholm et al. (2007), in their analysis of industrial wastewater from pulp and paper mill, found that dissolved forms predominated in 86% of the samples and where 63% corresponded to phosphate represented as DRP. Leiviskä et al. (2008) found similar results, as in between 14% and 30% of the wastewater samples the TP was bound to particles. Particulate P concentrations vary according to their origin. For example, Ichihashi and Hirooka (2012) reported that in a swine influent 86% of TP corresponded to particulate P, with a total concentration of 670 mgTP/L. In contrast, in a pulp and paper mill influent, particulate P accounted for 27% of TP, with a concentration of 0.46 mgTP/L (Ekholm et al. 2007).

In comparison with industrial wastewater, domestic wastewater has lower concentrations of P. Domestic wastewater presents TP concentrations varying from 5 to 30 mg/L depending on urban or rural wastewater (Andres et al. 2018; Dueñas et al. 2003; Li et al. 2018; Luo et al. 2016; Pronk et al. 2015). However, these concentrations are not sufficiently low, as eutrophication in continental water bodies such as rivers and lakes is triggered by concentrations of 0.03 to 1 mgTP/L (Vollenweider and Kerekes 1982). Generally, most particulate P (~78%) is removed in the primary treatment stage of the domestic wastewater treatment plant (Dueñas et al. 2003). Therefore, the total P concentration in the effluent consists mainly of dissolved P, with the phosphate ion accounting for 80-100%.

Domestic wastewater is generally composed of 57-95% inorganic phosphate (Andrés et al. 2018; Drenkova-Tuhtan et al. 2017; Gu et al. 2011; Sengupta and Pandit 2011; Pronk et al. 2015). However, other authors, such as Dueñas et al. (2003) and Venkatesan et al. (2018) found that phosphate accounted for only 40 and 20% of TP. Gu et al (2011), through P analysis, characterized a primary treatment effluent of which 57% (1.569 mg/L) corresponded to DRP, 17% (0.466 mg/L) to PRP, 21% to hydrolyzable or labile P and a smaller portion (2.8%) to organic P. These results show that P fractions are variable according to the origin and type of wastewater treatment. To better choose from among available technologies or disposal and recovery treatment mechanisms it is necessary to better understand the characteristics of both P fractions and concentrations in water, previously defining P discharge limits and recovery targets.

3. PHOSPHORUS RECOVERY MECHANISMS

From a global perspective and analyzing the transformations of P in the ecosystem, it is necessary to differentiate the mechanisms of P elimination and recovery. P elimination was originally aimed at avoiding eutrophication, and later the reuse of P-rich sludge in agriculture was examined (Cornel and Schaum 2009). Thus, sustainable P management, which involves the elimination and possible recovery of P, emerged. In general, recovery is based on a design model and techniques that produce a product containing P that can be easily reused (European Commission 2013; Desmidt et al. 2015; Venkiteshwaran et al. 2018). It should be noted that all removed P is not necessarily recovered. For example, Guisasola et al. (2019) removed 98% of P using a biological reactor and recovered about 60% through supernatant extraction from the anaerobic system.

P recovery occurs in both phases of wastewater: the liquid phase (water column) and the sludge phase (Tarayre et al. 2016). In the sludge phase, approximately 90% of the total P load is retained after tertiary or advanced treatment in WWTPs (Cornel and Schaum 2009; Egle et al. 2016). The potential for P recovery in sludge depends on the treatment it is subjected to. For example, in sewage sludge between 80% and 90% of P can be recovered, in sewage leachate 40% and in sewage sludge ash >90% (Cieřlik and Konieczka 2017; Cornel and Schaum 2009; Egle et al. 2016; Desmidt et al. 2015). P fractions in sludge depend on the metal added as a precipitating agent (coagulant, flocculants, precipitating salts). In raw sludge, inorganic P accounts for about 70% of TP, while the phosphate ion accounts for about 50%, mainly bound by the particulate fraction (Li et al. 2019). After the application of sludge treatment, inorganic P generally increases. Li et al. (2019), in an anaerobic digestion treatment and chemical precipitation with Mg and Fe, found that inorganic fractions of P increased by 83.9% and 79.6%, respectively. In addition, the inorganic P digestion ratio increased from 59.8% to 63.8%, which implies excellent mobility and bioavailability of P. Liu et al. (2019) also demonstrated that the addition of lime (CaO) to biochar derived from sewage sludge increased the bioavailable fraction of inorganic P from 21.2 to 33.6%.

If the main objective is to maximize P recovery, then the focus should be on solids rather than liquid streams. However, there is a possibility that sewage sludge may contain potentially hazardous organic pollutants, e.g., aromatic hydrocarbons, and heavy metals. Concentrations of metals such as Cd, Hg, As, Co, Ni, Pb, Cr in sludge can reach values of 3.0, 3.0, 6.0, 7.0, 22, 47 and 60 mg/kg,

respectively (Cieřlik and Konieczka 2017). Nonetheless, most current techniques aim at P recovery from the liquid phase of wastewater, in which there is a recovery potential of 40-60% (Cornel and Schaum 2009; Pratt et al. 2012; Ye et al. 2017). However, P concentrations in domestic wastewater are generally low (~15 mgTP/L). Therefore, a process is needed to increase the concentrations and optimize P recovery and reuse. From an economic point of view, the recovery of the sludge phase generally costs approximately 4-6 €/PEyear, while the liquid phase costs between 0.8- 6 €/PEyear. However, variables such as type of treatment process, annual costs, annual production load per person, among others, must be considered (Cornel and Schaum 2009; Egle et al. 2016).

The notable processes that have been most widely used for P recovery from wastewater are adsorption by support, chemical precipitation and enhanced biological phosphorus removal (EBPR) (Melia et al. 2017). These processes incorporate physical (Loganathan et al. 2014), chemical (Ye et al. 2017) and biological mechanisms (Tarayre et al. 2016). However, recent studies have shown that the P recovery using combined mechanisms has been particularly successful (Li et al. 2018; Ye et al. 2019; Zou and Wang 2016). Combined mechanisms have been shown to promote the conversion and recovery of different forms of P, decreasing effluent concentrations to less than <0.1 mg/L TP (Zou and Wang 2016; Qiu and Ting 2014). In addition, a release of phosphate to soluble state has been demonstrated, reaching up to 77.4% of TP (Kim et al. 2016) and a P recovery of 99% (Sengupta et al. 2015). Gu et al. (2011) combined EBPR and chemical removal of P with chemical addition and tertiary filtration; the combined mechanism system effectively reduced TP concentrations in a WWTP effluent from 2.77 mg/L to 0.054 mg/L.

Figure 3.3 groups the different processes associated with physical, chemical and/or biological mechanisms with the various technologies used for P recovery. Some technologies can be based on more than one process, e.g., constructed wetlands are based on adsorption by support, P precipitation and assimilation of plants and bacteria. This also implies that P can be retained by more than one mechanism.

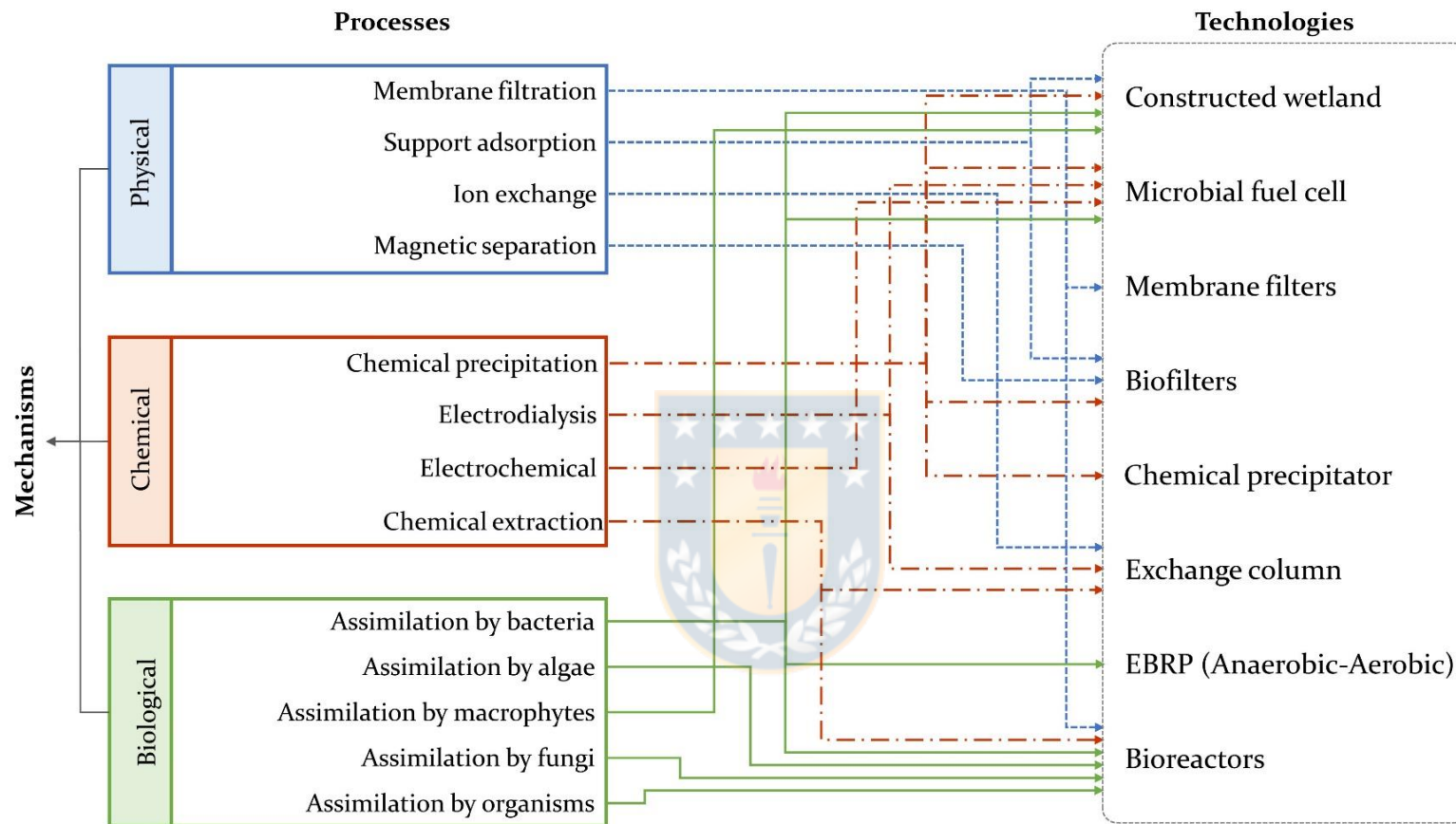


Figure 3.3. Different processes associated to physical, chemical and/or biological mechanisms, with the different technologies used for the recovery of P. Each arrow links each mechanism (on the left) to the relying technology (on the right).

3.1. Technologies based on physical mechanisms

Figure 3.3 illustrates the processes for treating P through physicochemical mechanisms, including filtration (osmosis, microfiltration or ultrafiltration), support adsorption, ion exchange and magnetic separation (Perera et al. 2019; Venkiteshwaran et al. 2018). Some experimental technologies that have been developed using physical mechanisms are: membrane filtration (Luo et al. 2016), wetlands constructed with zeolite as a support medium (Vera et al. 2014), calcite filter adsorption (Arias et al. 2003; Perera et al. 2019) magnetic separators (Prot et al. 2019), nanoparticle columns (Shahid et al. 2019) and ion-exchange columns with resins (Johir et al. 2011). These technologies have presented P retention efficiencies varying between 50 and 97%. However, they have generated effluents with concentrations between 1 and 4 mgP/L (Vera et al. 2014; Johir et al. 2011), values that exceed the established limits. For example, TP limits for wastewater discharges in Europe are between 1-2 mgP/L, for China 0.5 mgP/L, and in protected waters in Europe and the USA 0.05 and 0.01 mgP/L, respectively (Zou and Wang 2016; AWWA 1970). One of the limitations of these technologies is the load capacity or saturation of the adsorbent medium; therefore, they are recommended for effluents with low P concentrations (<10 mgP/L). Another alternative is the use of a pre-treatment or combining the technologies with other processes such as chemical precipitation (Prot et al. 2019) or a membrane bioreactor (MBR) (Johir et al. 2011) for optimization (Loganathan et al. 2014).

3.1.1. Membrane filtration

Membrane filtration technology based on physical mechanisms selectively separates constituents (particles, salts or ions) from wastewater without transforming them, taking advantage of particle size and water reactivity (Mehta et al. 2015). Membrane filtration can remove and recover both dissolved and particulate P (Sengupta et al. 2015). For the removal of P in particle form (< 0.1 μm), the most appropriate technologies are micro- or ultrafiltration (MF or UF) (Luo et al. 2016). Meanwhile, for dissolved P the best technologies are nanofiltration or reverse/direct osmosis (NF or RO/FO) (Qiu and Ting 2014). Membrane rejection provides an easily recoverable source of P (Sengupta et al. 2015). Nur et al. (2018) used effluent from a membrane bioreactor with a concentration of 35 mgPO₄³⁻/L and water treated by reverse osmosis with a concentration of 10

mgPO₄³⁻/L as sources of P for recovery. Another characteristic of these technologies is the low P concentration of 0.04 mgP/L in tertiary membrane and MBR effluents, and as low as 0.008 mgP/L for reverse osmosis systems (Sengupta et al. 2015).

Qiu and Ting (2014) managed to enrich the rejection stream by 98%, reaching a P concentration of 94.4 mgPO₄³⁻-P/L (including dissolved and particulate P), using an osmotic membrane bioreactor (OMBR) system. A promising approach has been the implementation of hybrid membrane systems. Luo et al. (2016) developed an osmotic membrane bioreactor–reverse osmosis (OMBR–RO) hybrid system integrated with periodic microfiltration (MF) extraction that was evaluated for simultaneous P and clean water recovery from raw sewage. This system was able to recover P in the form of amorphous calcium phosphates with a P content of 15-20% (w/w) at pH 10 in 24 h. A disadvantage of membrane filtration is that the membranes are sensitive to pH variation, generally operating in the range of 6.0-8.0 to reduce inorganic scaling and maximize shelf life (Mehta et al. 2015). The high costs associated with these technologies are another major disadvantage. Estimated membrane costs are 20 €/m², along with energy costs of 0.065 €/kWh (Cornelissen et al. 2011).

3.1.2. Support adsorption

Sorption is based on a reversible process (adsorption/desorption) through which the stream (liquid) is fixed in a solid material. The adsorbent/sorbent is the surface on which the adsorption takes place, whereas the adsorbate/sorbate is the substance that is adsorbed on the surface (Bus and Karczmarczyk 2015; Markou et al. 2016). For P adsorption, the adsorbed element is phosphate; organic P adsorption using this method has not been studied.

Table 3.2 shows a summary of different support materials that have been evaluated for P adsorption. Certain properties such as adsorption capacity, mineral content and physical-chemical characteristics such as particle size, porosity and surface area of the material are to be considered when choosing good support material.

Table 3.2. Characteristics of different types of support materials for phosphorus retention.

Type of material	Support	Study Type	Particle size (mm)	Porosity (%)	Superficial area (m ² /g)	Mineral content	pH	P retention (mg P/g)	References
Artificial	Filtralite	Batch	0-4	65	-	Ca-Mg	10	3.3	Ádám et al. (2005)
	Polonite	Column and batch	2-6	45	14	CaSiO	13.4	1.14	Nilsson et al. (2013)
	Magnetite synthesis	Column and batch	11.64 ^a	-	75.77	Fe ₃ O ₄	8.3	11.78	Shahid et al. (2019)
Waste	Opoka	Batch	2-5	50	-	Ca	10-12	45.6	Kasprzyk and Gajewska (2019)
	Gastropod shell	Batch	-	-	1.96	CaCO ₃	7.0-8.0	8.4	Oladoja et al. (2017)
	Active slag	Full-scale	10-20	45	-	Al ₂ O ₃ -TiO ₂	-	1.23	Shilton et al. (2006)
Natural	Zeolita	Batch	1-13	-	243	Al-SiO	7.0	0.33	Andrés et al. (2018)
	Apatite	Pilot-scale	4.02	50	690	Ca	7.4	1.1	Harouiya et al. (2011)
	Gravel	Batch	19-25	48	-	Al-Fe	7.0	0.02	Vera et al. (2014)
	Sand	Batch	0.21	33	0.08	SiO ₂ -Ca	6.9	0.121	Prochaska and Zouboulis (2006)
	Limestone	Mesocosm	12-25	-	-	Ca	7.5-8.5	0.46	DeBusk et al. (2004)
	Dolomite	Batch	1.2	35	0.14	CaMg (CO ₃) ₂	7.8	0.168	Prochaska and Zouboulis (2006)
	Modified	Calcined dolomite	Batch	0.18-0.425	-	0.14	Ca-Mg	3.54	12.5
Pretreated bentonite		Batch	0.3-1	-	-	SiO ₃ Ca (OH) ₂	7	8	Markou et al. (2016)
Hydroxy-aluminum pillared bentonite		Batch	1.88 ^a	-	200	[Al ₁₃ O ₄ (OH) ₂₄ H ₂ O ₁₂] ⁺	3-5	12.7	Yan et al. (2010)
Natural-Artificial	Limestone - Activated carbon	Batch	2.36-4.75	46	-	Ca	6.78	3	Hussain et al. (2011)

Different materials can classify as natural, waste, modified or artificial. Natural materials are commonly used due to their local availability, low purchase, and pre-treatment costs. However, the adsorption capacity of most natural materials is usually very low (<1 mgP/g). Some studies reported the application of natural materials in constructed wetlands, with P removal efficiencies of 45 to 80% obtained. The highest removal efficiencies were achieved with zeolite, at 70% (Vera et al. 2014), and apatite, at 80% (Harouiya et al. 2011). In contrast, lower efficiencies of 45 to 50% were obtained with sand, dolomite, limestone and gravel (DeBusk et al. 2004; Prochaska and Zouboulis 2006; Vera et al. 2014).

Some waste materials that have been tested for P recovery are fly ash, slag and gastropod shells (Tang et al. 2017; Shilton et al. 2006; Vohla et al. 2011). Slag materials such as steel (Shilton et al. 2006) and magnesium (Tang et al. 2017) have presented P retention efficiencies of 77% and 72%, respectively. A waste material that has presented high removal efficiencies (99%) and high P holding capacity (45.6 mgP/g) is opoka, which is a waste material resulting from heat treatment of silica carbonate rock at a temperature above 700°C (Kasprzyk and Gajewska 2019). One of the disadvantages of reuse is that a pretreatment of the waste materials becomes necessary due to the high alkalinity of the ashes (9.0-12) and the possibility of co-precipitation with some heavy metals (Kasprzyk and Gajewska 2019; Shilton et al. 2006; Tang et al. 2017; Vohla et al. 2011).

One method of optimizing P adsorption is the modification of certain natural materials. The modification can be carried out with acid treatments, ion exchange and surface modifications, among other methods, and thus increases the adsorption and specific capacities of the support materials (Loganathan et al. 2014). Markou et al. (2016) modified bentonite by chemically treating it with $\text{Ca}(\text{OH})_2$, obtaining a significant increase in P absorption from 0.3 mgP/g in untreated bentonite to 8 mgP/g in pretreated bentonite at an initial P concentration of 100 mg/L. Karaca et al. (2006) analyzed the feasibility of using calcine dolomite; it was observed that P retention decreases from approximately 23 to 12.5 mgP/g at an initial concentration of 8 mgP/L, with dolomite calcination at 350 °C. This is due to the changes that occur in the structure and pore size distribution, which generate a change in the interaction mechanism between P ions and the surface (Karaca et al. 2006).

Emerging supports have resulted from the synthesis of materials or the creation of active nanoparticles (0.1 microns) for P adsorption (Pratt et al. 2012). Shahid et al. (2019) synthesized magnetite particles using iron oxide residues through reverse precipitation. Approximately 11.78 mg of P was adsorbed into 1 g of synthesized magnetite, obtaining a P retention efficiency of 96%. A similar study synthesized bentonite with hydroxy-aluminum (Al-Bent), obtaining a large surface area of 200 m²/g and adsorption capacity of 12.7 mgP/g (Yan et al. 2010). Although artificial products have shown great affinity for P (> 80%), the production and pretreatment of these materials, their cost and the possibility of recycling P-saturated support materials as fertilizers must be considered (Melia et al. 2017; Vohla et al. 2011).

It is important to note that studies do not always operate under the same conditions and that differences in certain parameters such as initial concentration (mgP/L), particle size and amount of support material (g) make it difficult to compare and relate to different types of support materials (Karaca et al. 2006; Loganathan et al. 2014; Markou et al. 2016). However, some conclusions have been drawn from research. For example, in studies conducted in our laboratory, Andres et al. (2018) related the particle size ratio (1-13 mm) to the quantity of zeolite (20 and 50 g) and initial phosphate concentrations (1, 5, 10, 15 mgPO₄³⁻-P/L). The authors concluded that when the amount of zeolite increased from 20 g to 50 g, the percentage of P accumulation in zeolite increased by between 30% and 50% for initial concentrations higher than 5 mgPO₄³⁻-P/L and for the same size of zeolite. No correlation has been found between material size and adsorption capacity (Adam et al. 2005). However, a mixture of zeolite particle sizes (e.g., 1 to 13 mm) could provide more favorable conditions since more active sites could be used (Andres et al. 2018).

Regarding P adsorption capacity and initial P concentration, the adsorption capacity generally increases (20 - 48 mgP/g) as the initial concentration increases (10 - 100 mgPO₄³⁻/L) (Karaca et al. 2006). Oladoja et al. (2017) used gastropod shells as a support medium to evaluate P adsorption capacity in tests in which the initial concentration was increased (3.3 to 30.5 mgP/L). The researchers observed that the amount of P adsorbed increased proportionally from 1 to 4 mgP/g and noted that the process half-life drastically neared equilibrium at 5 h. However, Andres et al. (2018) observed that when the initial concentration was increased from 5 to 15 mgPO₄³⁻/L the adsorption was variable and decreased by between 10 and 40% in a support material such as

zeolite. In addition, Adám et al. (2005), using an artificial material, filtralite, showed that the adsorption velocity could depend on the initial P concentration, but that it was not correlated with the hydraulic loading velocity. For example, at an initial concentration of 15 mgP/L and different hydraulic loading velocities (5 and 1.25 L/d), approximately the same amount of P (90%) can be absorbed in time periods of 150 days and 18 months, respectively. Hussain et al. (2011) investigated the adsorption behavior of activated limestone-carbon in an upward-flowing column and found that a higher flow (0.003 L/min), an alkaline pH (11) and a higher initial concentration (22 mgP/L) produced a shorter column saturation time (7 h).

Other parameters such as pH, temperature (°C) and agitation (rpm) are important in P adsorption. At a pH between 4.5 and 5.0, precipitation of exchangeable cations is mainly due to Fe and Al, whereas under neutral and alkaline conditions between 6.0-8.0, precipitation is mainly due to Ca and Mg (Vera et al. 2014). In the case of temperature, Markou et al. (2016) did not find any significant differences in adsorption capacity at temperatures of 15, 25, 35 or 45 °C. Similarly, Karaca et al. (2006) observed a small decrease in adsorption capacity of approximately 47 to 43 mgP/g with a temperature increase of 20 to 40 and 60 °C in dolomite. Adsorption tests are usually performed between 15-25 °C (Harouiya et al. 2011; Prochaska and Zouboulis 2006), and agitation between 100 and 200 rpm is recommended. However, Hussain et al. (2011) showed that limestone has the potential to remove approximately 90% of phosphate at a higher stirring rate (300-400 rpm), with the increased stirring rate inducing better surface contact between the adsorbent and the aqueous solution, thereby improving the adsorption rate.

One of the disadvantages of support materials is that after a period of use, they become saturated and their P-retention efficiency decreases. Therefore, the saturated material must undergo a backwash or dewatering process (Loganathan et al. 2014). Shilton et al. (2006) a full-scale steel slag filter covering 28,830 m², removed 77% of TP, adsorbing 22.4 t P in 11 years operation, 19.7 t of which were removed in the first 5 years period. Increasing the filter capacity could prolong the hydraulic retention time (HRT) and thus the useful life of the filter (Pratt et al. 2012). However, a very long HRT can generate P desorption from the support material, which is why short-term storage is greater (0.011 to 0.022 gP/m²d) compared to long-term storage (5 years and 0.0025 gP/m²d) (Vymazal and Kröpfelová 2008).

Once the materials exceed their adsorption capacity, they can be a potential source of recovery and used as fertilizers. Saturated backing material can be desorbed, and release P. de Boer et al. (2018) used zeolite with struvite as fertilizer, finding a TP concentration of 13 gP/kg, of which 5.3 gP was assimilated by the plant. It should be noted that the mobility and bioavailability of P in these materials has not yet been sufficiently studied (Melia et al. 2017). It is important that, at the time of reuse, both the bioavailability P and possible contamination with emergent contaminants or heavy metals be evaluated (de Boer et al. 2018; Ebberts et al. 2015).

P concentration values in the effluent show values between 1 - 4 mgP/L independent of the influent concentrations which do not exceed concentrations above 25 mgP/L (Luo et al. 2016; Vera et al. 2014; Arias et al. 2003; Pront et al. 2019; Johir et al. 2019; Shahid et al. 2019; Drenkova-tuhtan et al. 2017). Even so, effluent concentrations are above the norm. In Europe P discharges between 1-2 mgP/L must be complied with, in China 0.5 mgP/L, protected waters in Europe and USA 0.05 and 0.01 mgP/L respectively (AWWA 1970; Zou and Wand 2016). However, in Latin American countries concentrations <10 mgP/L comply with established discharge standards (Mayer et al. 2013).

3.1.3. Ion exchange

P ion exchange is a process where ions (PO_4^{3-}) are transferred from an aqueous solution to charged surfaces of a selective medium, allowing the production of a P- impoverished effluent, while maintaining charge neutrality in the solid medium (Perera et al. 2019). Ion exchange is considered a type of adsorption that uses the electrostatic force of physical attraction between the ion and the adsorbent (Loganathan et al. 2014). In this process, suitable adsorbent materials are used, i.e., porous media with a large surface area and active sites with a positively or neutrally charged surface to selectively adsorb the ions. Typical materials include resins such as polymeric anion exchangers (purolite) (Johir et al. 2011), styrene-DVB matrix anion exchangers, Dowex 21K XLT (Nur et al. 2018) and hybrid anion exchangers (HAIX) (Sengupta and Pandit 2011). Other materials used are synthesized products such as granular activated alumina or waste products such as zirconium oxide and iron oxide tailings (Perera et al. 2019; Sengupta and Pandit 2011).

The ion-exchange process has allowed P accumulation and recovery, presenting efficiencies above 90% (Sengupta and Pandit 2011; Johir et al. 2011). Johir et al. (2011) used an ion-exchange process to recover N and P from an MBR effluent. In their study, macroporous anionic resins called A200P and A520E purolite were used; the P removal efficiency was higher for A500P purolite, at 50-90%, compared to A520E purolite, which presented an efficiency of 10-30%. In another similar study, Nur et al. (2018) used an anionic resin column (Dowex 21K XLT) for P accumulation, obtaining after 30 minutes a phosphate concentration 14 times higher than that of the original MBR water. Generally, WWTPs have a neutral pH, so the predominant P species are HPO_4^{2-} and H_2PO_4^- ; both species are strong ligands for oxides of polyvalent metals. Hence, Sengupta and Pandit (2011) used an anion-exchange polymeric resin impregnated with iron oxide nanoparticles to carry out the selective retention of P from wastewater and its possible recovery as fertilizer.

3.1.4. Magnetic separation

One of the characteristics of orthophosphate is its negative charge (PO_4^{3-}), which confers it magnetic properties. This recovery process is based on similar principles as adsorption, where phosphate is adsorbed by an adsorbent material with magnetic properties. Once the phosphate has been sequestered from the solution, the P-charged carrier material can recover by capturing the magnetic particles with a magnetic field in high-gradient magnetic separators (Mehta et al. 2015). Melia et al. (2017) reviewed some types of modified or synthetic adsorbent materials with magnetic properties, including zirconium-charged fibers, silica magnetite with amine, bimetallic nano ferrites (CuFe_2O_4 green synthesis), cerium-zirconium binary oxide nanoparticles and binary oxide (magnetic Fe-Zr), which have retention capacities ranging from 13 to 36 mgP/g.

Prot et al. (2019), inspired by technologies used in the mining industry, developed a magnetic separation procedure based on paramagnetism to extract magnetic fractions from sludge streams. They used magnetic separator equipment called Jones on a laboratory scale with an emphasis on recovered vivianite from wastewater treatment. They were able to separate up to 62% of vivianite, from which 80% of the P could be recovered. Likewise, Drenkova-Tuhtan et al. (2017) recovered > 90 % of phosphate from wastewater by means of magnetic particles coated with ZnFeZr. The optimal operating conditions were a 20 min HRT, pH 6.0-8.0 and an influent concentration of 10

mgPO₄³⁻-P/L. In addition, this process was able to guarantee effluent concentrations <0.5 mgPO₄³⁻-P/L.

Magnetic separation has not been widely studied, so more information and application are needed to fill the knowledge gap. Even so, it is presented as a potential process for P recovery because it is easy to operate and does not require high energy consumption, produce sludge or interfere with biological mechanisms (Perera et al. 2019). The main focus in this type of process is to be able to further investigate low-cost adsorbent materials with the properties mentioned above and the possible recovery of P in the materials used.

3.2. Technologies based on chemical mechanisms

Chemical mechanisms are widely applied in the recovery of P from wastewater because they are highly reliable, stable and efficient. However, their feasibility of use varies, as it sometimes depends on the type of precipitate and its bioavailability (Ye et al. 2017). According to the properties that characterize the phosphate ion, various chemical approaches have been developed for its recovery, such as chemical precipitation processes, chemical extraction, crystallization and electrochemical, among other emerging technologies (Fig. 3.3) (Cao et al. 2019; Dai et al. 2017; Ichihashi and Hirooka, 2012; Johir et al. 2011). Chemical technologies have presented a recovery efficiency of 63-99%, with P crystallization proving to be the most effective (99 %) and widely used treatment.

3.2.1. Chemical precipitation

Chemical precipitation of phosphate is one of the most commonly used methods of recovering P from the liquid stream of wastewater. Chemical precipitation consists of choosing an appropriate chemical as a precipitator agent that can be added before, after or during water treatment (Ye et al. 2017).

Table 3.3. Summary of the main characteristics of phosphorus recovery by chemical precipitation.

Type of influent	Chemical additions	Chemical formula	Operational conditions				P recovery (%)	References
			Molar ratio	pH	HRT (h)	P input (mg PO ₄ ³⁻ -P /L)		
Alkaline brines	Calcium chloride	CaCl ₂	Ca:P = 1.6:1.0	11.5	6-24	500	99	Hermassi et al. (2015)
Industrial wastewater	Seawater - Ammonia diluted	Mg ²⁺	N:P=4.0:1.0	8.0 - 8.5	2	84	64	Crutchik and Garrido (2011)
Fertilizers industry wastewater	Magnesium and ammonium chlorides	MgCl ₂ -NH ₄ Cl	Mg:N:P= 1.0:1.0:1.0	8.5 - 10	0.25-1	1483	98-99	Hutnik et al. (2013)
Anaerobic swine lagoon	Magnesium chloride	MgCl ₂	Mg:P= 1.0:1.0 Mg:P= 1.6:1.0	7.5 - 9.5	24	50.5 - 63.8	91-96	Nelson et al. (2003)
Synthetic wastewater	Magnesium chloride Calcium chloride	MgCl ₂ - CaCl ₂	Mg:Ca=1.0:0 Mg:Ca=0:1.0	5.0 - 11	24	50, 100, 500	71-95	Muster et al. (2013)
Anaerobic supernatant	Calcium chloride	CaCl ₂	Ca:P = 2.5:1.0	8.0 - 8.5	0.58	23	87	Dai et al. (2017)
Synthetic urine	Magnesium oxide	MgO	Mg:P=1.0:1.0	9.1	2	460	95	Wilsenach et al. (2007)
Secondary effluent domestic	Potassium ferrate (VI)	K ₂ FeO ₄	15 mg Fe/L	7.85	0.33	0.252	92	Kwon et al. (2014)
Swine wastewater	Magnesium chloride hexahydrate	MgCl ₂ ·6H ₂ O	Mg:N:P = 1.2:1.0:1.1	8.0 - 9.5	3.1	221	95	Kim et al. (2016)
Industrial wastewater	Brucite	Mg(OH) ₂	Mg:P = 1.3:1.0	8.5	1.5	176	93	Huang et al. (2012)
Membrane-bioreactor effluent (MBR)	Seawater - ammonium chloride	Mg ²⁺ - NH ₄ Cl		7.0 - 7.5		35		
	Seawater - Sodium carbonate	Mg ²⁺ - Na ₂ CO ₃	Mg:N:P= 1.0:1.0:1.0	7.0 - 7.5	3		95-99	Nur et al. (2018)
Reverse osmosis concentrate (ROC)	Seawater - Ammonium chloride	Mg ²⁺ - NH ₄ Cl		7.5 - 7.8		10		
Domestic wastewater	Iron sulphate	FeSO ₄	Fe: P = 1.5: 1.0	7.0 - 8.0	24		50	
	Aluminum sulfate	Al ₂ (SO ₄) ₃	-	7.0 - 8.0	23	0.4 - 2.8 ^a	63	Dotro et al. (2015)
Anaerobic supernatant	Metal salts	Fe ²⁺		6.5			72	
		Fe ³⁺	Fe ²⁺ :Fe ³⁺ :Al ³⁺ : P =1.0:1.0	4.5	0.5	148	78	Huang et al. (2017)
		Al ³⁺		5.0			87	

Table 3.3 shows several studies of P recovery by chemical precipitation in the treatment of different wastewater streams. Based on the main chemical additions and operating conditions as molar ratio, pH, HRT, P input, showing recovery efficiencies ranging between 63% and 99%. Are recorded this method is based on the crystallization of phosphate ions (PO_4^{3-}) that are dissolved and converted into a particulate inorganic compound (Mehta et al. 2015). Therefore, this process focuses on phosphate ions represented as DRP or PRP. However, chemical precipitation of P has been proven to be optimal for non-inorganic fractions such as dissolved non-reactive phosphorus (DNRP). Abel-Denee et al. (2018) observed an average removal of 81% for DNRP, with the inorganic polyphosphate fraction presenting a retention rate of 92% and organic P 74%.

The crystallization mechanism follows three chemical stages: oversaturation, nucleation (crystal birth), crystal growth and agglomeration. Crystallization initiates with a high ion supersaturation, with crystalline nuclei rapidly forming on surfaces. Sequential growth of the crystals follows, with the molecules joining together to begin forming an orderly structure. Finally, the size of the precipitates increases, with small crystals binding to larger and/or agglomerated crystals (Crutchik and Garrido 2011; Kataki et al. 2016). The nucleation of crystals is also generated by seed crystals that induce and promote phosphate crystallization through a support for crystal growth (Rugaika et al. 2019). For example, the use of seeds from a precipitate such as struvite improves recovery by 5% and the crystallization rate by 19-21% and increases the size of the crystals (from 1.72 to 2.08 nm) compared to seedless crystallization. In addition, induction time can be reduced by up to 75 min depending on oversaturation (Kataki et al. 2016). Several studies have analyzed the presence of seed crystals for the crystallization of phosphates in different materials such as sand (Rugaika et al. 2019), calcite (Dai et al. 2017) and industrial $\text{Mg}(\text{OH})_2$ (Crutchik et al. 2017). Harris et al. (2008) studied the mobility of P precipitation using seed material at different pH with an added source of Mg. Their results showed that a treatment with sand as a seed material, an elevated pH (7.0 to 8.9) and MgSO_4 as a source of Mg improved the precipitation of P, which led to a significant reduction in DRP (25 to 5.0 mg/L), with a P conversion from liquid to solid of 72 to 80%.

Phosphate precipitate is generally formed by adding metallic salts of Al, Fe, Mg or Ca as chlorides (CaCl_2 ; MgCl_2) or sulphates ($\text{Al}_2(\text{SO}_4)_3$; FeSO_4) (Melia et al. 2017). Where there are two main crystallization processes, calcium phosphate precipitating as hydroxyapatite (HAP) ($\text{Ca}_5(\text{PO}_4)_3\text{OH}$)

and Mg phosphate precipitating as struvite ($\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$) (Muster et al. 2013; Peng et al. 2018). Other less common additives are potassium ferrate (K_2FeO_4) and iron chloride (FeCl_3). Potassium ferrate at doses of 5-25 mg/L retained over 80% of TP (Kwon et al. 2014). Likewise, FeCl_3 at doses of 0-20 mg/L achieved TP retention efficiencies 39.6-96.4% (Li et al. 2018). For struvite precipitation a source of Mg is indispensable. Some of the most common sources are MgCl_2 (Hutnik et al. 2013; Nelson et al. 2003), MgO (Wilsenach et al. 2007) and $\text{Mg}(\text{OH})_2$ (Huang et al. 2012); less common sources of Mg that have been used are seawater (530 mgMg/L) (Nur et al. 2018) and industrial wastewater (505 mgMg/L) from a frozen fish factory (Crutchik and Garrido 2011).

Studies have shown that certain parameters such as pH and molar ratio can be manipulated for the formation of pure struvite crystals instead of amorphous calcium magnesium phosphate precipitates (Crutchik and Garrido 2011; Muster et al. 2013). However, co-precipitation with Ca and Mg can generate a struvite of higher purity (95-98%), provided that the previous precipitation takes place with Ca. In addition, co-precipitation presented a high (71-95%) P recovery efficiency, due to the higher amount of precipitates (Muster et al. 2013; Nur et al. 2018). Struvite is the most desirable precipitate for P recovery based on purity and bioavailability (97-99% purity and 94% bioavailability). It is therefore comparable to a high-quality fertilizer (Melia et al. 2017). Quantitative analysis showed that struvite was obtained with a purity higher than 98% when $\text{Mg}:\text{Ca} > 4:1$ and $\text{pH} > 7.9$. Conversely, when the pH decreases below 7.5 or $\text{Mg}:\text{Ca} < 4:1$, significant impurities in struvite are likely to occur, whether in the form of HAP, brushite or newberryite (Muster et al. 2013).

The theoretical molar ratios of the participating ions (PO_4^{3-} , NH_4^+ , Ca^{2+} and Mg^{2+}) are equimolar ($\text{Mg}:\text{N}:\text{P}:1:1:1$) for struvite and 1.6:1 ($\text{Ca}:\text{P}$) for HAP (Peng et al. 2018). However, some researchers have shown that the experimental relationship between $\text{Mg}^{2+}/\text{Ca}^{2+}$ and PO_4^{3-} should be greater than the theoretical molar relationship due to the combination of Mg/Ca with some chemicals or organic matter associated with wastewater. Nelson et al. (2003) and Kim et al. (2016) showed Mg:P molar ratios of 1.6:1 and 1.2:1.1, achieving a 95% struvite precipitation efficiency. Dai et al. (2017) showed a higher molar proportion of Ca:P of 2.5, achieving a precipitation efficiency of 86% for HAP. The concentration of NH_4^+ has also proven to have an important role in struvite formation due to the

buffering effects of P (Ye et al. 2017). Crutchik and Garrido (2011) promoted a molar ratio of $\text{NH}_4^+:\text{PO}_4^{3-}$ around 4, obtaining P efficiencies of 64% and monocrystals in needle form of 1 mm.

The pH of the solution is one of the most determining parameters for the crystallization of Ca-P or struvite due to its influence on the solubility of the precipitates and the supersaturation of the solution (Peng et al. 2018). Precipitation can be generated in a pH range of 7.0 to 11.5, although the most appropriate pH is alkaline, from 8.0 to 9.5 (Muster et al. 2013). The precipitation of pure struvite occurs at an almost neutral pH. Hao et al. (2013), through an elemental analysis of crystals, confirmed that highly purified struvite (99.7%) formed at a pH of 7.0-7.5 over a longer time period (three months) at room temperature (25-30°C). A higher pH (> 10) may reduce the efficiency of P recovery due to ammonia volatilization and the amount of ions that are reduced (Ye et al. 2017). Also, a high pH in struvite induces the appearance of smaller crystals and a greater variety of sizes. This is due to an increase in supersaturation in the nucleation process and, consequently, to an increase in the growth rate of the crystals (Peng et al. 2018). Hermassi et al. (2015) proved this, as at pH 11.5 they observed a higher precipitation of hydroxyapatite (96%) compared to 78% at pH 8.0 and 81% at pH 10. However, they observed a lower degree of crystallinity in HAP powders, because the degree of crystallinity of Ca-P decreases through the formation of calcium carbonate.

In addition to factors such as pH and molar ratio, other factors such as temperature, speed or intensity of aeration and mixing; influence P reaction and nucleation processes, although they are less discussed (Peng et al. 2018). They influence the rate of spontaneous nucleation by changing the number of crystals, induction time and product size, as well as the morphology and composition of the precipitates. Wilsenach et al. (2007) in a fluidized bed reactor precipitated struvite from urine with an initial PT concentration of 750 mg/L. They observed that at an agitation rate of 50-300 rpm the concentration of PT in the effluent was lower (51 mg/L) than at an agitation rate of 600 rpm (78 mg/L). This is because as ions decrease, the precipitate flows directly into the settler, resulting in a greater loss of fine materials. Dai et al. (2017) used recirculation at 2.5 L/min, increasing the recovery efficiency to 86%, improving the level of supersaturation i.e. greater nucleation and maintaining the pH (8.0-8.5) and a good mix in the reactor. Temperature generally oscillates between 18 and 30°C (Huang et al 2012; Muster et al. 2013; Nelson et al. 2003). As for the costs associated with chemical precipitation, they are estimated to be worth about 2.2 to 8.8 euros/kg of

P. One of the problems with the cost of producing struvite, for example, is that it covers about a third of the cost of chemical inputs. The market for struvite moves with values between 0,38 and 0,46 euros/kg which are too low to compete with the production of fertilizers from phosphate rock (Peng et al. 2018; Mayer et al 2016). However, as the total value of P considers valuable social and environmental protection services the recovery and reuse become more valuable.

Despite all the foregoing, there are some disadvantages of chemical precipitation such as the need for and cost of chemical additions, inhibitory effects on further biological processing, pH adjustment and the generation of large volumes of sludge that often co-precipitate with toxic ions such as arsenic and fluoride, as well as with organic contaminants, pathogens or viruses (Melia et al. 2017; Perera et al. 2019). For example, de Boer et al (2018) studied the bioaccumulation of pharmaceutical microcontaminant carbamazepine in plant tissues fertilized with adsorbent materials + struvite recovered from human urine. They found that the bioaccumulation in tomato fruit each of the fortified fertilizers in the growing test was ~ 0.003 mg/kg tomato, a level well below the Acceptable Daily Intake (ADI) levels of 0.033 mg/kg/day.

3.2.2. *Electrodialysis*

Another chemical mechanism for recovering P from domestic wastewater is electrodialysis. This technology is based on the extraction that selectively separates anions (PO_4^{3-} , SO_4^{2-} , Cl^-) and cations (NH_4^+ , K^+ , Na^+ , Ca^{2+} , Mg^{2+}), concentrating them in separate solutions. This occurs through an ion-exchange membrane, driven by an electric field applied between electrodes. Zhang et al. (2013) concentrated a wastewater flow of up to 72%, with a concentration of approximately 279 mg PO_4^{3-} -P/L. Some authors, such as Ebbers et al. (2015) and Zhang et al. (2013), have used electrodialysis to recover P from wastewater with efficiencies of 85 and 93%. For this type of process, liquid streams with an acid to slightly alkaline pH (<8.0) tend to have better nutrient solubility and better ion transfer (Mehta et al. 2015).

An advantage of this process is its duality to recover nutrients and remove heavy metals. Ebbers et al. (2015) used a three-compartment electrodialysis method to simultaneously remove heavy metals and recover P from anaerobically digested sludge. P recovery was most effective (95%) at a low pH (2.0). This anaerobic process allowed easier extraction of heavy metals Cd (31%), Cr (6%), Cu

(22%), Ni (56%), Pb (1%) and Zn (85%), as they had fewer adsorption sites, and improved P availability and extraction capacity. Some of the drawbacks of this technology are high energy consumption (1 kWh can produce 60 g of PO₄) and the need for chemical additives for membrane regeneration.

3.2.3. *Electrochemical*

An emerging technology for P recovery consists of microbial fuel cells that use an electrochemical method for the accumulation of phosphate and its subsequent recovery through precipitation. This process is based on the transfer of chemical energy contained in organic matter into electrical energy through microorganisms. The anode and cathode single chambers are optionally separated by an ion-exchange membrane to prevent mixing of oxidation and reduction products (Ichihashi and Hirooka 2012; Ye et al. 2019). This technology is a balanced system in energy and dosage as the pH (alkaline) value of the electrolyte at cathode can be raised without the addition of chemicals. In addition, the use of Mg anodes can generate struvite precipitation in currents with sufficient ammonia (Perera et al. 2019; Ye et al. 2019).

Microbial fuel cells contribute to pH adjustment for subsequent P precipitation, in this case alkaline, conversion of organic P to inorganic P and release of dissolved P. For example, Ichihashi and Hirooka (2012) using a single-chamber microbial fuel cell for swine wastewater. They showed a P release where the dissolved P concentrations of the influent were 100 mgP/L and increased to an average of 170 mgP/L in the effluent at the anode outlet. This result indicates that the particulate P was dissolved in the liquid phase during operation. Therefore, P in suspended solid form was first dissolved and then precipitated on the cathode; this process generated greater availability of dissolved P for possible recovery.

Ichihashi and Hirooka (2012) observe in the cathode of the microbial fuel cell presented P elimination of 70-82% of P and observed struvite precipitation of 4.6-27%. It was concluded that P precipitated on the cathode because the pH was higher (7.2) than other reactor sites. The molar ratio of P:Mg:Ca in the precipitate was 1:0.89:0.94. This means that P precipitated in a slight excess relative to Mg, so the Mg would not be the limiting reagent in P precipitation. Ye et al. (2019) studied nutrient recovery in a double-chamber microbial fuel cell, achieving improvements in P recovery

efficiency of 94%, with P accounting for 2.6% of the total precipitate weight. It was also found that aeration up to 6.22 mgO₂/L could increase the pH (8.0-8.4) due to oxygenation at the cathode, where oxygen is the electron acceptor and thus facilitates the precipitation of P with Mg and Ca (Park et al. 2017; Ye et al. 2019). Final concentrations of PO₄³⁻-P/L decreased by about 0.05 mg/L (Ye et al. 2019).

Other electrochemical methods have also shown efficiencies over 90% recovery of P (Huang et al. 2016; Kruk et al. 2014). Huang et al. (2016) used an electrochemical process combined with an electrochemical precipitation reactor for the recovery of P from pig wastewater. They managed to recover 93% in struvite form and to decrease from an initial concentration of 103 mg/L to an effluent of 7 mg/L. Also, Kruk et al. (2014) precipitate struvite using magnesium sacrificial anode which did not require the addition of chemicals. They noted that an increase in electrical current from 1.14 to 4.5 mA/cm² resulted in a 13% increase in struvite purity and a 98% recovery of P. In contrast, Huang et al. (2016) analyzed the struvite purity obtained at different current densities of 1-5 mA/cm². Whereas current density and electrolysis time increased, struvite purity decreased rapidly. Huang et al. (2016) achieved 95.7% purity at a current density of 2 mA/cm², while Kruk et al. (2014) achieved 90% purity at 4.5 mA/cm². However, in both studies the current density improved the recovery of P.

3.2.4. Chemical extraction

Wet chemical extraction wastewater treatment implies that P in wastewater sludge is solubilized by adding acid or alkali, in combination with heating if necessary (Cornel and Schaum 2009). One of the advantages of using alkali in extraction, unlike acid extraction, is that the release of heavy metals/metalloids can be suppressed, thereby eliminating the need to add another process for metal retention. The decontamination potential (98%) for heavy metals, therefore, it shows a low transfer (<5%) of heavy metals into the recovered product (Egle et al. 2016). However, alkali treatment can also reduce P recovery by up to 30% (Cornel and Schaum 2009; Melia et al. 2017). However, one of the disadvantages may be the associated economic cost of required chemicals, including acids, caustics and precipitating agents. For example, the cost of 1 kg P recovered produced through wet chemical processes is 9-16 € (Egle et al. 2016).

Alkaline hydrolysis can also allow 42% of P to be released from sludge supernatant at pH <10.5 and 16% to be recovered as struvite at a molar ratio (Mg:P) of 1.8 and pH 9.7 in 15 min (Bi et al. 2014). Kim et al. (2016) used an acid-alkaline pre-treatment (pH: 2.0-12) for the recovery of PO_4^{3-} -P from swine wastewater through struvite precipitation. Concentrations of TP and PO_4^{3-} -P increased to up 97% as pH increased linearly in swine wastewater, with the maximum release observed at pH 8.0-9.0. Meanwhile, Qiu and Ting (2014) indicated that when the pH increased (close to 9) in an MBR, it resulted in a decrease of PO_4^{3-} -P dissolved in the bioreactor. Therefore, a relatively lower pH in the bioreactor (preferably <6.5) was essential to maintain PO_4^{3-} -P in dissolved form for later recovery of P.

Advanced oxidation processes (AOP) are another mechanism for solubilizing P. They consist of the generation of hydroxyl radicals ($\text{HO}\cdot$), a potent oxidizing species that mineralizes P into phosphates or phosphoric acid. AOPs have shown release percentages of 24% to 90% depending on the oxidizing agent used (Venkiteshwaran et al. 2018). These acid/alkali conversion technologies and AOPs are effective for solubilizing P in sludge streams and above all for converting non-bioavailable fractions or NRP into RP, which is more susceptible to possible recovery.

3.3. Technologies based on biological mechanisms

This mechanism consists in the biological absorption of P by organisms, microorganisms or plants, known as P assimilation. These mechanisms are based on the transfer, absorption and accumulation of P to recycle it or optimize its retention through the physiological process (Bunce et al. 2018).

Table 3.4 summarizes some technologies that have been developed for P recovery using biological mechanisms. Among them are biodigesters with enhanced biological phosphorus removal (EBPR) (Pronk et al. 2015), constructed wetlands (Adhikari et al. 2015), facultative tanks (Chen et al. 2010), algae reactors (Sukačová et al. 2015), fungal inocula (Ye et al. 2015) and zooextraction (Jones et al. 2001), which have presented efficiencies of 25 to 97%.

3.3.1. Assimilation of phosphorus by bacteria

Assimilation by bacteria depends on microorganisms, specifically a group known as polyphosphate-accumulating organisms (PAO) able to absorb intracellular P as polyphosphates (Poly-P) over the

needs of their growth requirements (Yuan et al. 2012; Melia et al. 2017). This type of process is called EBPR and is enabled by alternating anaerobic and aerobic conditions; PAOs take volatile fatty acids in the anaerobic phase, which are stored as polyhydroxyalkanoates (PHA). They are then metabolized in the aerobic phase to provide the energy needed for the PAO to build up P (Yuan et al. 2012). Because the amount of Poly-P stored in microorganisms is greater than that released under anaerobic conditions, a 10- to 50-fold increase in soluble P is achieved in the biomass of sludge systems (Yuan et al. 2012; Desmidt et al. 2015).

Li et al. (2019) observed that after anaerobic digestion the organic P content in the sludge decreased (from 7.9 mg/g to 4.37 mg/g). This is due to hydrolysis and possible release of orthophosphate. Furthermore, the highly PAO-enriched sludge can accumulate up to 20% dry weight of cells as P, compared to 1-2% in sludge not enriched with PAO (Yuan et al. 2012). Optimal EBPR operating parameters include pH in the range of 6.0-8.0, temperature between 20-25°C, dissolved oxygen (DO) concentration of 0.2-4.5 mg O₂/L, hydraulic retention time (HRT) between 6.5-15 h, solids retention time (SRT) of 10-38 days, and COD/P ratio of 10-60 (Guisasola et al. 2019; Li et al. 2018; Melia et al. 2017; Pronk et al. 2015).

The addition of carbon is fundamental for EBPR, as without the addition of carbon, PAOs can be affected. Ge et al. (2015) observed that phosphate release was strongly linked to the absorption of dissolved carbon (sCOD). Li et al. (2018) recirculated the membrane bioreactor (MBR) sludge through fermenters. This co-fermentation helped recover P and alleviate the problem of inorganic build-up in the MBR. In contrast, Guisasola et al. (2019) were able to treat wastewater influents with a low COD/P ratio of 7.5 in an anaerobic-aerobic SBR, achieving a P recovery of 33%. As for dissolved oxygen, an increase in DO leads to a higher aerobic volume of biofilm which is composed of PAOs and these release P. In contrast, low concentrations (< 0.2 mg O₂/L) can inhibit denitrification and PAOs store P (Wong et al. 2015). Pronk et al. (2015) studied the use of aerobic granular sludge technology in a WWTP. They observed that the system operating with an initial concentration of 4.4 mg/L of PO₄³⁻-P increased to 15 mg/L of PO₄³⁻-P with aeration to 2.5 mg O₂/L. By contrast, when aeration decreased to 1.8 mg O₂/L the concentration could reach 0 mg PO₄³⁻-P /L.

Recent applications of EBPR include incorporation into MBR (Li et al. 2018), granular sludge reactors (Pronk et al. 2015) and sequencing batch biofilm (SBR) reactors (Guisasola et al. 2019). It has been reported that domestic wastewater treatment with EBPR in these reactors can yield P conversion rates of 4 to 24 gP/m³d sludge at laboratory scale and 240 gP/m³d at full scale. P concentrations in domestic wastewater effluents have also been reduced, reaching values less than 1 mg/L of TP (Guisasola et al. 2019; Li et al. 2018; Pronk et al. 2015). Recently, new configurations have been developed for EBPR systems. Guisasola et al. (2019) proposed an EBPR² (biological phosphorus removal and recovery) modified to include an extraction of the supernatant after the anaerobic phase, through which the concentration of the influent was increased from 20 to 40 mg/L of P with 6 h cycles. It should be noted that the system was able to maintain its recovery capacity (33-69%) with a biomass P assimilation that increased from 4.9 to 9.6 mgP/gVSS. Therefore, an alternative to EBPR followed by P recovery is to apply anaerobic treatment in advance to recover P in the anaerobic treatment effluent stream.

3.3.2. Assimilation of phosphorus by algae

In addition to microorganisms, P assimilation by microalgae and cyanobacteria has also been studied, demonstrating the ability to grow and reduce P concentrations in wastewater to approximately 1 mgTP/L (Sukačová et al. 2015). Algae absorb P in excess of growth requirements, with P taken as orthophosphate and stored as polyphosphate granules for use. When inorganic orthophosphate is not available, algae absorb organic P, converting it to orthophosphate on the cell surface through the enzyme phosphatase (Bunce et al. 2018). Another way of storing microalgae polyphosphate is through "luxury catchment;" this mechanism occurs when microalgae absorb more phosphorus than required for growth without a previous starvation stage, i.e., P deficiency in the water body (Brown and Shilton 2014). Brown and Shilton (2014) reviewed P accumulation over the amount required for cell growth in microalgae.

Table 3.4. Summary technologies of recovery by biological mechanisms.

Technology	Biological organism	Type of influent	Operational conditions				P conversion rate	P removal (%)	References
			HRT (d)	T(°C)	pH	P input (mg TP/L)			
Sequencing batch reactors (SBR)	Anaerobic microorganisms	Swine wastewater	0.0034	-	-	1729	3.42 g P	25	Massé et al. (2007)
Membrane bioreactor (MBR)	Aerobic microorganisms	Domestic wastewater	0.5	25	6.0-6.9	6.35	24.2 g P/m ³ d	96	Li et al. (2018)
Constructed wetland	Macrophyte: duckweed (<i>Lemna minor</i>)	Dairy wastewater	22.5	15-22	-	0.05-14	0.02 g P/m ² d	45	Adhikari et al. (2015)
Photobioreactor	Filamentous cyanobacteria, diatoms, green algae	Synthetic and real domestic wastewater	0.0048	19-24	7.5-9.9	3	0.16 g P/m ² d	97	Sukačová et al. (2015)
Zooextraction	Oyster (<i>Saccostrea commercialis</i>)	Shrimp effluent	1	20-23	-	0.65	0.55 g P/kg	86	Jones et al. (2001)
Facultative tank	Macrophyte: Water hyacinth (<i>Eichhornia crassipes</i>)	Swine wastewater	1, 7, 27	12-36	-	81.5	0.32 g P /kg	36	Chen et al. (2010)
Vertical subsurface flow constructed wetlands	Macrophyte: cattail (<i>Typha latifolia</i>)	Eutrophic river water	152	23-25	7.7-7.8	0.04-0.22	14.8 and 41.6 g P/m ² d	35-75	Tang et al. (2011)
Reactor SHARON	Aerobic microorganisms	Domestic wastewater	0.27-0.70	20	-	6.7	240 g P/m ³ d	87	Pronk et al. (2015)
Photobioreactor	Benthic algae	Dairy manure wastewater	0.66	22	7.0-7.5	303	0.11 g P/m ² d	93	Wilkie and Mulbry (2002)
Screening	Fungal strains (<i>Mucor circinelloides</i>)	Domestic wastewater	5	27	-	127 ^b	7.08 % Cellular P content	53	Ye et al. (2015)
Sequencing batch reactors (SBR)	Anaerobic and aerobic microorganisms	Synthetic wastewater	0.25-0.5	25	7.5	20	4-12.3 g P/m ³ d	60	Guisasola et al. (2019)
Hydroponics	Macrophyte: duckweed (<i>Spirodela punctata</i>)	Swine lagoon water	0.08	23	7.0	31 ^a	31.92 g PO ₄ -P/m ² d	-	Cheng et al. (2002)

The most common microalgae found in the natural ecosystem are the green microalgae *Scenedesmus* sp. and *Chlorella* sp. (Bunce et al. 2018). Sukačová et al. (2015) studied different groups of algae such as filamentous cyanobacteria (*Phormidium autumnale*, *Chroococcus* sp. and *Pseudanabaena* sp.), diatoms (*Cymbella minuta*) and coccal green algae (*Scenedesmus acutus* and *Monoraphidium contortum*) (Sukačová et al. 2015). Algae that are rich in P can be processed with nutrient (N and P) release techniques such as anaerobic digestion, thermochemical methods, or can be used directly as animal feed or fertilizer (Mehta et al. 2015). For P removal microalgae and cyanobacteria are cultivated and grown mainly in suspension, although the use of benthic algae has also been studied. Benthic (attached) algae can grow as biofilms on solid surfaces and have an advantage over planktonic (suspended) algae in the ease of biomass separation and recovery (Wilkie and Mulbry 2002). These biofilms are composed of autotrophic organisms that play a key role in the self-purification of aquatic ecosystems. Phototrophic biofilms are a technology also known as photobioreactors, which have demonstrated an efficiency of over 90%, obtaining absorption rates of 0.11 to 0.16 gP/m²d (Sukačová et al. 2015; Wilkie and Mulbry 2002).

The P content of dry algal biomass varies between 1.5 and 3.3% under certain conditions such as light intensity, pH, P concentration in the water and temperature (Brown and Shilton 2014; Wilkie and Mulbry 2002; Mehta et al. 2015). For example, the optimal temperature for algae growth is between 15 and 30°C and the optimal pH is in the range of 7.0-8.5. Sukačová et al. (2015) studied the light regimes in a photobioreactor, where algae were able to retain 97% of TP after 24 h under continuous artificial lighting. Meanwhile, when solar radiation (12 h sunlight–12 h night) was used, algae reduced their TP removal efficiency by 36-41%. Therefore, the P removal efficiency could be increased by imposing a regime of sunlight during the day and artificial light during the night.

3.3.3. Assimilation of phosphorus by macrophytes

Another way to assimilate P is through macrophytes; this process consists of harvesting P in the macrophyte biomass. Some widely used and examined macrophytes are water hyacinth (*Eichhornia crassipes*), duckweed (*Lemna* spp., *Spirodela* spp., *Wolffia* sp.), cattail (*Typha* spp.), reed (*Phragmites* spp.) and junk (*Schoenoplectus* spp.) (López et al. 2016; Adhikari et al. 2015). Studies in our laboratory showed that the concentration of P in macrophytes varied between 0.15%

and 0.24% dry weight, eliminating between 5% and 10% of P in wastewater effluent (Vera et al. 2014). Some of the technologies that use macrophytes are CWs, facultative tanks and hydroponics (Adhikari et al. 2015; Chen et al. 2010; Cheng et al. 2002; Tang et al. 2011).

In constructed wetlands, removal capacity will depend on hydraulics, flow direction and macrophyte type. According to the hydraulics, the CWs are classified as surface flow, also called free water flow (FWS), and subsurface flow (SSF). Subsurface flow wetlands can be classified according to the direction of water flow as horizontal (HSSF) or vertical (VSSF) (Carrillo et al. 2019). In FWS, an extraction rate of 0.02 gP/m²d has been observed (Adhikari et al. 2015), while in VSSF it has reached 41.6 gP/m²d (Tang et al. 2011). P retention by water hyacinth (*E. crassipes*) reached up to 45 gTP/m² (Vymazal 2007) and duckweed (*L. minor*) an annual mean of 13 gTP/m² (Adhikari et al. 2015). In an HSSF, Lopez et al. (2016) used macrophytes such as junk (*Schoenoplectus*) and reed (*Phragmites*); the TP content varied from 0.12 to 0.83 g/m² in junk and from 0.08 to 0.23 g/m² in reed. Meanwhile, Cheng et al. (2002), obtained assimilation of 31.92 gP/m²d through the duckweed for synthetic lagoon treatment of swine wastewater, reducing the P concentration in the effluent to 0.4 mgTP/L.

3.3.4. Assimilation of phosphorus by fungi

Fungi have also been shown to be an option for P assimilation. Filamentous fungi are much easier to harvest than bacteria due to their growth in the mycelial structure (Tarayre et al. 2016). These organisms have demonstrated an ability to accumulate P in poly-P granules. Hultberg and Bodin (2019) found a total amount of 13.2% dry weight biomass in *P. ostreatus*. Ye et al. (2015) investigated the potential of *M. circinelloides* for P removal from wastewater, obtaining removal efficiencies of 53% and 7.08% for cellular P content. In addition, Hultberg and Bodin (2019) treated wastewater from a brewery with high concentrations of TP (320-600 mg/L) using fungi and observed a maximum TP retention of 30.8% with *P. ostreatus* and 16.6% with *T. harzianum*. Therefore, the authors observed that for this type of effluent additional techniques such as pre-treatment or combination with other processes are required for efficacy.

3.3.5. Assimilation of phosphorus by organisms

A process called zooextraction based on biological mechanisms facilitated by organisms such as animals is one of the least studied processes for P removal. Zooextraction harvests P through animal biomass, thus contributing to P recycling. For example, mussel cultivation can store 1 gP per dry mussel (Spångberg et al. 2013), while oyster cultivation can store 0.55 gP per pearl oyster (Jones et al. 2001), achieving P retention efficiencies of 86%. Other organisms that use this process are earthworms in vermicomposting, which consists of composting waste. However, the process has not been studied directly with wastewater, as we generally work with sludge to improve soil fertility (Tarayre et al. 2016). Yadav and Garg (2011) reviewed vermicomposting for the conversion of organic matter and nutrients of industrial waste. They reported that worm-treated sludge increased the P content of the sludge by 25%. The increase is due to the direct action of intestinal enzymes of the worm and indirectly by stimulation of microflora that increases P bioavailability through the process of mineralization of P.

3.4. Combined technologies

Although P recovery could be obtained through the technologies reviewed above (physical, chemical and biological), it is important to recognize the recovery potential of all P fractions, including non-reactive, recalcitrant and labile fractions. For example, organic P is normally not susceptible to recovery technologies, which generally rely on physical-chemical mechanisms and recover only inorganic P. Therefore, the recovery capacity of P can be improved by processes such as accumulation, release or conversion of organic to inorganic P, which can be eliminated, extracted and/or recovered for later reuse (Mehta et al. 2015; Venkiteshwaran et al. 2018). To date, several laboratory-scale treatments with combined technologies for P recovery from wastewater have been developed; they are summarized in Table 3.5.

Technologies such as membrane filters (Qiu and Ting 2014), ion-exchange columns (Johir et al. 2011), magnetic separators (Prot et al. 2019), microbial fuel cells (Ye et al. 2019), biological reactors (Cai et al. 2018), membrane bioreactors (Li et al. 2018) or electrodialytic cells (Ebbers et al. 2015), together with chemical precipitation, are among the most prominent combined technologies, obtaining P recovery efficiencies between 62 and 97%. Studies indicate that one of the most

implemented combinations is biological systems with chemical precipitation. EBPR systems are improved by a combination of P accumulation and transformation techniques (Section 4.1.1) (Venkiteshwaran et al. 2018). Zou and Wang (2016) proposed a process called EBPR-PR (EBPR-Crystallization) from domestic wastewater, which consists of enriching PAO in the anaerobic phase, offering the opportunity to recover P through crystallization in the internal process of the EBPR instead of the external process. This process was able to release P and enrich the stream from 5.00 mgPO₄³⁻-P/L in the influent to 15.82 mgPO₄³⁻-P/L in the anaerobic effluent. Recovery of 59% by crystallization improved the EBPR yield, with the P concentration in the effluent gradually decreasing from 1.24 to 0.41 mgPO₄³⁻-P/L.

Another less common technology is the combination of bioreactors with iron dosage for P recovery from sludge, which has presented retention efficiencies of <90 % (Cai et al. 2018; Li et al. 2018). Iron dosage is widely used in WWTP due to the rapid granulation, accumulation and bioavailability of P. Cai et al. (2018) studied the influence of ferrous iron (Fe²⁺) on granulation of activated sludge and the bioavailability of P accumulated in sludge. The results indicated a P accumulation efficiency of 92% with a bioavailability of 95%, especially with a high non-reactive inorganic P content of 36.2 mg/g suspended solids, which was quantified by the Standards, Measurements and Testing (SMT) extraction protocol (Boenke 1998). An innovative technology in this process is MBR with iron dosing and acidic co-fermentation of side-flow sludge, with P recovery occurring through the sludge and iron precipitates. The aerobic MBR converts part of the phosphate into organic P by biosynthesis. The sludge subjected to acidogenesis produces a drop in pH, increasing the solubility of the Fe-P complex, so P and Fe are released in the supernatant. The average ratio for P concentrations (CP, soluble/CP, total) in long-term operations (190 days) was approximately 0.44, while the TP recovery from the wastewater influent 62.1%, which was bound to the iron oxides in the sludge (vivianite) (Li et al. 2018). One of the advantages of combined systems is the recirculation of their processes.

In particular, it is possible to reduce the costs of chemical additives that are required to reach the optimal pH for P precipitation. Qiu and Ting (2014) achieved an effluent <0.2 mgPO₄³⁻-P/L through an Osmotic membrane bioreactor (OMBR) without the addition of Mg and Ca, by combining the process with advanced filtration technology (forward osmosis membrane) in which the ions PO₄³⁻, NH₄⁺, Ca²⁺ and Mg²⁺ are concentrated in the reactor. This P-rich supernatant was enriched to 40.4

mgPO₄³⁻-P/L in 7 days and precipitation of P was carried out at pH 9.0, allowing P recovery of 95%. A similar study (Johir et al.2011) combined an MBR with an ion-exchange column for nutrient recovery. The configuration was advantageous as it allows for a smaller MBR reactor volume, and a correspondingly smaller footprint, as well as less contamination to the ion exchange membrane.

According to the analyzed combined recovery studies shown in Table 3.5, chemical precipitation is the preferred approach for P recovery. Some types of P precipitates have been recovered in the form of calcium phosphate or amorphous magnesium, hydroxyapatite, vivianite and most commonly struvite. Recovered precipitates depending on pH and precipitator type may P contain from 2 to 40% (w/w) (Luo et al. 2016; Nur et al. 2018; Ye et al. 2019). Luo et al. (2016), at a pH adjusted to 10 obtained between 15 and 20% (w/w), mainly in the form of amorphous calcium phosphates. Likewise, Qiu and Ting (2014) obtained amorphous calcium phosphate precipitates with a P content > 11.0 %. Nur et al. (2018) reached higher values, between 32 and 40% (w/w), which resemble the reference struvite (38% w/w) with sea water as Mg source. Some studies evaluate the amount of P in the precipitates from the influent. Ichihashi and Hirooka (2012) estimate that the amount of P contained in these precipitates was equivalent to 27% of the influent, and Li et al. (2018) determined that 66.7% of the P contained in the precipitates came from the domestic wastewater influent. Meanwile, Li et al. (2019), through an analysis of the precipitates in sludge after anaerobic digestion with P precipitation with Mg²⁺ and Fe³⁺, detected quartz, vivianite and struvite precipitates, where

Table 3.5. Phosphorus recovery technologies combined with other processes.

Type of influent	Technology	Process	Operational conditions				Recovered product	P recovery (%)	References
			pH	T (°C)	HRT (h)	P input (mg TP/L)			
Domestic wastewater	Microfiltration (MF)	Membrane filtration + chemical precipitation	10	22	30-80	24 ^a	Amorphous calcium phosphate	15-20 ^b	Luo et al. (2016)
Swine wastewater	Microbial fuel cells (MFC)	Assimilation by bacteria + chemical precipitation	7.78-8.42	25	-	780	Struvite	4.6-27	Ichihashi and Hirooka (2012)
Synthetic wastewater	Sequencing batch reactor (SRB)	Assimilation by bacteria + chemical precipitation	-	-	4.17	10	Sludge	92	Cai et al. (2018)
Domestic wastewater	Membrane bioreactor (MBR) + acidogenic co-fermentation	Assimilation by bacteria + chemical precipitation	8.0	25	12	6.35	Sludge/ Vivianite	62.1	Li et al. (2018)
Swine wastewater	Chemical extraction with MgO	Chemical extraction + chemical precipitation	7.5-11	40	3	114.9	Magnesium ammonium phosphate	96.7	Cao et al. (2019)
Synthetic wastewater	Enhanced removal of biological phosphorus (EBPR)	Assimilation by bacteria + chemical precipitation	8.5	16-21	12	5 ^a	Hydroxyapatite	59.3	Zou and Wang (2016)
Synthetic wastewater	Double chamber microbial fuel cell	Assimilation by bacteria + chemical precipitation	7.0	25	24	1 ^a	Estruvite	94	Ye et al. (2019)
Synthetic wastewater	Membrane	Assimilation by bacteria + ion exchange	-	-	2.4	3.11–4.18 ^a	Anionic resin	95-97	Johir et al. (2011)

	bioreactor (MBR) + ion exchange column								
Swine wastewater	Ultrasonic	Alkaline hydrolysis + chemical precipitation	8.0-9.0	25	3.24	612	Estruvite	95	Kim et al. (2016)
Domestic wastewater	Electrodialytic cells	Assimilation by bacteria + Electrodialysis	2.0-10	25	48	186	Sludge	95	Ebbers et al. (2015)
Synthetic wastewater	Ion exchange column	Ion exchange + chemical precipitation	8.0	20	48	4.25	Calcium phosphate/struvite	> 90	Sengupta and Pandit (2011)
Synthetic wastewater	Pellets reactor + constructed wetland	Chemical precipitation + adsorption	7.0-11	25	4	16-124 ^a	Calcium phosphate	62	Rugaika et al. (2019)
Membrane-bioreactor effluent (MBR)			7.0-7.5			35 ^a		33.5 ^b	
Reverse osmosis concentrate (ROC)	Ion exchange column	Ion exchange + chemical precipitation		24	3		Struvite		Nur et al. (2018)
			7.5-7.8			10 ^a		40.2 ^b	
Domestic wastewater	Osmotic membrane bioreactor (OMBR)	Membrane filtration + chemical precipitation	8.0-9.5	23	15.4-22.6	7.1 ^a	Amorphous calcium phosphate	95	Qiu and Ting (2014)

^amg PO₄-P / L; ^b % (w/w)

quartz represents 30% of the inorganic component of the sludge. Vivianite was the dominant species of inorganic P, in which about 70-90% of the total P

De Boer et al. 2018 combined adsorbent materials such as zeolite and biochar with struvite precipitation, obtaining high recovery efficiencies of 96-98%. Their study on combinations indicated that P recovery was predominantly controlled by struvite precipitation, rather than adsorption by the adsorbent materials. It should be noted that the product recovered with zeolite could be used as a fertilizer, as it has a high buffer capacity; thus, in a later application as a fertilizer on farmland, the adsorbed P would be transferred according to the need of the plants or microorganisms as they consume it (Vera et al. 2014; de Boer et al. 2018).

A similar process occurs in constructed wetlands; this technology occupies all three types of mechanisms: biological through assimilation of plants and microorganisms and physical chemical through precipitation and adsorption of P (Vymazal and Kröpfelová 2008). However, it has been observed that P in wastewater is not sufficiently retained, with only 40-55% P removal in constructed wetlands (Vymazal 2007). Wood et al. (2008) observed that constructed wetlands are optimal for the treatment of dissolved phosphate from dairy wastewater. Over 48 months, the treatment showed TP and DRP retention efficiencies of 53.7% and 52.7%, respectively. However, to improve retention efficiency in these systems, seed material filters have been incorporated as pretreatment (Arias et al 2003; Rugaika et al. 2019). With a calcite filter, Arias et al. (2003) obtained a good initial removal rate (75%), with a high hydraulic load rate (HLR) that varied between 13-50 m/d, but after three months all P filters were saturated. Calcite increased the pH from 7.2 to 7.8 and average calcium from 127 to 193 mg/L. In addition, Rugaika et al (2019) used a pellet reactor for the crystallization of P as calcium phosphate with optimal parameters such as pH 9.0, a molar Ca/P ratio of 1.5. However, a decrease in removal efficiency from 65.9 to 54.2 % was observed with an increase in HLR from 1.8 to 2.9 m/d.

Some of the most common P recovery products are precipitates such as HAPs and struvite; and less common precipitates such as Amorphous calcium phosphate and vivianite (Ye et al. 2019; Luo et al. 2016; Li et al. 2018). Another recovered is P-containing products in biomass such as sludge and plants (Cai et al. 2018; Adhikari et al. 2015). Li et al. (2018) through a mass balance could obtain the proportions of P, where the effluent, the recovered precipitates (vivianite) and the disposal

sludge obtained 3.9%, 66.7% and 29.4%, respectively. Recycling of products may have limitations in their comparison because of different characteristics of the P products present, such as P content expressed in different units, contaminants and bioavailability of P. The bioavailability of P could be the common factor of comparison between the recovered products. However, the authors do not specify this value since their test involves evaluation, i.e., using extractants or more directly in pot or field trials or with algae (Melia et al. 2017). Liu et al. (2019) made a comparison of rice seedling biomass growth between KH_2PO_4 fertilizer and a CaO-modified biochar in a crop. The CaO-modified biochar showed improved growth with an increase in biomass dry weights of 7.7% - 9.5% in contrast to KH_2PO_4 .

In summary, there has been considerable progress in technologies for P recovery in recent years. Biological mechanisms are presented as a good type of pretreatment increasing P solubility rates, resulting in higher recovery rates. Chemical precipitation is an effective and environmentally sustainable method for P recovery. P-loaded materials are a new source of P which can be used as fertilizer for agricultural production. However, there is still a need to pool knowledge on the release and availability of P either in the recovered product or in soils and plant operation. More progress is needed on the final products recovered, their economic, social and environmental impacts in order to close the P cycle.

4. CONCLUSIONS AND PERSPECTIVES

This review has shown that the P recovery technologies focus mainly on the phosphate ion, while other P fractions such as organic P, which causes damage to the ecosystem, are generally not considered. Only TP and $\text{PO}_4\text{-P}$ are mentioned as measures of P and efficiencies, making it difficult to more thoroughly review how the different technologies impact on the different P forms. However, the main conclusions on recovery technologies are:

- Physical technologies have shown effluents with concentrations between 1 and 4 mgP/L, which exceed standards. It is recommended that these technologies be used for low P concentrations (<10 mgP/L) or combined with other treatments.
- Chemical precipitation has been the preferred technology for P recovery; combined with other technologies, it has achieved efficiencies of 62-67%.

- As a pre-treatment, the biological mechanism was optimal for later recovery, accumulating and converting the P fractions from 44 to 77%.

Combined technologies can be considered as the best alternative for P recovery, reaching efficiencies of 99% and effluent concentrations <0.1 mg/L of TP. In general, there is a need to integrate, apply and demonstrate that combined processes can improve the efficiency of P recovery and decrease the total P fractions contributing to the eutrophication of aquatic ecosystems. However, the application of these technologies requires a better understanding of the characteristics of P in water. It is important to note that certain operational factors and recent developments have promoted the combined recovery of P, showing a high recovery rate, the treatment of different forms of P, the economic efficiency of the process and, finally, the obtaining of a useful P product with low environmental risks.

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CAPÍTULO IV

EVALUATION OF LONG-TERM PHOSPHORUS UPTAKE BY *SCHOENOPLECTUS CALIFORNICUS* AND *PHRAGMITES* *AUSTRALIS* PLANTS IN PILOT-SCALE CONSTRUCTED WETLANDS



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Evaluation of long-term phosphorus uptake by *Schoenoplectus californicus* and *Phragmites australis* plants in pilot-scale constructed wetlands

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Abstract

The aim of this study was to evaluate long-term phosphorus (P) retention in a pilot-scale system made of four horizontal subsurface flow (HSSF) constructed wetlands for wastewater treatment. Each wetland had an area of 4.5 m² and was operated for nearly 8 years (2833 days). Two wetlands with *Schoenoplectus californicus* (HSSF-Sch) and the other two with *Phragmites australis* (HSSF-Phr) were planted. The P removal efficiency was 18% for both types of HSSF wetlands. The primary factors that correlated with long-term P retention efficiency in HSSF were phosphorus loading rate (PLR), hydraulic loading rate (HLR) and dissolved oxygen (DO). Average biomass production of HSSF-Phr and HSSF-Sch was 4.8 and 12.1 kg dry weight (DW)/m², respectively. The P uptake by the plant increased over the years of operation from 1.8 gP/m² to 7.1 gP/m² for *Phragmites* and from 3.2 to 7.4 gP/m² for *Schoenoplectus* over the same periods. Moreover, the warm season (S/Sm) was more efficient reaching 14% P uptake than the cold season (F/W) with 9%. These results suggest that both plants' P retention capacity in HSSF systems represents a sustainable treatment in the long term.

Keywords: Constructed wetlands, Plant uptake, Phosphorus removal, *Schoenoplectus californicus*, *Phragmites australis*

1. INTRODUCTION

Constructed wetlands (CW) are a technology for natural, environmental and sustainable wastewater treatment. In terms of P treatment, they have shown removal efficiencies ranging from 10 to 80%, depending on the type of wetland, plant species or supporting media (Vymazal 2007; López *et al.* 2016; Maucieri *et al.* 2020; Jóźwiakowski *et al.* 2018). P removal mechanisms occur through interactions between supporting media, plants, and microorganisms (Vymazal 2007). The plants play an important role in P reduction in HSSF through their effect on P transformations (Cheng *et al.* 2009). Key functions are associated with physicochemical effects such as oxygen release to the rhizosphere, regulation of hydraulic conditions, and stimulation of productivity, diversity, and microbial activity in the rhizosphere (Leiva *et al.* 2018; Burgos *et al.* 2014; Zheng *et al.* 2020).

The commonly used plants in CW are *Phragmites australis*, *Typha spp.* and *Scirpus spp.* (Vymazal 2020). The uncommon species *Schoenoplectus californicus* is distributed along the Atlantic and Pacific coasts of the Americas from California to Chile (Macía and Balslev 2000). Similar to *Schoenoplectus californicus* is *Schoenoplectus validus* which is distributed in northern America and has been less widely used in CW (Greenway and Woolley 2001; Zhang *et al.* 2008). However, the effect of this plant species on P uptake in CW has not been thoroughly investigated.

The P uptake by plants has shown contradictory results on CW treatment efficiency. Lee *et al.* (2012) found that P uptake by plants was less than 1% in a six-cell surface flow CW planted with three species (*Phragmites australis*, *Miscanthus sacchariflorus*, *Typha orientalis*). Wu *et al.* (2012) treated river water in a microcosmic CW and demonstrated a P uptake of 4 to 22% by four types of plants (*Trema orientalis*, *Phragmites australis*, *Schoenoplectus validus*, *Iris pseudacorus*). In contrast, Leiva *et al.* (2018) reported 41% P uptake by plants for a HSSF planted with *Cyperus papyrus*. Therefore, P uptake capacity by plants is also influenced by factors such as CW configurations, plant type, and input P concentration.

The CW systems have shown finite retention capacity by plants and supporting media for long-term sustainable P removal (Wu *et al.* 2013). However, most studies evaluating the performance of CW systems for domestic wastewater treatment have been limited in time (1-3 years) (Arias *et al.* 2003; Bolton *et al.* 2019; Tondera *et al.* 2020). Therefore, they have not reached the maximum long-term

nutrient treatment capacity, which precludes knowledge of the long-term performance of CWs. Notably, plants need to reach maturity before differences in treatment performance can be detected (Calheiros *et al.* 2007). For example, Zheng *et al.* (2020) showed that P removal in a free surface flow CW increased from about 9% in the first year to 42% in the sixth year. Furthermore, a study by Lv *et al.* (2017) showed that aeration and plants could influence long-term P removal and alter the substrate structure to extend the time of saturation by uptake.

Therefore, this study aims to evaluate P uptake by *Schoenoplectus californicus* and *Phragmites australis* in a general way in CW treatment. Taking into account the basis of in situ and operational parameters, the biomass production by each species, especially the adsorption and retention of P in the long term. This content will provide a real and original scientific contribution on the P treatment capacity of the plants in a pilot scale CW system for wastewater treatment.

2. MATERIALS AND METHODS

2.1. Design parameters of HSSF pilot-scale system

The treatment system was located in Hualqui, Biobío Region, Chile (36°59'26.93" S latitude and 72°56'47.23" W longitude). The influent originated from a wastewater treatment plant in the rural community of 20,000 inhabitants. The wastewater was first subjected to a sand degreaser (630 L) as pre-treatment, and then to a septic tank (1200 L) and a pumping tank (630 L) as primary treatment. The resulting wastewater was then stored in a 1000 L distribution tank, where it was distributed by gravity to four HSSF CW (López *et al.* 2016; Leiva *et al.* 2018; Sepúlveda-Mardones *et al.* 2017). Two HSSF wetlands were planted with *Phragmites australis* (HSSF-Phr; HSSF-Phr2) and the other two with *Schoenoplectus californicus* (HSSF-Sch1; HSSF-Sch2).

Figure 4.1 provides details of the design and characteristics of each pilot-scale HSSF CW. Each HSSF unit had an area of 4.5 m², a total volume of 1.28 m³ and an average height of 0.57 m. The effective volume was 0.76 m³ and the water table was at a depth of 0.3 m. The support medium used was 19–25 mm gravel with a porosity of 0.57% (Rojas *et al.* 2013; Vera *et al.* 2014). Each HSSF was divided into three zones with a sampling tube in the middle of each zone: Zone A (inlet zone) with the sampling tube 0.65 m from the inlet; Zone B (middle zone) with the sampling tube 1.4 m from the inlet; and Zone C (outlet zone) with the tube 2.25 m from the inlet. The gravel used

in this study had the same characteristics as that described in Andrés *et al.* (2018), with a P adsorption capacity of 0.03-0.05 gP/kg.

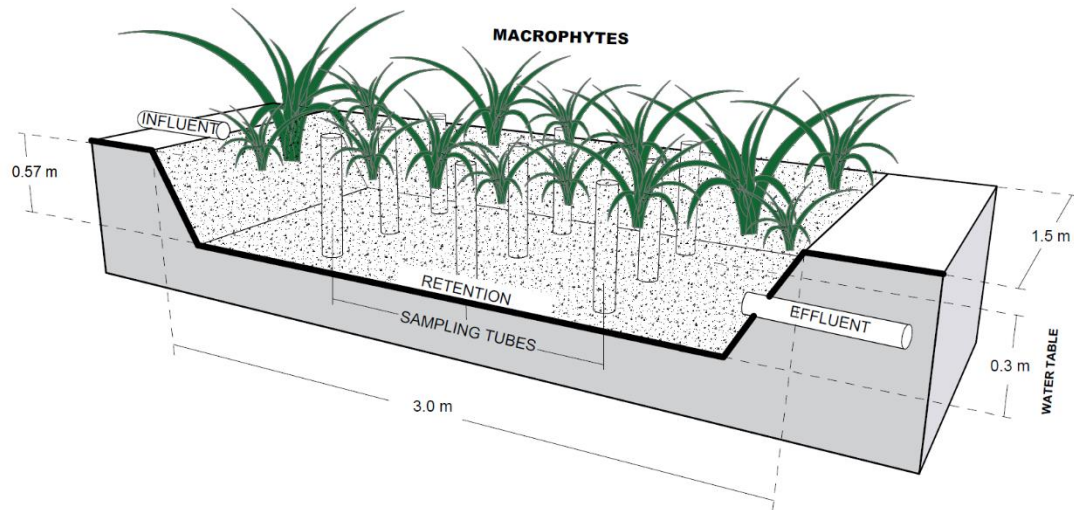


Figure 4.1. Overview of each pilot-scale HSSF showing dimensions, characteristics and sampling tubes in situ.

2.2. Monitoring and operating conditions

The system was launched in July 2011. The stabilization time was 85 days during the winter season, and the HSSF ran from 2011 to 2019, for 2833 days in total. Monitoring consisted of collecting samples by season (spring (S), summer (Sm), fall (F) and winter (W)) during the entire period of operation. There were 72 samples, which were variable and there were at least 2 samples per season and a maximum of 6 samples. Due to the large number of samples, by zones (A, B, C) and by HSSF (HSSF-Phr1; HSSF-Phr2; HSSF-Sch1; HSSF-Sch2), the parameters are presented in periods from I to VIII for each year, according to the days of operation elapsed. Each period represents an average of the fall-winter cold season (F/W) and the spring-summer warm season (S/Sm). However, in period II of the year 2012, samples were only collected during the cold season F/W. Moreover, in the year 2018 no samples were collected, so period VIII corresponds to the year 2019. During the periods of operation, average temperatures were 10.4°C in F/W (March to September) and 15.1°C in S/Sm (September to March). There were marked seasonal trends in rainfall, with higher average rainfall in F/W of 3.6 mm/d and a minimum of 0.6 mm/d in S/Sm.

Evapotranspiration (ET) presented minima between 1-1.5 in winter and maxima of 4.0-4.8 mm/d in summer. The meteorological data were provided by the climate explorer of the Climate and Resistance Science Center (CR)², Chile.

Table 4.1 shows the operating conditions for both HSSF-Phr and HSSF-Sch during the monitoring periods. However, the data are presented in periods because the values between the hot and cold seasons were similar. The hydraulic loading rate (HLR) varied between 19.6 and 30.7 mm/d, the organic loading rate (OLR) in the range of 2.4-6.7 gBOD₅/m²d, the phosphorus loading rate (PLR) was 0.3 to 0.6 g/m²d and the hydraulic retention time (HRT) varied between 5.6 and 8.7 days. Water samples from influent and effluents were collected each season and period and stored under refrigeration (4 °C) until physicochemical analysis. In addition, for each HSSF, the following parameters were monitored on site: temperature (T), pH, oxidation reduction potential (ORP) and dissolved oxygen (DO).

Table 4.1. Operating conditions for HSSF-Phr and HSSF-Sch during the different periods of operation.

Days of operation	Period	HLR [mm/d]	OLR [g/m ² d]	PLR [gP/m ² d]	HRT (d)
85-248	I	19.6±0.0	3.6±0.1	0.3±0.0	8.7±0.0
272-399	II	19.6±0.0	3.6±0.0	0.3±0.0	8.7±0.0
640-855	III	30.7±0.0	4.6±0.6	0.4±0.0	5.6±0.0
999-1286	IV	30.2±0.6	4.6±0.3	0.4±0.0	5.7±0.1
1330-1574	V	29.8±0.0	5.3±1.5	0.4±0.0	5.7±0.0
1707-1945	VI	22.3±1.7	4.9±0.1	0.3±0.0	7.7±0.6
1974-2285	VII	29.8±0.0	6.1±0.9	0.5±0.0	5.7±0.0
2650-2833	VIII	27.8±0.6	3.0±0.8	0.5±0.1	6.2±0.1

2.3. Analytical methods

In situ parameters such as T, pH and ORP were measured through sampling tubes using OAKTON (PC650–480485) portable equipment. DO concentration was analyzed by a portable oxygen sensor (HANNA OXI 330i/set HI 9146-04). The water samples were made in triplicate and were filtered using a 0.45 µm pore size membrane. Physicochemical parameters were determined according to APHA (2012). Chemical oxygen demand (COD) (colorimetric method, 5210-B) biological oxygen demand (BOD₅) (modified Winkler azide method, 5210-B), total suspended solids (TSS) and volatile

suspended solids (VSS) (gravimetric method, 2540-D and 2540-E, respectively), phosphate phosphorus ($\text{PO}_4^{3-}\text{-P}$) (colorimetric method), total phosphorus (TP) and total nitrogen (TN) (Spectroquant-Nova 60, Merck kits). The term P is presented as TP value in the results of this paper.

2.4. Macrophyte analysis

Macrophyte analyses were performed in different seasons and periods. The period II was in spring after 482 days of operation, the period III in winter after 745 days, the period IV in summer after 1286 days, the period VI in summer after 1675 days, and in winter after 1842 days, the period VII in fall after 2080 days and in spring after 2284 days, the period VIII in winter after 2695 days and in summer after 2833 days. Therefore, no leaf analyses were performed in the initial period (I) or period V. Biomass analysis was not carried out in the initial period (I) or in period V, due to the reduced biomass. Biomass analysis was not carried out in the initial period (I) or in period V, due to the reduced biomass. As for harvesting, 2 manual harvests were carried out in spring, the first in period IV and the second in 2018, which was not considered within the periods.

The *Phragmites* and *schoenoplectus* macrophytes were randomly considered by counting the number of individuals in a PVC quadrat of 0.0625 m² (0.25 m x 0.25 m) (López *et al.* 2016) to calculate the density (individuals/m²) by zone A, B and C (Each zone had an area of 1.5 m²) (Leiva *et al.* 2018). Coverage was determined by measuring the square meters that were unplanted in each of the zones of the HSSF, and subsequently, the percentage of coverage was determined considering the total area. In addition, plant samples of aboveground biomass (stems) and belowground biomass (roots) were taken and a proximal analysis was performed to obtain the concentration of TP in plant tissues. For the total TP content in the plant, only the TP contained in the stem and root were considered. Following the protocol described by Sadzawka *et al.* (2007), the separated biomasses were powdered and analyzed for nutrient content. P content was determined by calcination (500 °C) and then by colorimetry (466 nm). P content in plant tissues was calculated using equation (1) (Lee *et al.* 2012):

$$\text{P content (g/kgDW)} = \text{mass P (g)} / \text{dry weight (kg)} \quad (1)$$

2.5. Mass balance

Mass balances were calculated in terms of TP. Equation (2) explains the procedure for calculating balances as follows:

$$(C_i \cdot Q_i \cdot Do) / A - C_{i+r} - C_p = (C_e \cdot Q_e \cdot Do) / A \quad (2)$$

where C_i = influent concentration of TP (g/m^3); Q_i = input stream wastewater (L/d); Do = operation time (d); A = surface area (m^2); C_{i+r} = intake by microorganisms or retention in HSSF (g/m^2); C_p = plant uptake (g/m^2); C_e = effluent concentration of TP (g/m^3); and Q_e = effluent output stream (L/d). This procedure was modified from Kadlec and Wallace (2009).

2.6. Statistical analyses

Statistical analysis compared influent and effluent concentrations, removal efficiency and *in-situ* parameters during different seasons (F/W and S/Sm) and periods (I-VIII). First, the data were subjected to a test of normality (the Shapiro-Wilk test). The following tests were performed: a) for data with a normal distribution, an ANOVA test, and b) for data without a normal distribution, a Kruskal-Wallis test. To compare the differences between HSSFs, we used a t-test. Principal component analysis (PCA) was carried out with the first three principal components. Data was standardized and P removal efficiencies were correlated with the *in situ* and operational parameters. Then, the Fisher's Least Significant Difference (LSD) was performed to discriminate between periods and stations for P removal efficiency when the ANOVA results were significant. Statistical analyses were carried out using the statistical program Rstudio (Version 1.3.959) with a level of significance of $p = 0.05$.

3. RESULTS AND DISCUSSION

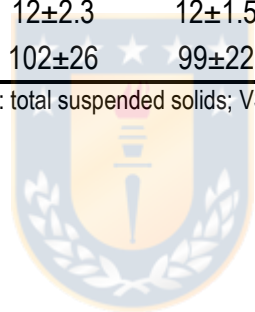
3.1. Influent characteristics and phosphorus removal efficiency

Table 4.2 shows the results of the physical-chemical characterization of the influent wastewater throughout the period of operation (2833 days). The influent showed mean BOD_5 concentrations in the range 48–348 mg/L. The mean COD influent concentration were in the range of 115–465 mg/L. The minimum biodegradability coefficient (BOD_5/COD) found in this study was 0.36, the maximum 0.92. These low ratios indicate that the organic matter was simple to degrade (Henze *et al.* 2002).

Table 4.2. Physicochemical characteristics of the wastewater influent for HSSF-Phr and HSSF-Sch during periods of operation.

Parameters	Range [mg/L]	Average [mg/L] ± SD							
		Period I	Period II	Period III	Period IV	Period V	Period VI	Period VII	Period VIII
BOD ₅	48-348	187±72	184±58	149±50	153±64	179±66	220±85	204±34	108±41
COD	115-465	281±69	324±97	222±101	297±81	293±73	303±93	327±77	212±69
TSS	40-565	259±126	408±141	199±85	177±65	256±92	179±61	282±105	68±24
VSS	33-513	145±100	346±167	146±77	150±60	236±74	211±87	277±117	103±66
TP	10-21	15±3.5	15±1.7	14±2.2	14±1.3	13±1.2	13±2.3	16±2.8	17±1.5
PO ₄ ³⁻ -P	5-17	7±2.2	12±1.8	12±2.3	12±1.5	12±1.5	11±2.3	11±2.2	16±1.3
TN	41-142	73±22	91±37	102±26	99±22	100±21	94±14	107±22	84±40

BOD₅: biological oxygen demand; COD: chemical oxygen demand; TSS: total suspended solids; VSS: volatile suspended solids; TP: total phosphorus; PO₄³⁻-P: phosphate phosphorus; TN: total nitrogen; SD: standard deviation



No significant differences ($p > 0.05$) in mean BOD₅ and COD concentrations between seasons and period were observed. The ratio of organic carbon to P in the influent (COD/TP) varied from 11 to 26 mgCOD/mgTP, what is a low COD/TP ratio (10-20 mgCOD/mgTP) that is favourable to phosphate-accumulating organisms (PAO) and P removal (Oehmen *et al.* 2007). As regards the inorganic load applied in the HSSFs expressed as ammonium and phosphate was 2.1 ± 0.8 gNH₄⁺-N/m²d and 0.3 ± 0.1 gPO₄³⁻-P/m²d respectively.

Figure 4.2 shows the long-term trend of influent TP and PO₄³⁻-P concentration. TP influent concentrations ranged from 10-21 mg/L, with no significant differences between periods and seasons ($p > 0.05$), while PO₄³⁻-P presented a higher variation, between 5-17 mg/L, with significant differences between periods ($p < 0.05$). In period I, the average PO₄³⁻-P concentration was 36% lower than the overall average (11 ± 2.9 mg/L). In contrast, in period VIII, PO₄³⁻-P concentration increased by 42% compared to the overall average. The variation of PO₄³⁻-P was also expressed in the TP/ PO₄³⁻-P ratio in the influent, with an overall average of 80% of TP, and a range of 50% (period I) to 95% (period VIII). Dzakpasu *et al.* (2015) and Yang *et al.* (2007) reported similar observations, where the range varied over the days of operation. In general, influent wastewater concentrations were similar to those found by Józwiakowski *et al.* (2020), between 5-42 mg/L for TP and Bolton *et al.* (2019) between 7-30 mg/L for PO₄³⁻-P.

Figure 4.3 shows the average effluent concentrations and removal efficiency of P for both HSSF-Phr and HSSF-Sch, respectively, during the F/W and S/Sm seasons during the periods of operation. Effluent TP concentrations averaged 12.2 ± 3.1 mg/L for HSSF-Phr and 11.9 ± 3.2 mg/L for HSSF-Sch, with no significant differences between species. The P values measured in the effluent are still too high for the discharge of wastewater and thus avoid eutrophication of water. The required limits for P discharges from wastewater reach P values between 1-2 mg/L in Europe, 0.5 mg/L in China, 0.05 mg/L, protected waters in Europe and the USA 0.05 mg/L and 0.01 mg/L respectively. In Europe, according to Directive 91/271/EC, the requirements depend on the size of the wastewater treatment plant (WWTP) expressed in population equivalent (PE) and also by its sensitivity to eutrophication. Countries such as Italy, Ireland, Spain, Portugal and the United Kingdom, among others, only selected water areas as sensitive (Preisner *et al.* 2020). Other countries, such as Switzerland, require zero discharge, which makes it mandatory to recover P. In Latin American

countries such as Chile, the allowable P discharge varies from 2 to 15 mg/L, depending on the dilution capacity of the receiving water body (AWWA 1970; Zou and Wand 2016; WWAP 2017). Therefore, in such treatment context, reuse of the treated wastewater by CWs should be encouraged.

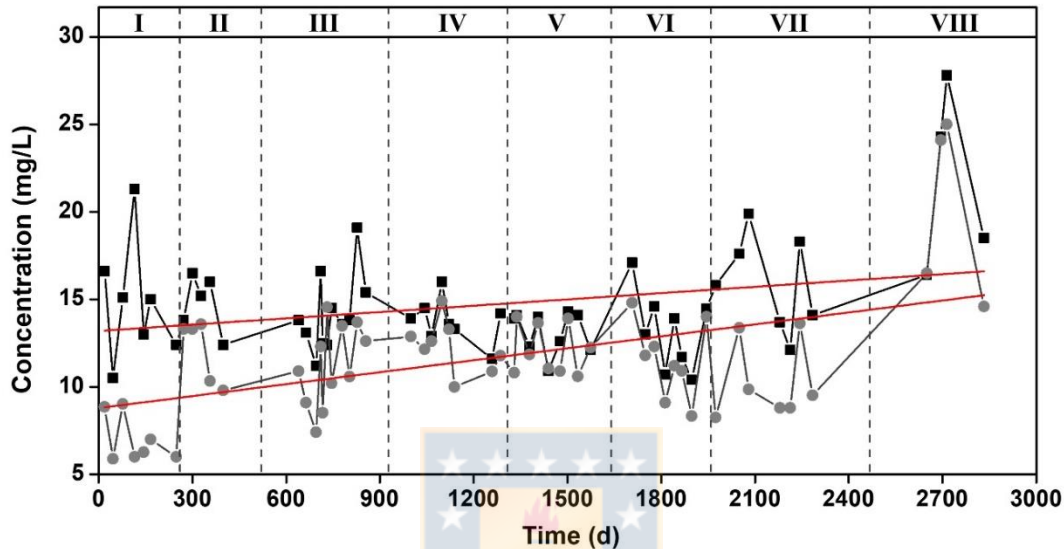


Figure 4.2. Average concentrations of TP (—■—) and PO₄³⁻-P (—●—) in the influent during the periods of operation. The red line (—) shows the long-term trend.

Comparison of the two seasons in the HSSF shows that they differ by 14%, with a mean of 12.8 ± 3.2 mg/L in S/Sm and 11.2 ± 3.1 mg/L in F/W ($P < 0.05$). This difference can be attributed to the TP concentration in the effluent, which is accentuated by evapotranspiration in summer. In this case, high temperatures ($> 20^\circ\text{C}$), reduce water solubility, which may be an influential factor in P removal efficiency. This was represented in period IV, because it showed the highest TP concentrations in the effluent, with 14.5 ± 2.7 mg/L for HSSF-Phr and 14.2 ± 3.4 mg/L for HSSF-Sch. Overall it represented 21-23% above the annual mean, which was associated with the high temperatures in the S/Sm season. Also, in a study on the effect of seasons on a CW, Józwiakowski *et al.* (2020) found that, in spring, TP concentrations were 2.3 to 4 mg/L higher. Over the periods, no clear trend could be observed for any of the HSSFs.

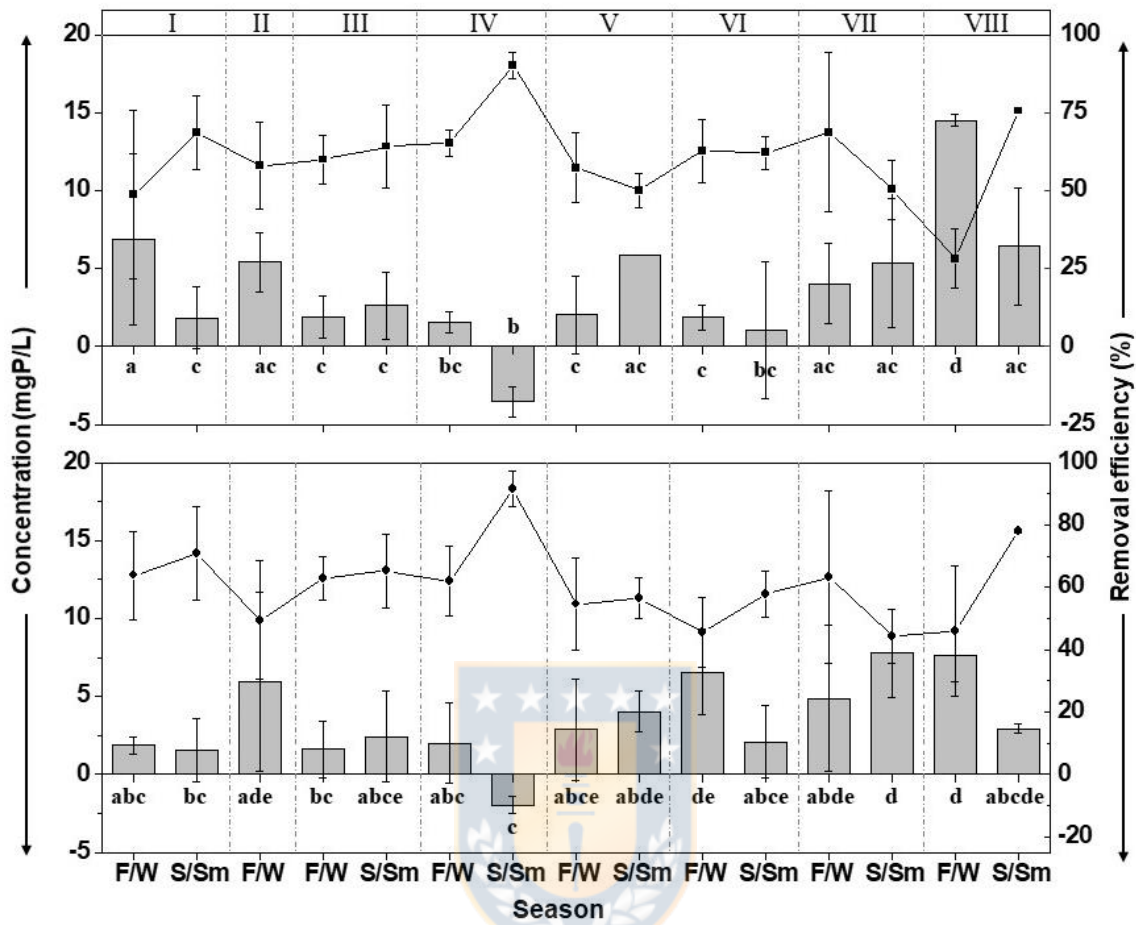


Figure 4.3. Average concentration (line) and removal efficiency (bar graph) for TP in effluent by season and monitored periods. a) HSSF-Phr (—■—) and b) HSSF-Sch (—●—). Different letters indicate significant differences in P retention efficiencies between periods and season.

In both HSSF systems, TP removal efficiency averaged 18%, with greater variation (-10 ± 5.0 to $61 \pm 5.8\%$) for HSSF-Phr than HSSF-Sch (-10 ± 2.8 to $44 \pm 0.0\%$). Therefore, no significant differences were observed between species and seasons. However, significant differences were observed between periods ($P < 0.05$). Generally, gravel-based CW has demonstrated low TP removal efficiency, ranging from -40% to 40% (Vohla *et al.* 2011). The data obtained on removal efficiency were irregular, similar to the results reported by Mateus and Pinho (2010) and Shilton *et al.* (2006). In 14 years of operation, a CW studied by Józwiakowski *et al.* (2018) achieved highly varied removal of TP (mg/L), with a standard deviation of ± 19.9 mg/L as in the present research (± 18.5 mg/L).

3.2. In situ parameters of HSSF-Phr and HSSF-Sch

Figure 4.4 shows the behavior of the *in-situ* parameters pH, T, ORP and DO for HSSF-Phr and HSSF-Sch. There were no significant differences between HSSF-Phr and HSSF-Sch for any *in situ* parameters measured. The pH values did not change significantly between F/W and S/Sm, averaging 6.9 ± 0.4 and 6.9 ± 0.3 respectively for both species. However, a significant effect occurred over the course of the experiment, with the initial pH value of 7.0 ± 0.3 decreasing to 6.4 ± 0.1 after 2833 days of operation. Similar results were obtained in a study by Hench *et al.* (2003), where the pH decreased from 7.05 to 6.58. This decrease in pH in CW may be due to the interaction between plants and microorganisms, to the mineralization of organic matter, to the release of ions (H^+) and to the production of organic substances that acidify the medium (Garcia *et al.* 2010; Shan *et al.* 2011). The temperature for both species showed a significant difference between seasons with a mean of $12.4\pm 3.3^\circ C$ for F/W and $19.0\pm 3.6^\circ C$ for S/Sm. It has been observed that increased temperature may benefit P assimilation by microorganisms. A study conducted in the same pilot-scale HSSF showed a higher growth of bacteria (38%) and archaea (50%) during the S/Sm season than in the F/W season. In addition, the species *Schoenoplectus californicus* showed a higher amount of bacteria (4-48%) and archaea (34-43%) than *Phragmites australis* (López *et al.* 2019). Differences were also observed between period I and period IV, where the difference between the seasons was greater, with 10.6 and $8.2^\circ C$ respectively. However, for the rest of the periods, the difference between seasons was lower, with an average of $4.0^\circ C$. This trend could be due to the development of the macrophytes, which provided a lower coverage during the stabilization period and an increasingly higher coverage over time, along with better thermal insulation (Sepúlveda-Mardones *et al.* 2017; Vymazal and Kröpfelová 2005).

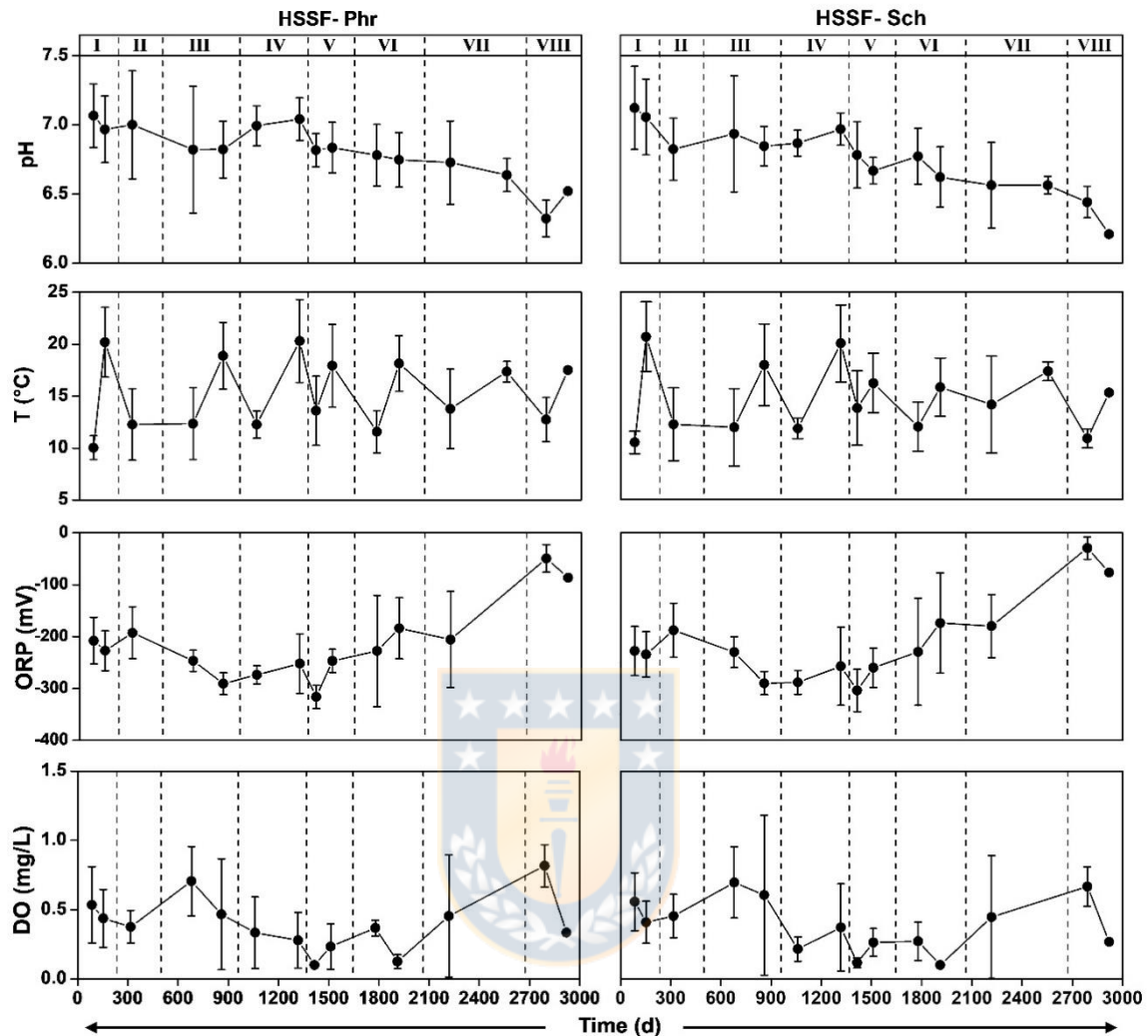


Figure 4.4. *In situ* parameters such as pH, temperature (T), oxide reduction potential (ORP) and dissolved oxygen (DO) of HSSF-Phr and HSSF-Sch in the different periods of operation.

The ORP fluctuated, with mean values from -316.6 ± 23 mV to -29.5 ± 21 mV on both HSSF systems while in operation. No significant differences were observed between seasons, but there were differences between periods of operation. The ORP values for periods III, IV, V were 33.2-58.5 for HSSF-Phr and 22.2-63.1 mV for HSSF-Sch, lower than their averages of -236.0 and -229.1 mV, respectively. This increase in ORP may be related to the increase in temperature between 15-16 °C in these periods. In contrast, in period VIII, there was an increase in average ORP values, with -54.6 ± 25.9 mV for HSSF-Phr and -38.9 ± 23.3 mV for HSSF-Sch. This behavior of the ORP can be attributed to the variations of the OLR during the period of operation, since these decreased from

4.9 g BOD₅/m²d (period III, IV, V) to 3.0 gBOD₅/m²d (period VIII) (Leiva *et al.* 2018). It is also attributed to the decrease in pH to 6.3 ±0.2, because of the pH decreases there is an increase in ORP (Shan *et al.* 2011). Likewise, DO concentrations showed values of 0.1±0.0 to 0.8±0.1 mg/L (average 0.4±0.3) for both species. A significant difference was observed between periods. In period III, the mean of 0.67±0.4 mg/L was higher than that in period I and II, and in period V, the mean decreased to 1.5±0.1 mg/L DO. The highest DO values (0.6-0.7 mg/L) were achieved during the F/W season. Similarly, Oliver *et al.* 2017 recorded the lowest DO values in summer and the highest values were recorded in winter. During that colder period of the year, higher DO concentration was measured in HSSF, resulting in higher P retention. Ilyas and Masih (2018), reported that aeration strategies could be responsible for P removal by enhancing DO levels to benefit precipitation and P uptake. In addition, DO concentrations determine the aerobic or anaerobic conditions of the wetland, thus to the associated microorganisms and in turn to the rhizosphere of plants (Ilyas and Masih 2018; Lopez *et al.* 2019). These HSSF DO concentrations (< 0.8 mg/L) and ORP values (-300 and -100 mV) indicate anaerobic conditions.

3.3. Influence of parameters on phosphorus removal

Some *in situ* or operational parameters, such as seasonal fluctuations (HLR), PLR and HRT, can affect long-term monitoring. Figure 4.5 shows the result of PCA of operational and *in situ* parameters related to Phr (E_Ph) and Sch efficiency (E_Sch). The first three principal components (PC1, PC2, PC3) explain 82.75% of the variation in the data. The 42.33% of variance is explained by PC1. This component is positively associated with PLR variables (0.40), operations days (0.42) and negatively with pH (-0.45). Oliver *et al.* (2017), and a positive relationship between P mass removal efficiency and PLR. In this case, the PLR increased 0.2 g/m²d over the days of operation. The 27.03% of variance is explained by PC2, which is positively associated with variables such as HRT (0.48) and negatively to HLR (-0.48). The removal efficiency of TP is reported to increase with increased HRT. Maximum removal efficiency values were achieved in period VIII for HSSF-Phr, with an average of 39.5±30.4% and in period VII for HSSF-Sch with an average of 31.5±10.4%. The increase in period VIII is related to an increase of HRT to 6.2 days and a decrease of HLR to 27.8 mm/d.

Finally, PC3 represented *in situ* parameters with variables like DO (0.57) and temperature (-0.42), which explained less variation in the data (13.39%). DO and temperature can influence CW

efficiency as they affect several P biogeochemical processes (Oliver *et al.* 2017). DO oscillated inversely with temperature, due to lower solubility and higher biochemical oxygen demand as temperature increases. Seasonal variation was observed with respect to these parameters. During the F/W season and higher DO concentration (0.6-0.7 mg/L), the average efficiency was higher at $22.5\pm 18.5\%$ for HSSF-Phr and $21.6\pm 13.2\%$ for HSSF-Sch, while at the S/Sm season lower DO concentration (0.1-0.3 mg/L), the efficiency averaged $13.1\pm 9.1\%$ and $13.6\pm 6.0\%$, respectively. In the last years the DO increased the mean to 0.5 mg/L hence the removal efficiency (30-40%), therefore DO may be an important parameter to consider in CW in the long term. Ilyas and Masih (2018), found a positive relationship between TP and $PO_4^{3-}\text{-P}$ with improvement in DO levels due to redox manipulation and with aeration strategies could rejuvenate CW with fresh air recovering phosphorus removal processes. Despite the apparent differences observed, there were no significant seasonal differences, due to the high variability of the efficiencies in the seasons throughout the periods, which is evidenced by the standard deviations. The same pattern was observed in Lee *et al.* (2012), Oliver *et al.* (2017) and Józwiakowski *et al.* (2020).

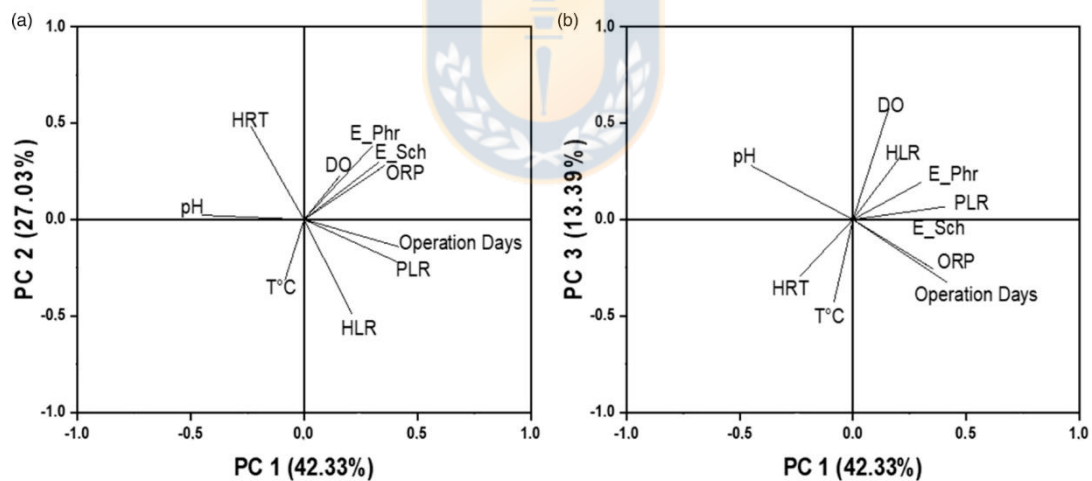


Figure 4.5. Principal component analysis (PCA) of operational and in situ parameters related to Phr (E_Phr) and Sch efficiency (E_Sch), explaining results of (a) principal components PC1 and PC2, (b) principal components PC1 and PC3.

3.4. Biomass production

Table 4.3 shows the growth characteristics and total biomass production of HSSF-Phr and HSSF-Sch during the periods of operation. Biomass production was significantly different between species,

with a mean of 2.2 ± 1.1 kgDW/m² for HSSF-Phr and 4.9 ± 2.2 kgDW/m² for HSSF-Sch. The total biomass of HSSF-Sch was twice that of HSSF-Phr, with an average percentage of cover of $89 \pm 15\%$ compared to $70 \pm 14\%$. In this research, the biomass production of HSSF-Phr was similar to that reported by the studies of Maucieri *et al.* (2020) and Liu *et al.* (2012), which is in the range of 1.6 - 5.7 kgDW/m², as reported by Vymazal and Kröpfelová (2005). As for HSSF harvesting or pruning, the first one took place in period IV, which had negative effects on the HSSFs, decreasing biomass, and consequently negative efficiencies (-10% for both HSSFs) in the S/Sm season in that period. Frequent harvesting has been observed to reduce biomass by 27-32% and may influence CW performance (Ingrao *et al.* 2020). On the other hand, harvesting strategies have been proposed to improve long-term performance in CW. Therefore, between 2 or 3 harvests may benefit plant tissues or environmental conditions of growth (Zheng *et al.* 2018).

Table 4.3. Growth and biomass production characteristics in HSSF-Phr and HSSF-Sch during periods of operation.

Period	Season	Density [individuals/m ²]		Coverage [%]		Total Biomass [kgDW/m ²]	
		HSSF-Phr	HSSF-Sch	HSSF-Phr	HSSF-Sch	HSSF-Phr	HSSF-Sch
II	S/Sm	1200±92	431±367	80±20	55±33	1.9±0.3	1.3±1.2
III	F/W	3610±2005	2279±9	52±32	81±10	4.2±2.2	4.1±0.1
IV	S/Sm	981±981	2366±371	65±38	86±14	1.1±0.4	5.3±0.8
VI	S/Sm	1113±206	2764±28	52±32	96±7	1.4±0.1	5.4 ± 0.2
	F/W	2815±297	5472±209	69±27	100±0	3.2±1.0	8.9±1.0
VII	F/W	4681±506	5807±347	92±14	92±13	2.5±0.8	4.9±0.8
	S/Sm	3372±809	6970±710	78±16	98±6	1.5±1.1	6.0±0.9
VIII	F/W	1255±388	1760±80	74±19	100±0	1.4±1.0	3.0±0.1

No significant seasonal differences were found, with a F/W coverage of 71% for HSSF-Phr and 93% for HSSF-Sch, and a S/Sm cover of 68% and 83%, respectively. In the S/Sm season of period IV, HSSF-Phr was affected by aphids, with a cover declining to $65 \pm 38\%$ and biomass decreasing to 1.1 ± 0.4 kgDW/m² in HSSF-Phr. Meanwhile, HSSF-Sch was not affected by aphid attack and biomass reached 5.3 ± 0.8 kgDW/m², representing a 27% increase compared to the previous period. Biomass production showed no correlation in P removal in both species (HSSF-Phr= 0.14; HSSF-

Sch=0.36). However, in the case of HSSF-Sch, when a biomass production of 8.9 kgDW/m² was reached, P removal efficiencies were higher than average with a range of 24.5-38.8% during the period VI and VII. Regarding the relation between biomass production and P uptake, a moderate correlation was found with 0.42 for HSSF-Phr and 0.66 for HSSF-Sch. This behavior was shown for *Schoenoplectus* in period VI where the biomass production reached 8.9 kgDW/m² and an P uptake of 7.2 g/m². Vymazal (2020), indicated in a study of 4 HSSF in operation between 9 and 25 years that the high production of biomass (6.6 kgDW/m²) is the main reason for P uptake.

3.5. Plant phosphorus uptake

Figure 4.6 shows the TP contents in different plant tissues for both HSSF systems during the monitoring period. The total TP content of the dry plant biomass averaged 1.53±0.95 gP/kgDW for *Phragmites* and 1.72±0.8 gP/kgDW for *Schoenoplectus*, with no significant differences between species. The TP values in plant tissues were in the range of 0.2 and 4.0 gP/kgDW, as reported by some authors in the literature, varying according to the plant species, soil conditions, water availability, nutrient load and other factors (Vincent *et al.* 2018; Shan *et al.* 2012; Rycewicz-Borecki *et al.* 2017; Liu *et al.* 2012; Malecki-Brown *et al.* 2010). As for TP distribution in plant tissues, it was lower in stems than in roots, reaching 36% of total biomass for *Phragmites* and 48% for *Schoenoplectus*. The results found in this study, between 0.1-1.5 gP/kgDW for stems and 0.1-2.0 gP/kgDW for roots, are similar to those of Shan *et al.* (2012), who reported a TP content of 1.46 gP/kgDW in *Phragmites* stems and 1.88 gP/kgDW in its roots. However, the values for *Schoenoplectus* in this study, 0.1-1.4 gP/kgDW for stems and 0.2-2.2 gP/kgDW for roots, were lower than those of 2.1-3.2 and 1.7-1.7 gP/kgDW, respectively, found by Zhang *et al.* (2008). This may be because the concentration of nutrients in the plant gradually decreased and became diluted as biomass increased (Lee *et al.* 2012). Furthermore, these results differ from those of Zhang *et al.* (2008), who found that P content was higher in stems than roots. This difference may be attributable to the phase the plants were in. When plants go into dormancy, nutrients like N and P are translocated from the stems to the roots and rhizomes. In contrast, in growth phase, P content is concentrated in stems (Liu *et al.* 2012; Zheng *et al.* 2020).

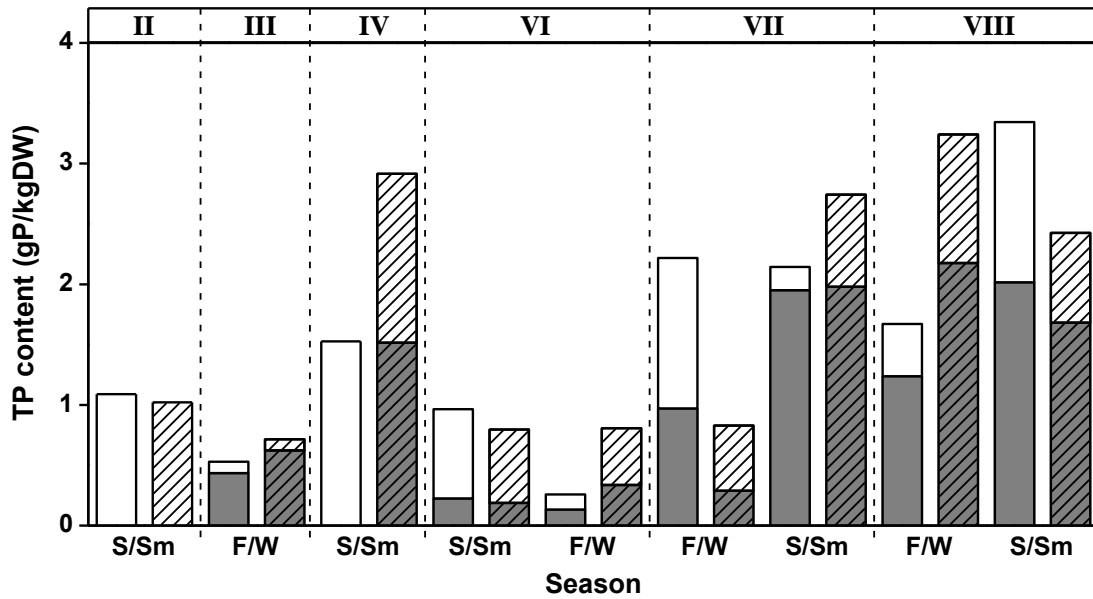


Figure 4.6. Distribution of TP content in different plant tissues in root (■) and stem (□) for *P. australis* (without any line, left) and root (▩) and stem (▨) for *S. californicus* (with line, right) for HSSF system.

The range of P uptake by plants was 1.3–7.9 g/m² for HSSF-Phr and 1.3-9.3 g/m² for HSSF-Sch during the monitoring period. These values are similar to those found by Vincent *et al.* (2018), with an average of 4.5 gP/m² for *Phragmites*, and by Greenway and Woolley (2001), with an average of 2.8 gP/m² for *Schoenoplectus*. Likewise, the maximum values of P uptake by roots were 4.8 gP/m² for *Phragmites* and 6.7 gP/m² for *Schoenoplectus* in this study. No significant differences were observed between F/W and S/Sm seasons. *Phragmites* averaged 3.9±2.2 gP/m² for F/W and 3.2±2.7 gP/m² for S/Sm, while for *Schoenoplectus*, the P uptakes in F/W and S/Sm were 5.4±2.2 gP/m² and 5.4±3.0 gP/m², respectively. In contrast, Lopez *et al.* (2016) in the same HSSF but during the first three years of operation observed a significant difference where P uptake was higher in S/Sm than in F/W. From these contradictions it can be inferred that some parameters such as operation time are fundamental to CWs. Moreover, other parameters that can influence are the scale of the CW, the plant species, the region where it is built and its climatic conditions. During the last monitoring periods, an increase in P uptake was observed. The P uptake in *Phragmites* increased from an average of 1.8 gP/m² in the first three periods (II, III, IV) to 7.1 gP/m² in the last period (VIII), while *Schoenoplectus* increased from an average of 3.2 to 7.4 gP/m² in the same

periods. These results are consistent with findings by Zheng *et al.* (2020) in a CW with *Phragmites*, where the uptake of P by plants also increased from 5.5 gP/m² in 2011 to 15.0 gP/m² in 2014. This suggests that plant uptake of P plays an important role in the long-term elimination of P from CWs. This highlights the important role of roots in creating suitable conditions for microbial activity, increasing the surface area of the substrate in the water, oxygenating the environment around the roots and facilitating the filtration and sedimentation of P (Kadlec and Wallace 2009).

3.6. Mass balance

Table 4.4 shows the mass balance of P in HSSF-Phr and HSSF-Sch during monitoring periods with no significant difference between the two HSSF systems. The average annual load of P input was 31.8 to 55.0 gP/m², represented by the TP of influent. The highest P load was in period IV (55.0±2.7 gP/m²) and resulted in negative P removal efficiency. Some authors, such as Stefanakis and Tsihrintzis (2012) and Oliver *et al.* (2017), have shown a significant correlation between P load and P removal. Zhao and Piccone (2020) observed that, when annual P load was low, annual TP output in the effluent was low. As shown, P at effluent throughout the experiment was 22.2-55.5 gP/m² for HSSF systems. Average P retention was 6.5±8.0 gP/m² for HSSF-Phr and higher for HSSF-Sch, with an average of 8.4±11.4 gP/m². This value is similar to those found by Shan *et al.* (2011) in a pilot scale HSSF planted with *Phragmites*, resulting in P removal of 8.35 gP/m². In addition, P uptake by the plant reached values of 1.3-7.4 gP/m².

Table 4.4 Phosphorus mass balance for HSSF-Phr and HSSF-Sch according to periods of operation.

Period	Influent [gP/m ²]	Effluent [gP/m ²]		Retention [gP/m ²]		Plant uptake [gP/m ²]	
		HSSF-Phr	HSSF-Sch	HSSF-Phr	HSSF-Sch	HSSF-Phr	HSSF-Sch
I	31.8±11.8	22.2±9.5	25.1±6.8	5.2±2.2	2.4±0.4	-	-
II	36.7±0.0	27.6±0.0	23.5±0.0	7.6±0.0	11.6±0.0	1.8±0.0	1.3±0.0
III	39.7±5.1	30.3±8.7	31.4±9.6	4.7±0.4	3.6±1.3	1.6±0.0	3.0±0.0
IV	55.0±2.7	55.5±12.4	54.9±14.7	-7.1±15.8	-6.5±18.1	1.8±0.0	5.2±0.0
V	42.7±19.4	32.3±20.8	32.3±17.6	6.1±0.0	6.1±3.2	-	-
VI	37.0±10.1	34.9±11.3	28.1±4.4	3.0±2.2	9.8±9.1	1.9±0.8	5.6±2.2
VII	48.9±24.2	25.8±15.4	23.5±14.7	8.0±1.3	10.3±2.1	4.5±1.6	6.6±3.7
VIII	41.1±29.7	23.6±24.4	26.3±22.5	10.7±2.1	8.0±0.2	7.1±1.3	7.4±0.3

According to the literature, P concentration in plant tissue varies from 0.1 to 19 gP/m² depending on species and location, and also varies during the season (Vymazal 2007). As for the values expressed annually (g/m²year) these had an average P load of 78±22 g/m²year with a minimum of 37 g/m²year and a maximum of 111 g/m²year. The effluent from HSSF-Phr had a lower P load with 58±25 g/ m²year, while HSSF-Sch with 62±22 g/m²year. The P removal load was 20±16 g/m²year and 21±15 g/m²year for HSSF-Phr and HSSF-Sch respectively. These values are lower than those presented by Vymazal (2007) in full-scale HSSF with retention values between 45 g/m²year as a function of P input load, which was considered to be 141 g/m²year. However, our results were superior to those presented by Dzakpasu *et al.* (2015) treating domestic wastewater with a low P input load 16 g/ m²year, obtaining a P retention of 15 g/m²year.

Figure 4.7 shows the proportion of influent TP through the different phosphorus removal pathways for the season F/W and S/Sm in a) HSSF-Phr and b) HSSF-Sch. From the total P entering the influent (100%), it is distributed into P that is uptaken by plants, P that is retained in the HSSF (media support and microbial uptake) and finally P removed by the effluent. P retention by HSSF was 6.2-19.8%, plant uptake removed 7.8-13.5% of total P input, while P discharge to effluent was 71.9-78.2% of influent P. These results are consistent with P removal efficiency values, which were shown to be higher (8%) in the F/W season than in S/Sm. The effluents showed a lower P content in the F/W season, with 75% for HSSF-Phr and 72% for HSSF-Sch. There was a small but not significant difference between the seasons in the uptake of P by plants, with 13% in both HSSF in S/Sm, but, in F/W, 9.3% for HSSF-Phr and 7.7% for HSSF-Sch. This distribution is explained by the translocation of the plants, where in cold seasons like F/W, the plants go into dormancy, while in S/Sm they resume their growth, and at that time there is a greater uptake of P due to the development of the plants (Zheng *et al.* 2020). Wu *et al.* (2013) reported plant uptake removed 4.8-22.3% of P input based on mass balance calculation, a rate comparable to that found in the present study. In general, P removal by plants has been reported to be low (< 20%) but could be substantial for systems with lower P loads (10-20 gP/m²). Accordingly, plants may be able to contribute to long-term sustainable P removal (Vymazal 2007).

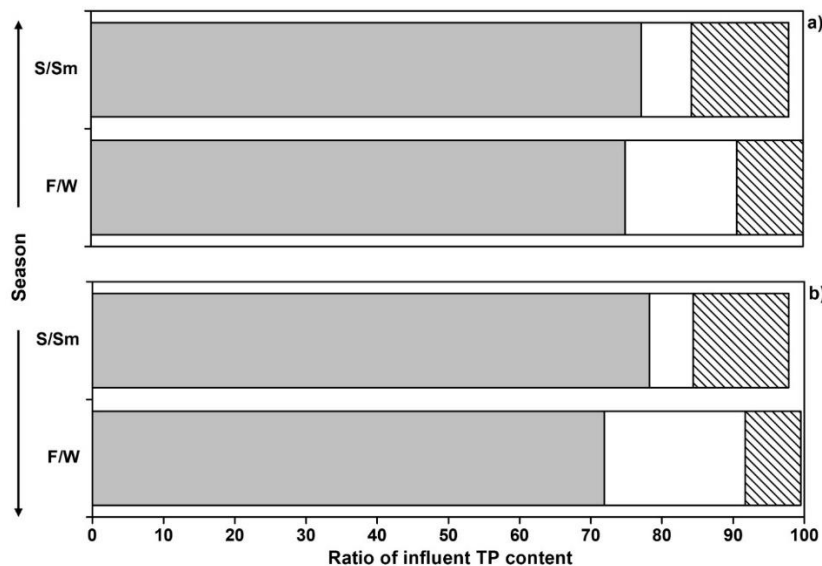


Figure 4.7. Ratio of influent TP content in effluent (■), retention (□) and plant uptake (▨) for season F/W and S/Sm in a) HSSF-Phr and b) HSSF-Sch.

4. CONCLUSIONS

The average TP removal efficiency during long-term operation (2833 days in total) was 18% for both HSSF. The F/W station obtained a higher efficiency of 22%, while the S/Sm station with 13%. There were negative efficiencies of -10% in the S/Sm season of period IV which was influenced by high temperatures ($<20^{\circ}$) and higher P input load. The main factors that correlated with long-term P retention efficiency in HSSF were positively with PLR, and DO, and negatively with HLR. It is recommended that P input load be monitored and regulated according to seasonal flows (HLR). P retention stabilized during the last periods of operation (VI, VII, VIII), which were associated with P accumulation by plants. The species *Schoenoplectus californicus* showed a better performance in terms of biomass production and showed a positive correlation with P uptake reaching 9.3 gP/m^2 in the last years. P content was higher in the root with 36% for HSSF-Phr and 48% for HSSF-Sch than in the stem. The P retention in the HSSF varied between 6-20% with higher retention in the F/W season. On the other hand, in the S/Sm season, P adsorption by the plants was more significant, contributing 14% in P removal, which is attributed to its resumption in the growth stage. These highlights highlight the important role of plants in P removal; however, it is important to consider the right conditions to generate a sustainable long-term P treatment in HSSF systems.

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CAPÍTULO V

PHOSPHORUS UPTAKE BY MACROPHYTE PLANTS IN MONOCULTURES AND POLYCULTURES IN CONSTRUCTED WETLANDS FOR WASTEWATER TREATMENT



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Phosphorus uptake by macrophyte plants in monocultures and polycultures in constructed wetlands for wastewater treatment

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Abstract

Phosphorus uptake by common and ornamental plants was studied in pilot-scale horizontal subsurface flow (HSSF) constructed wetlands (CWs) with monocultures and polycultures. Three HSSF CWs were planted with monocultures of *Phragmites australis* (HSSF-Phr), *Schoenoplectus californicus* (HSSF-Sch) and *Cyperus papyrus* (HSSF-Cyp), and one polyculture was planted with *Cyperus papyrus* and *Zantedeschia aethiopica* (HSSF-Cyp/Zant). During the experimental period, removal efficiency, growth characteristics, biomass production and phosphorus uptake were evaluated in the cold season (fall/winter) and warm season (spring/summer). In general, the cold season showed better performance with an order of HSSF-Cyp/Zant > HSSF-Cyp > HSSF-Sch > HSSF-Phr in the evaluated parameters. The removal efficiencies were 33%, 27%, 23% and 12%, respectively. The biomass production and density of the HSSF treatments ranged from 1.5 to 5.4 kg dry weight (DW)/m², and 435 to 1298 individuals/m² with higher values for HSSF-Sch. The tissue phosphorus content was 5 to 20% higher belowground in all plants, including ornamentals. Phosphorus uptake was higher for polyculture (HSSF-Cyp/Zant) and monoculture (HSSF-Cyp) planted with ornamentals, with a mean of 30 g P/m². Also, the polyculture was not affected by the seasons, reaching up to 27% phosphorus uptake by the plants. According to our results, the ornamental species of the polyculture contribute to the phosphorus uptake.

Keywords: Phosphorus uptake, Ornamental plants; Monoculture; Polyculture; Constructed wetlands.

1. INTRODUCTION

Human intervention in the global phosphorus cycle has generated anthropogenic sources, such as municipal wastewater, runoff from agricultural areas and terrestrial leachates in lakes, rivers and coastal areas, constitute a risk for water quality reduction and eutrophication (Rittmann et al., 2011, Vera et al., 2013). Constructed wetlands (CWs) have been widely used as a promising advanced technology for the treatment of these types of wastewater due to their advantageous characteristics, such as low cost, high efficiency and easy operation (Vymazal and Kröpfelová, 2008, Vera et al., 2014). Subsurface CW systems are known to be poor in phosphorus removal (Arias et al., 2003). According to Vymazal (2020) nutrient (nitrogen and phosphorus) removal does not exceed 50% for municipal wastewater. Generally, phosphorus removal in a CW is attributed to substrate adsorption, plant uptake, and microbe assimilation (Vera et al., 2014). Substrates and plants are the main removal pathways of phosphorus compounds in a CW, with 4 to 22% assimilation and uptake by plants, while substrates accumulate approximately 36 to 50% (Wu et al., 2013). Therefore, mainly different substrates that can increase phosphorus removal have been studied (Vohla et al., 2011). However, only a few studies have focused on the effect of plants on phosphorus removal in CW (Abbasi et al., 2019; Shan et al., 2011).

Common plants include *Phragmites* spp., *Typha* spp. and *Scirpus* spp., which are the most commonly used species in horizontal subsurface flow (HSSF) CWs (Sandoval-Herazo et al., 2018; Vymazal and Kröpfelová, 2008). *Phragmites australis* have shown its benefits, such as its great capacity for long term invasion, its vertical root development increasing hydraulic conductivity in a CW, its rhizomes and the great variety of life it harbors, which enhances the complete treatment of CW scrubbing (Uddin and Robinson, 2018; Zheng et al., 2020). An uncommon and lesser known species is *Schoenoplectus californicus*, which is distributed along the Atlantic and Pacific coasts of the Americas, from California to Chile (Macía and Balslev, 2000). Similar to *Schoenoplectus californicus* is *Schoenoplectus validus*, which is distributed in northern America and has been less commonly used in CWs (Greenaway and Woolley, 2001; Zhang et al., 2007b).

On the other hand, an emerging alternative is the use of ornamental plants that have shown phosphorus removal efficiencies of 49 to 70% (Sandoval et al., 2019). In addition, they have the advantage of aesthetically improving the treatment system and have the added value of

commercialization of flowers or fibers (García-Ávila et al., 2019; Sandoval et al., 2019). Some ornamental plant species that have been used in CW are *Zantedeschia* spp, *Canna* spp, *Cyperus* spp, *Iris* spp, *Agapanthus* spp, *Strelitzia* spp, *Heliconia* spp. (Burgos et al., 2017). *Cyperus papyrus* stands out for having a great potential in nutrient uptake due to the permeability of its thin roots that allow a great root-water interaction, assimilating especially nitrogen and phosphorus (Kyambadde et al., 2004). While *Zantedeschia aethiopica* can reach heights of 1.5 m and produces 2 to 3 white flowers. It grows in humid, shady areas with temperatures between 12-15°C, however it can still resist frost (Calheiros et al., 2015; Morales et al. 2013).

At the same time, recent studies have shown that polyculture systems are a treatment alternative in CWs (Liang et al., 2011; Marín-Muñiz et al., 2020). Polycultures have been shown to be less susceptible to seasonal variation and therefore more stable (Calheiros et al., 2015). However, this has been controversial, as they have been shown to be unstable due to competition and/or interactions between plant species (Leiva et al., 2018; Rodriguez and Brisson, 2016). Zheng et al. (2020) studied the effects of microbial communities and interactions among them in polycultures, concluding that interspecific competition intensified plant contributions from 9.9% to 41.9% to phosphorus removal, generating an interactive effect on phosphorus removal.

Considering the above, the objective of this study was to compare phosphorus uptake by common plants such as *Phragmites australis* and *Schoenoplectus californicus* and ornamentals such as *Cyperus papyrus* and *Zantedeschia aethiopica* in HSSF monoculture and polyculture treatments.

2. MATERIALS AND METHODS

2.1. Pilot-scale constructed wetland

The pilot-scale HSSF CW is located in Hualqui (36°59'26.93" S and 72°56'47.23" W), Biobío Region, Chile, a rural community of 20,000 inhabitants. Figure 5.1 shows a schematic diagram of the HSSF pilot system. The influent from the domestic wastewater was extracted from preliminary pretreatment (40 mm chamber bars), which was then applied to the primary treatment system of the pilot plant. This system consists of three parts: a desanding-degreasing tank (630 L), a septic tank (1200 L) and a pumping tank (630 L). Water is distributed from the pumping tank to a new

distribution tank (1000 L) that distributes it to the six units of the HSSF (Leiva et al., 2018; López et al., 2016).

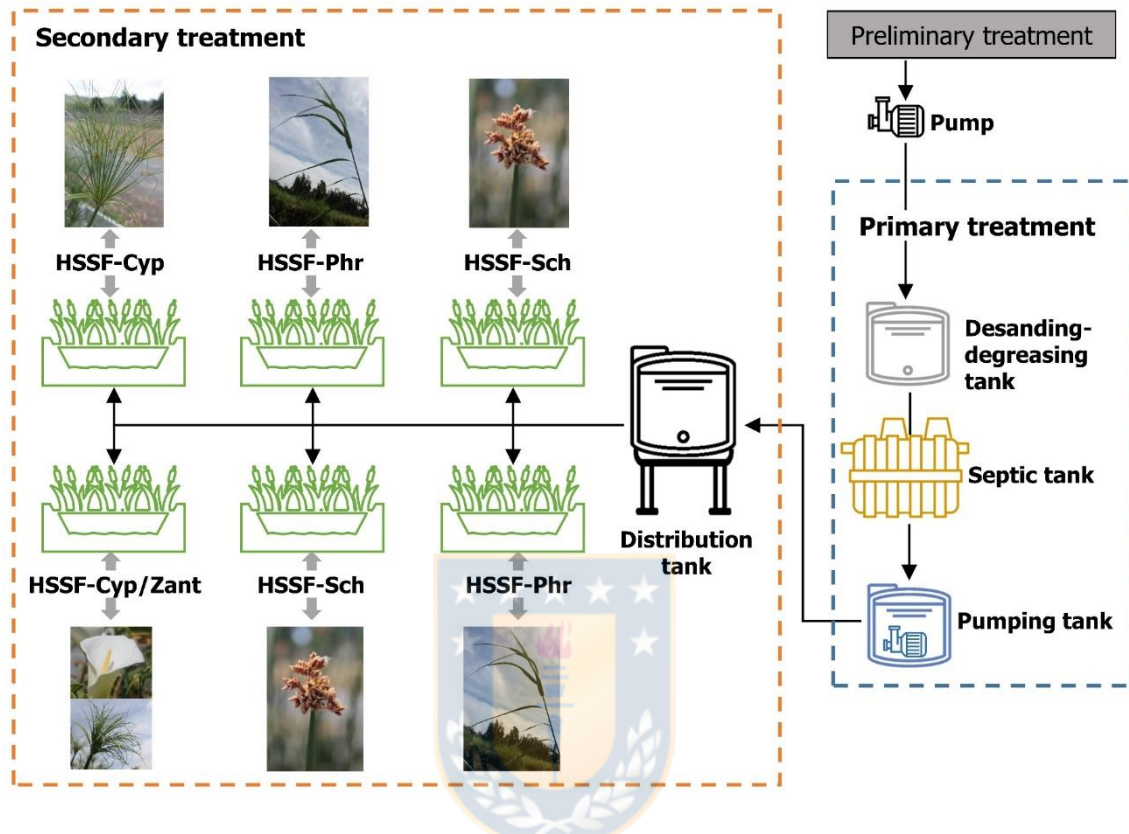


Figure 5.1. Schematic diagram of the pilot-scale wastewater treatment plant horizontal subsurface flow (HSSF) constructed wetlands.

Table 5.1 shows the distribution of plant species by culture type. Two HSSF were planted with a monoculture of *Phragmites australis* (HSSF-Phr). One of the most cosmopolitan and widely used species in CW (López et al., 2016). Two other HSSFs with a monoculture of *Schoenoplectus californicus* (HSSF-Sch), this species is rare because it is only found in the South American region where it is widely distributed (Carrillo et al., 2021). In addition, another HSSF had a monoculture of ornamental plants such as *Cyperus papyrus* (HSSF-Cyp), which in a study by Burgos et al. (2017) was recommended for CW application of HSSF over other ornamental plants. While the latest HSSF had a polyculture of ornamentals with a mixture of *Cyperus papyrus* (11 plantlets) and *Zantedeschia aethiopica* (7 plantlets) (HSSF-Cyp/Zant). It has been demonstrated that *Zantedeschia aethiopica* can be useful in CW treatment and prevent algal growth as well as flower production due to its striking white flower (Morales et al., 2013; Leiva et al., 2018; Zurita et al., 2009). It should be noted

that in the area where the pilot plant is located, *Schoenoplectus californicus* and *Zantedeschia aethiopica* is a common species in the area and has developed well.

Table 5.1. Distribution of plant species by culture types and treatment systems.

Type culture	Plant type	Plant species	Treatment
Monoculture	Common	<i>Phragmites australis</i>	HSSF-Phr
	Common	<i>Schoenopletus californicus</i>	HSSF-Sch
	Ornamental	<i>Cyperus papyrus</i>	HSSF-Cyp
Polyculture	Ornamental	<i>Cyperus papyrus</i> ; <i>Zantedeschia aethiopica</i>	HSSF-Cyp/Zant

Table 5.2 shows the design and operational parameters of the HSSF system. The HSSF cell has a surface area of 4.5 m², a volume of 1.28 m³ and a depth of 0.57 m. The substrate adsorption in the CW was gravel with a 19 to 25 mm particle size and porosity of 0.6% (Andrés et al., 2018). It should be noted that the HSSF was not constructed mainly for phosphorus removal. The average organic loading rate (OLR) was 7.2±2.5 g COD/m² d, and the phosphorus loading rate (PLR) was 0.4±0.1 g P/m² d. The average hydraulic loading rate (HLR) and hydraulic retention time (HRT) were 25.7±4.8 mm/d and 6.6±1.3 days, respectively. The HSSF pilot system was implemented in July 2011 with HSSF-Phr and HSSF-Sch and had an operating time of 2,695 days (Rojas et al., 2013) while monoculture (HSSF-Cyp) and ornamental polyculture HSSF-Cyp/Zant treatment was implemented in December 2014 and had an operating time of 1,673 days (Leiva et al., 2018).

Table 5.2. Design and operational parameters of the horizontal subsurface flow constructed wetland (HSSF) pilot plant.

Design parameter	Units	Values	Operational parameter	Units	Values
Surface area	m ²	4.5	OLR	g COD/m ² d	7.2±2.5
Total volume	m ³	1.8	PLR	g P/m ² d	0.4±0.1
Water level	m	0.3	HLR	mm/d	25.7±4.8
Effective volume	m ³	0.76	HRT	d	6.6±1.3
Substrate adsorption	-	Gravel	Days of operation	d	2,695

OLR: organic loading rate; PLR: phosphorus loading rate; HLR: hydraulic loading rate; HRT: hydraulic retention time. COD: chemical oxygen demand; TP: total phosphorus.

2.2. Sample collection

Influent and effluent water samples were collected every month during 2014–2019. The average of the cold season (Fall-Winter) and the warm season (Spring-Summer) was considered. The average between HSSFs planted with *Phragmites australis* and *Schoenoplectus californicus* was also considered. In addition, monthly in situ measurements were considered at each HSSF at three sampling points, as described in Leiva et al. (2018) and López et al. (2016). For the plant species samples, measurements were performed during the warm seasons from 2014 to 2017 and during the cold seasons from 2015 to 2019. The average concentrations of the analyzed physicochemical parameters in the wastewater influents (C_{inf}) and effluents (C_{eff}) were used to calculate the removal efficiencies of each HSSF parameter according to Eq. (1):

$$\text{Removal efficiency (\%)} = 100 \times (1 - \text{Ceff/Cinf}) (\%) \quad (1)$$

2.3. Analytical methods

The influent and effluent water samples were transported and stored under refrigeration (4 °C). To characterize the influent and effluent of each HSSF, the water samples were made in triplicate and were filtered using 0.45 µm pore size membrane pore size filters and analyzed according to standard methods (APHA, 1998). The physicochemical parameters considered were chemical oxygen demand (COD) (colorimetric method, 5210-B), biological oxygen demand (BOD₅) (modified Winkler azide method, 5210-B), total suspended solids (TSS) (gravimetric method 2540-D), total nitrogen (TN) and total phosphorus (TP) (Spectroquant-Nova 60, Merck kits), ammonium (NH₄⁺-N), and phosphate-phosphorus (PO₄³⁻-P) (colorimetric method). The *in-situ* parameters, such as pH, temperature (T), dissolved oxygen (DO) and oxidation-reduction potential (ORP), were measured in situ with all the samples using a multiparametric OAKTON-PC650 (Eutech Instruments; Singapore). The DO was measured using a portable oximeter (oxi 330i/set Hanna HI 9146-04).

2.4. Biomass sampling and analysis

To compare growth, percent cover (%) and density (individuals/m²) were calculated by counting the number of individuals in a polyvinyl chloride (PVC) pipes quadrat of 0.0625 m² (0.25 m x 0.25 m) (Leiva et al., 2018; Vymazal, 2020). Samples of plants of *Phragmites australis* (Phr), *Schoenoplectus californicus* (Sch), *Cyperus papyrus* (Cyp) and *Zantedeschia aethiopica* (Zant)

were taken at each HSSF. The dry biomass aboveground (stem) and belowground (roots) was considered, but in the case of ornamental macrophytes, the flowers were considered. In addition, a proximal analysis was performed to obtain the concentration of TP in plant tissues. All samples were dried in an oven between 80 °C and 100 °C for 24 h until a constant dry weight (DW) was achieved. The biomass of each plant was then pulverized and analyzed to determine the TP concentration in the plant tissue (López et al., 2016; Zhang et al., 2007b). The phosphorus content was determined by calcination (500 °C) and then by colorimetry (466 nm) (Sadzawka et al., 2007). Finally, phosphorus uptake in the macrophytes was estimated following Eq. (2) (Alayu and Leta, 2021).

$$\text{TP uptake (g P/m}^2\text{)} = \text{Biomass (kg DW/m}^2\text{)} \times \text{TP content (g P/kg DW)} \quad (2)$$

2.5. Mass balance

Mass balances were calculated in terms of TP. Equation (3) explains the procedure for calculating balances as follows:

$$(\text{C}_i \cdot \text{Q}_i \cdot \text{Do}) / A - \text{C}_{i+r} - \text{C}_p = (\text{C}_e \cdot \text{Q}_e \cdot \text{Do}) / A \quad (3)$$

where C_i = influent concentration of TP (g/m^2); Q_i = input stream wastewater (L/d); Do = operation time (d); A = surface area (m^2); C_{i+r} = intake by microorganisms or retention in HSSF (g/m^2); C_p = plant uptake (g/m^2); C_e = effluent concentration of TP (g/m^2); and Q_e = effluent output stream (L/d). This procedure was modified from Kadlec and Wallace (2009).

2.6. Statistical analyses

Statistical analyses were conducted using the statistical program Rstudio (Version 1.3.959) with a level of significance of $p = 0.05$. The TP effluent concentrations, removal efficiency, biomass and phosphorus uptake during the different seasons (cold and warm) were compared. First, the data were subjected to a normality test (the Shapiro–Wilk test). The following tests were performed: a) for data with a normal distribution, an ANOVA test, and b) for data without a normal distribution, a Kruskal–Wallis test. Fisher's least significant difference (LSD) was then performed to discriminate differences between treatments when the ANOVA was significant, where different letters represent the difference between treatments.

3. RESULTS AND DISCUSSION

3.1. Influent Characteristics and in situ parameters of HSSFs

Table 5.3 shows the average concentrations of the wastewater quality parameters of the influent from the HSSF treatment during the cold and warm seasons. According to the average organic matter content (183 mg BOD₅/L), the influent can be defined as concentrated wastewater. However, it can be easily degraded with a biodegradability coefficient (BOD₅/COD) of 0.69±0.27 (Henze et al., 2008). The TP and PO₄³⁻-P concentrations in the influent were 14±3 mg/L and 11±3 mg/L, respectively. The TP/PO₄³⁻-P ratio in the influent represented an average of 84±12%. In general, influent wastewater concentrations are consistent with the wastewater values described by (Carrillo et al., 2020; García et al., 2004).

Table 5.3. Physicochemical characterization of the quality of the influent wastewater from HSSF treatments during the cold and warm seasons.

Parameter	n	Cold season		Warm season	
		Range (mg/L)	Average ± SD (mg/L)	Range (mg/L)	Average ± SD (mg/L)
COD	69	129-465	282±92	115-457	282±80
BOD ₅	60	96-330	177±61	79-348	185±68
TSS	67	40-565	260±137	101-480	227±99
TN	59	41-138	91±26	74-139	99±20
TP	57	11-24	15±3	10-21	14±3
NH ₄ ⁺ -N	68	31-190	83±33	48-155	78±26
PO ₄ ³⁻ -P	64	6-17	11±3	5-14	10±3

n: Sample number; SD: standard deviation; COD: chemical oxygen demand; BOD: biological oxygen demand; TSS: total suspended solids; TN: total nitrogen; TP: total phosphorus; NH₄⁺-N: ammonium nitrogen; PO₄³⁻-P: phosphate phosphorus.

Table 5.4 shows a summary of the average in situ parameters in each HSS during the monitored period. The pH showed values between 6.2 and 7.0, which are in the optimal range for plant development in CWs (Calheiros et al., 2015; García-Ávila et al., 2019; López et al., 2016; Sandoval-Herazo et al., 2018). The temperature showed seasonal variability, with a minimum of 12 °C in the cold season and a maximum of 18 °C in the warm season. DO and ORP showed values lower than

0.5 mg/L and close to -250 mV, respectively, which represent anoxic-anaerobic conditions for HSSFs with ornamental and common plant species (Garcia et al., 2010; Leiva et al., 2018).

Table 5.4. In situ parameters for each HSSF treatment during the cold and warm seasons.

Parameter	Unit	Season	Average \pm SD			
			HSSF-Phr	HSSF-Sch	HSSF-Cyp	HSSF-Cyp/Zant
pH	-	Cold	6.8 \pm 0.2	6.8 \pm 0.2	6.7 \pm 0.2	6.6 \pm 0.3
		Warm	6.8 \pm 0.2	6.7 \pm 0.3	6.7 \pm 0.2	6.7 \pm 0.2
T	°C	Cold	12 \pm 1.2	12 \pm 1.3	13 \pm 4.4	13 \pm 3.9
		Warm	19 \pm 1.2	18 \pm 2.1	18 \pm 3.2	18 \pm 3.2
ORP	mV	Cold	-215 \pm 78	-210 \pm 84	-250 \pm 89	-230 \pm 100
		Warm	-215 \pm 72	-215 \pm 78	-225 \pm 72	-226 \pm 66
DO	mg/L	Cold	0.5 \pm 0.2	0.4 \pm 0.2	0.2 \pm 0.2	0.6 \pm 0.4
		Warm	0.3 \pm 0.1	0.3 \pm 0.2	0.1 \pm 0.1	0.2 \pm 0.1

SD: standard deviation; T: temperature; ORP: oxidation-reduction potential; DO: dissolved oxygen.

3.2. Phosphorus removal and HSSF performance

Figure 5.2 shows the effluent TP concentrations and phosphorus removal efficiencies of each HSSF treatment during the cold and warm seasons. In general, the HSSF-Cyp/Zant polyculture treatment presented the effluent with the lowest TP concentration with a mean of 9.3 \pm 3.5 mg/L in the warm season (Fig. 2b). The monoculture HSSF-Phr had the highest concentration of 12.5 \pm 2.7 mg/L in the cold season (Fig. 2a). HSSF-Sch and HSSF-Cyp showed similar TP values in effluents of 10.9 \pm 2.8 mg/L and 10.3 \pm 3.3 mg/L, respectively. Rodriguez and Brisson (2016) and Song et al. (2006) like this study, concluded that seasonality did not influence phosphorus removal from effluents.

Comparing the treatments, a significant difference in removal efficiencies by species was observed in the cold season. The polyculture HSSF-Cyp/Zant (b) showed the best performance with 33 \pm 19%, followed by the ornamental monoculture HSSF-Cyp (ab) with 27 \pm 18% (Fig. 2c). Among the common macrophytes, HSSF-Sch (ab) had better TP removal efficiency, with 23 \pm 17% compared to 12 \pm 10% for HSSF-Phr (a). The results were in agreement with the results found in many previous studies, where polyculture HSSF presented approximately 10% more efficient phosphorus removal

than those planted with monoculture (Marín-Muñiz et al., 2020; Zhou et al., 2017). Rodriguez and Brisson (2016) hypothesized that the combination of plant species could improve treatment efficiency and represent functional complementarity and/or seasonal or spatial compensation. On the other hand, there were no significant differences in the warm season due to the large variability of the efficiencies (Fig. 2d). TP removal efficiencies ranged from -6 to 25% for HSSF-Phr, -16 to 45% for HSSF-Sch, -17 to 50% for HSSF-Cyp and -12 to 79% for HSSF-Cyp/Zant. Similar results were reported by Józwiakowski et al. (2020) and Hijosa-Valsero et al. (2012) who showed higher data variability in the spring season (42%) and in the summer season (35.7%).

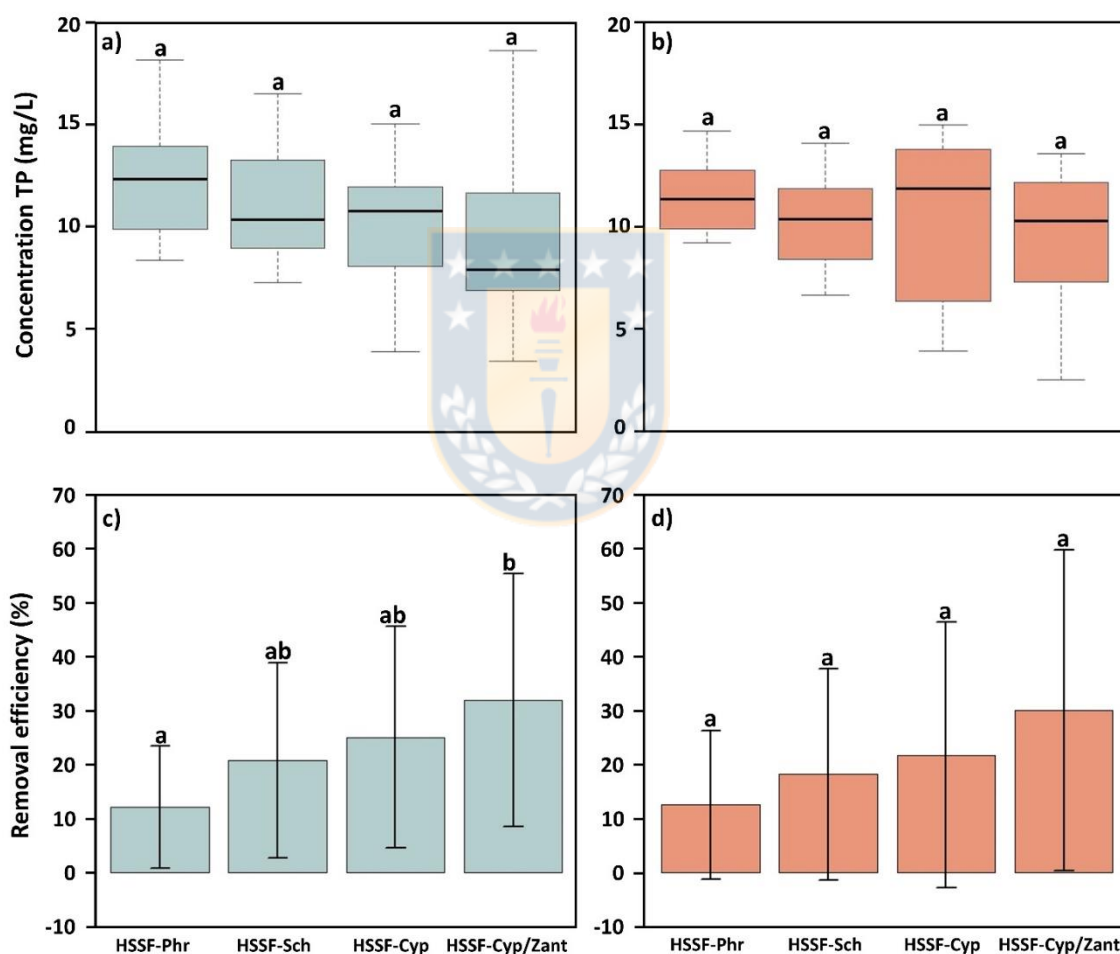


Figure 5.2. Effluent concentration (box plot) of phosphorus a) during the cold (■) and b) warm (■) seasons and removal efficiency (bar chart) of phosphorus in HSSF treatments c) during the cold (■) and d) warm (■) seasons. Different letters indicate significant differences among plant species.

3.3. Plant development in HSSFs

Figure 5.3 shows the growth characteristics in the HSSF for Phr, Sch, Cyp and Cyp/Zant during the cold and warm seasons. Regarding density (Fig. 3a), no significant differences were observed between species by season ($p \geq 0.05$). Monoculture HSSF reached a total density between 1.7-2.8 times higher than ornamental species HSSF, with a mean of 461 ± 308 individuals/m² for HSSF-Cyp and a mean of 620 ± 210 individuals/m² for HSSF-Cyp/Zant in the cold season. The HSSF-Sch was superior, with a mean of 1283 ± 733 individuals/m², followed by HSSF-Phr, with 879 ± 452 individuals/m² and HSSF-Cyp with 742 ± 286 individuals/m² in the warm season. These results show that the cold season slows vegetative growth, especially in the case of ornamental plants that develop the flowering phase in the summer months (Leto et al., 2013).

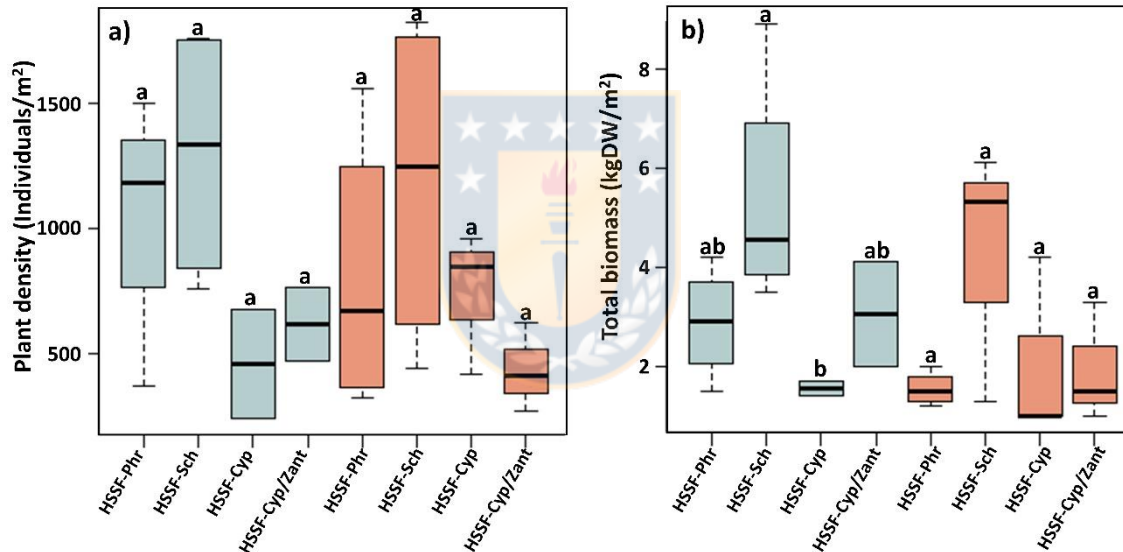


Figure 5.3. Plant growth characteristics in HSSF treatments. a) Plant density and b) total biomass production in dry weight (DW) during the cold (■) and warm (■) seasons. Different letters indicate significant differences among plant species.

Biomass yield (Fig. 3b) was not consistent with density due to significant differences between species for the cold season. The HSSF-Sch it developed the highest biomass with 5.4 ± 2.4 kg DW/m² which is one of its characteristics as a stable support plant for growth. In addition, for the warm season it also obtained the highest biomass with 4.5 ± 2.2 kg DW/m², being the species less latent to seasonal variations. This agrees with the background information that this species develops a net-like root system that stores nutrients and helps the plant survive during dry seasons and

adverse conditions (Hidalgo-Cordero and García-Navarro, 2018). On the other hand, the lowest biomass with a mean of 1.6 ± 0.2 kg DW/m² was for HSSF-Cyp. This species in general has a biomass between 2.2-3.1 kg DW/m² with abundant sunlight, which explains the low biomass in cold seasons (Perbangkhem and Polprasert, 2010). As for the HSSF-Cyp/Zant polyculture, biomass production was 1.9 ± 1.2 kg DW/m². In the warm season and improved in the cold season with 3.1 ± 1.5 kg DW/m². This result is consistent with polycultures being unstable due to competition and/or interactions between plant species when space is no longer available, generating a dominant species and decreasing or extinguishing the other species (Leiva et al., 2018; Zheng et al., 2020). In this case the dominance is by *Cyperus papyrus*, and the extinction of *Zantedeschia aethiopica*, which tends to be a long-term monoculture (Leiva et al., 2018).

3.4. Phosphorus content in plant tissue

Table 5.5 shows the plant tissue TP content and percent phosphorus concentration above and below the soil for each HSSF treatment in the cold and warm seasons. The TP content showed significant differences in the different plant tissues of HSSF-Phr (a) and HSSF-Sch (a) with HSSF-Cyp (b) and HSSF-Cyp/Zant (b) ($p < 0.05$). HSSF-Cyp/Zant presented the highest TP contents in both seasons (cold: 9.8 ± 2.0 g P/kg DW; warm: 8.2 ± 3.2 g P/kg DW), with better performance in the cold season. HSSF-Cyp, HSSF-Sch and HSSF-Phr had higher TP contents in the warm season than in the cold season. TP values in common plant tissues are between 0.22 and 5.03 g P/kg DW, as reported by some authors in the literature, varying according to plant species, soil conditions, water availability, nutrient loading, CW flux and other factors (Liu et al., 2012; López et al., 2016; Rycewicz-Borecki et al., 2017; Shan et al., 2011; Zhang et al., 2007b). In contrast, ornamental species have shown TP contents ranging between 7.9 and 17.0 g P/kg DW depending on the species (Haritash et al., 2017; Kyambadde et al., 2004; Leiva et al., 2018; Polomski et al., 2007). In the case of ornamental plants, flowers presented a higher P content, with a mean of 5.1 ± 1.5 g P/kg DW for *Zantedeschia aethiopica* and a mean of 2.5 ± 2.0 g P/kg DW for *Cyperus papyrus*. These results are similar to those found in the literature, where they reported a range of 2.2 to 4.6 g P/kg DW for TP content in flowers in ornamental species (Abou-Elela and Hellal, 2012; Haritash et al., 2017; Leiva et al., 2018).

Table 5.5. Phosphorus content in plant tissue and percent phosphorus concentration aboveground and belowground for each HSSF treatment during the cold and warm seasons.

Unit		HSSF-Phr	HSSF-Sch	HSSF-Cyp	HSSF-Cyp/Zant
Cold Season					
TP Content	g P/kg DW	1.3±0.7	1.3±1.0	5.4±3.6	9.9±2.0
Aboveground	P %	0.17±0.1	0.20±0.0	0.16±0.1	0.38±0.0
Belowground	P %	0.21±0.0	0.29±0.0	0.36±0.1	0.81±0.3
Warm Season					
TP Content	g P/kg DW	1.4±0.8	1.8±1.0	6.3±4.9	8.2±3.2
Aboveground	P %	0.16±0.1	0.32±0.0	0.31±0.1	0.43±0.0
Belowground	P %	0.29±0.0	0.33±0.1	0.29±0.1	0.73±0.2

DW: dry weight; TP: total phosphorus.

Likewise, the percentage of phosphorus in biomass for the common species *Phragmites australis* and *Schoenoplectus californicus* was in the range of 0.05-0.35%. Such values are similar to those of the common plants used in CWs (0.15-0.25% of DW) (Burgos et al., 2017; Maucieri et al., 2020). A higher percentage showed ornamental species with a range of 0.11-0.99%, where polyculture reached 0.99% with a mean of 0.76%. In addition, the percentage of phosphorus in belowground biomass was 5-20% higher for all species than aboveground. Rodriguez and Brisson (2016) explored the effect of combining two plant species in monoculture and polyculture, observing that phosphorus content in all combinations was higher by 0.1-0.2% for belowground biomass.

3.5. Phosphorus uptake by plants

Figure 5.4 shows TP uptake in HSSF treatment for all plants during the cold and warm seasons. The TP uptake in aboveground biomass showed significant differences between the HSSF-Cyp/Zant (b) polyculture with a mean of 5.5±2.8 g P/m² and the HSSF-Phr monoculture (a) (1.2±0.7 g P/m²) in the warm season ($p < 0.05$). Generally, in the warm season the growth phase is generated, where the phosphorus content is mobilized from the roots to the stems. In contrast, in the dormancy phase, nutrients such as nitrogen and phosphorus are translocated from the stems to the roots and rhizomes (Liu et al., 2012; Zheng et al., 2020).

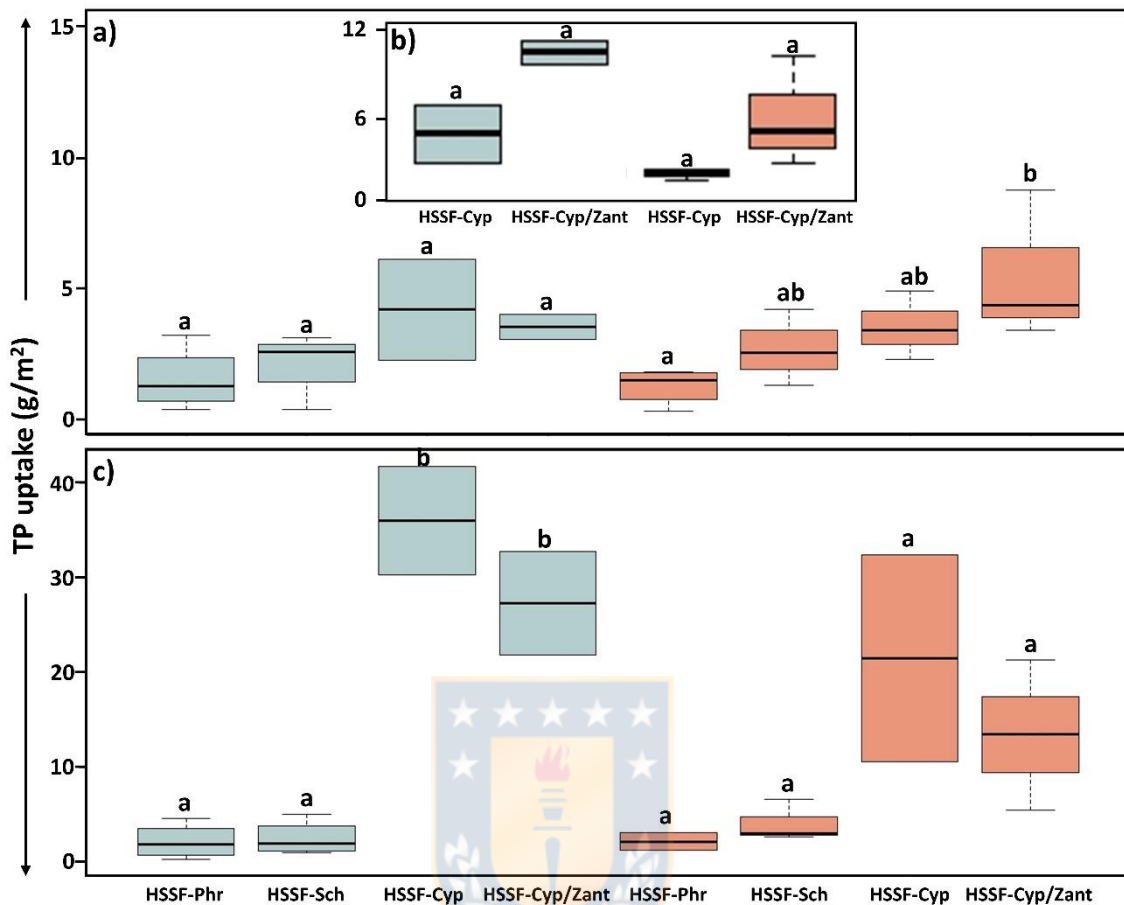


Figure 5.4. Total phosphorus (TP) uptake in HSSF treatments. a) Aboveground, b) flower for ornamental plants and c) belowground biomass during the cold (■) and warm (■) seasons. Different letters indicate significant differences among plant species.

On the other hand, belowground phosphorus uptake was significantly higher by 18 times for HSSF-Cyp (b) and 14 times for HSSF-Cyp/Zant (b) than HSSF-Phr (a) and HSSF-Sch (a) (2 g P/m^2) in the cold season ($p < 0.05$). This is consistent with the dormancy phase in the cold season. Furthermore, Haritash et al. (2017), Liu et al. (2012), Zhang et al. (2007b) and Zheng et al. (2020), observed that roots with higher belowground phosphorus uptake are known to take up soluble phosphate through epidermal cells and use it to synthesize organic materials for their own growth and reproduction (Ji et al., 2021). Likewise, polycultures and ornamental plants grow by the type of roots they develop. More roots are found when there is a mixture of plant species in a CW due to the greater root and vertical development (15-30 cm) in the competition generated by the plant species (Liang et al., 2011).

Likewise, belowground phosphorus uptake was higher for HSSF-Cyp, with a mean of 28.8 ± 13 g P/m². According to the root type, *Cyperus papyrus* has thin roots and does not develop deep roots forming networks that help to create a greater root area coverage for the absorption of contaminants or assimilation of plant tissues (Garcia et al., 2010). The accumulated phosphorus uptake was similar for HSSF-Cyp and HSSF-Cyp/Zant, with an average of 30 g P/m². These results were lower than those obtained by Abou-Elela et al. (2017) who reported a phosphorus uptake of 70.2 g P/m² by *Cyperus papyrus* on a full-scale HSSF (surface area 185.5 m²). However, they were superior to the CW at the polyculture pilot scale containing common species such as *Phragmites australis* and *Typha orientalis*, where the phosphorus uptake reached 15 g P/m² (Zheng et al., 2020).

3.6. Phosphorus balance

Table 5.6 shows the phosphorus mass balance for each HSSF treatment in the cold and warm seasons. Phosphorus uptake by common plants (HSSF-Phr, HSSF-Sch) was 5-9%, while that of ornamental plants (HSSF-Cyp, HSSF-Cyp/Zant) was 17-27%. Zheng et al. (2020) in a CW polyculture at the pilot scale reached a long-term phosphorus uptake rate by plants of 41.9%. Likewise, Zhang et al., (2007a) also achieved a plant uptake of 49% of input phosphorus in a polyculture with a low input concentration of 10 mg/L. These results are similar to our study, since in the winter season the input load was lower (60.8 g P/m²), and plant uptake of phosphorus reached 17-27% of the total retention for HSSF-Cyp and HSSF-Cyp/Zant.

In terms of seasonality, there were non-significant differences, except for the HSSF-Cyp/Zant polyculture which reached values of 17% for the warm season and 27% for the cold season in phosphorus uptake. It should be considered that phosphorus retention by plants is better in the warm season due to their development and growth stage. While in the cold season, as in winter, plants go into dormancy, a strategy that allows them to survive when climatic conditions are adverse. This coincides with our results where monocultures presented slight improvement in the warm seasons. Zhou et al., (2017) highlighted those monocultures tend to decrease nutrient uptake at lower temperature (8.9 °C), however, in polyculture systems they were better at lower temperature. In general, polyculture systems are more resilient and less susceptible to seasonal variation than a monoculture system (Licata et al., 2021). In addition, the polyculture planted with the species *Zantedeschia aethiopica* presents a summer dormancy and its flowering is at the end

of winter until spring (Morales et al., 2013; Zurita et al., 2009). This explains its better phosphorus uptake in the cold season. In addition, *Zantedeschia aethiopica* is a species that has adaptation mechanisms to flooding, obtaining a better management of flood stress in the winter season (Zurita et al., 2009).

Table 5.6. Phosphorus mass balance in the HSSF treatment for the cold and warm seasons.

Treatment	Season	Average (g P/m ²) ± SD			
		Influent	Retention	Plant uptake	Effluent
HSSF-Phr	Cold	60.8±4.9	10.2±9.8	2.9±2.4	47.7±8.7
	Warm	63.8±11.8	11.0±6.4	3.1±0.7	49.7±11.6
HSSF-Sch	Cold	60.8±4.9	17.3±9.5	4.7±0.6	39.8±5.1
	Warm	63.8±11.8	17.4±6.4	5.7±3.4	39.2±10.7
HSSF-Cyp	Cold	60.8±4.9	8.7±5.4	14.8±2.0	40.0±5.1
	Warm	63.8±11.8	9.3±11.0	14.4±7.0	39.9±16.8
HSSF-Cyp/Zant	Cold	60.8±4.9	9.2±8.6	16.3±4.5	38.5±7.2
	Warm	63.8±11.8	16.0±8.7	11.1±5.0	36.6±16.2

In general, phosphorus uptake by plants contributed to the HSSF treatment as a function of species and culture system. However, some differences were shown in each growth stage and their tissues. These variations are due to seasonal conditions, water availability, the growth phase of the plant, interspecific competence between them and environmental conditions (Liu et al., 2012; Zurita et al., 2009). Even so, some characteristics to consider are the adaptation time of the different species since HSSF-Phr and HSSF-Sch were planted in 2011 and the study considers monitoring from 2014 forward. On the other hand, it has been shown that biomass production varies annually in both monocultures and polycultures (Liang et al., 2011; Maucieri et al., 2020), therefore the results should be expressed in years and not by seasons since the plants must complete their cycle.

4. CONCLUSIONS

The type of plant species and the culture system can influence phosphorus removal in a HSSF. The HSSF-Cyp ornamental monoculture is presented as an alternative for phosphorus removal, demonstrating good phosphorus uptake and stable biomass development. It should be noted that the pilot-scale HSSF was not designed for phosphorus removal, so it is necessary to consider an optimal support material and a certain plant species for which a CW can improve its performance.

Additionally, HSSF-Sch proved to be a tolerant and stable plant for constructed wetlands, with good vegetation development. Regarding polyculture, which has been quite controversial, we emphasize that the combination of ornamental species and competition between them can be a good option for phosphorus treatment in CWs independent of seasonal conditions. Finally, adding the importance of the type of plant to be selected can be a key factor in phosphorus uptake considering that each plant has its natural cycles.

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CAPÍTULO VI

LIFE CYCLE ANALYSIS OF A CONSTRUCTED WETLAND FOR THE TREATMENT OF MUNICIPAL WASTEWATER UNDER COLD AND WARM SEASONS



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Life cycle analysis of a constructed wetland for the treatment of municipal wastewater in cold and warm seasons

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Abstract

Wastewater treatment is indispensable to reduce the content of pollutants in water bodies. In recent years, constructed wetlands (CW) have increasingly gained ground for wastewater treatment in rural areas. This study aims to estimate the potential environmental impact of a pilot-scale horizontal subsurface flow constructed wetland (HSSF) through a life cycle assessment. Four scenarios were evaluated, differentiated using two emergent aquatic macrophytes (*Phragmites australis* and *Schoenoplectus californicus*) and the seasonality during the systems operation (warm season, cold season) were evaluated. In addition, two different indicators were evaluated to compare with the LCA in the categories freshwater eutrophication and climate change. One based on the reduction of eutrophication (kgRemoved) (εP) and the other the net environmental benefit (NEB). The results indicate that infrastructures are responsible for more than 70 % of the total impact of human toxicity, land occupation, water, metals and fossil depletion, whereas in impact categories such as climate change and particle formation, the operational phase dominates with 65-75 % and 100 % for marine and freshwater eutrophication. The cold season and the *Schoenoplectus* species showed a better environmental performance while the hot season and the *Phragmites* species the worst environmental performance. The NEB showed a positive environmental benefit for freshwater eutrophication while a negative benefit for climate change. The CWs proved to be an attractive solution for environmentally friendly rural areas for wastewater treatment

Keywords: Constructed wetlands, Life cycle analysis; Wastewater treatment; Seasonality; *Phragmites australis*; *Schoenoplectus californicus*.

1. INTRODUCCION

Today, the focus of the wastewater treatment sector is to develop sustainable wastewater treatment capabilities, with a growing awareness of the potential impacts associated with the treatment processes (Ingrao et al., 2020). Wastewater treatment plants (WWTP) have been designed to reduce the direct pollution of wastewater produced by the population, contributing to the conservation of the aquatic environment. However, other environmental impacts are associated with their processes, due to infrastructure, resource, energy consumption, and solid waste generation (Hospido et al., 2004). This generates a potential trade-off in the environmental impacts of wastewater treatment, leading to situations where issues such as air quality and water quality can be conflicted (Fuchs et al., 2011).

In this sense, constructed wetlands (CWs) have been considered interesting options for decentralized wastewater treatment in small communities or distant locations. They are based on natural processes through physical, chemical, biological processes, where organic matter and nutrients combined with wastewater are purified (Vymazal, 2007). Therefore, they require low labor during operation and maintenance, no chemical additives, and limited energy consumption, being considered as a non-conventional technology with low environmental impact (Garfi et al., 2017; Ingrao et al., 2020). However, these systems generate gaseous compounds that are released into the atmosphere through microbial processes. Among the gases are carbon dioxide (CO₂), methane (CH₄) and nitrous oxide (N₂O) being the most dangerous because they act as greenhouse gases (GHG) (Mander et al., 2014; Maucieri et al., 2017; Ledon et al., 2017).

Over the last decade, life cycle analysis (LCA) has taken a significant interest in assessing the potential environmental impacts of WWTP (Zang et al., 2015; Corominas et al., 2020). LCA is a standardized and sophisticated tool for assessing the potential environmental impacts of product systems, helping to identify environmental hotspots and support decision making (ISO, 2006). There are several LCA studies that have compared the environmental impact of conventional technologies, such as aerobic treatments, versus nature-based solutions such as CW (Kalbar et al., 2013; Lopsik, 2013; Garfi et al., 2017; Gongora et al., 2021). However, little attention has been paid to the performance of CW itself. Some of them have compared different CW types (Fuchs et al., 2011), construction materials (Gkika et al., 2015), or type of support medium (Lopsik, 2013). While

the influence of operational aspects, such as seasonal variability like local climate, type of plant species and their potential environmental impact of treatment systems (specifically CW) have not been extensively evaluated in LCA studies.

An investigation by López et al. (2019) demonstrated in a horizontal subsurface flow (HSSF) CW planted with *Phragmites australis* and *Schoenoplectus californicus* that methane production was higher with 42% in the warm season. Likewise, Kataki et al. (2021) analyzed the CW and life cycle impact of the technology through literature review, where they mostly had a negative effect in the climate change category, where species and temperature are variables to be considered. However, the studies were not based on LCA data, but on emissions. On the other hand, one of the limitations is the available data set, which is difficult to extend from one territory to another, where they are focused on Europe and North America. In the Chilean context, some efforts have been made to evaluate CW from an environmental point of view, but the studies are still limited (Ledon et al., 2017; Livia et al., 2020).

To our knowledge, there are no existing studies that evaluate the environmental performance of different plant species and their seasonal variability. Therefore, the goal is to evaluate the influence of seasonality and the use of different plants on the environmental performance of CW wastewater treatment using the LCA.

2. MATERIALS AND METHODS

2.1. Description of the system constructed wetland

The treatment system was located in Hualqui, Biobio Region, Chile (36°59'026.93" S latitude and 72°56'047.23" W longitude). The capacity of the pilot facility is 804 L/d, which represents a wastewater treatment capacity of about 5 person-equivalents (p.e). The influent into the CW corresponded to wastewater from a rural community of 20,000 inhabitants. The wastewater is diverted to the CW after preliminary treatment (chamber with 40-mm bars), and it enters the pilot plant for primary treatment, consisting of a desander degreaser (630 L), a septic tank (1200 L), and a pumping tank (630 L) (Carrillo et al., 2021; Sepúlveda-Mardones et al., 2017). Finally, the wastewater is distributed in four units of HSSF: two units are planted with *Phragmites australis* (Phr), and two with *Schoenoplectus californicus* (Sch). Table 6.1 shows the design characteristics of the

CW system, and the operational parameters for the warm and cold seasons. For the plant species, there are no differences because the inflow is the same for both. The support medium used was 19–25 mm gravel with a porosity of 0.57% (Andrés et al., 2018).

Table 6.1. Design characteristics and input operational parameters of the HSSF units for the warm and cold seasons.

Design parameter	Units	Values/ Charters	
Surface area	m ²	4.5	
Total volume	m ³	1.8	
Water level	m	0.3	
Effective volume	m ³	0.76	
Support medium		Gravel	
Operational parameter			
		Warm Season	Cold Season
Flow rate	m ³ /d	0.500	0.528
Organic loading rate	gBOD ₅ /m ² d	4.5±1.5	4.8±2.1
Phosphorus loading rate	gTP/m ² d	0.37±0.08	0.40±0.1
Hydraulic loading rate	mm/d	27±3.3	29±1.9
Hydraulic retention time	d	6.5±1.2	6.7±1.5
Temperature	°C	12±1.8	20±3.2

BOD: Biological oxygen demand; TP: total phosphorus

2.2. Goal and scope definition

An attributional LCA was performed following the international standardization organization ISO (ISO 14040, 2006) guidelines. According to this ISO guidelines, LCA consists of four steps: goal and scope definition, life cycle inventory analysis, life cycle impact assessment, and life cycle interpretation. This study aims to evaluate and compare the potential environmental impacts generated in horizontal subsurface flow (HSSF) CW for wastewater treatment. The proposed scenarios were focused on two macrophyte species: (i) *Phragmites australis* and (ii) *Schoenoplectus californicus*, and two seasonal variability (warm and cold). The warm season corresponds to the spring/summer season considering the months of October to March, while the

cold season corresponds to the autumn/winter season considering the months of April to September. Therefore, four scenarios were established as follows:

- Phr_warm: *Phragmites australis*, warm season.
- Phr_cold: *Phragmites australis*, cold season.
- Sch_warm: *Schoenoplectus californicus*, warm season.
- Sch_cold: *Schoenoplectus californicus*, cold season.

The functional unit (FU), comprising a physical measure, was established as 1 m³ of treated wastewater. This is the most used unit for wastewater treatment (Rodríguez-García et al., 2011; Corominas et al., 2020). A lifetime of 20 years was considered for the treatment systems.

2.3. System boundaries

The scope includes cradle-to-grave input and output flows of wastewater, gaseous emissions, natural resources, and energy. The system boundaries included construction and operation phase of the CW. The construction phase only included the materials necessary for the infrastructure of the system because heavy machinery was not used. Although the construction phase contributes equally to all four scenarios, it is recommended to include construction inventories as part of the wastewater treatment LCA studies to assimilate its contribution (Corominas et al., 2020). Furthermore, previous studies show that for CW infrastructure can be significant (Fuchs et al., 2011; Resende et al., 2019; Lutterbeck et al., 2017; Lopsik et al., 2013). On the other hand, dismantling is not considered since the impact of the demolition/removal stage is insignificant (Rodríguez-García et al., 2011). The operation phase of the CW considers the pumping of wastewater from preliminary treatment, primary treatment, and secondary treatment of the HSSF, as shown in Fig. 6.1. In addition, electricity generation and transmission, sludge generation and dewatering, solid waste transportation (IT) and final disposal were included within the system boundaries. Solid waste was assumed to be disposed of in sanitary landfills.

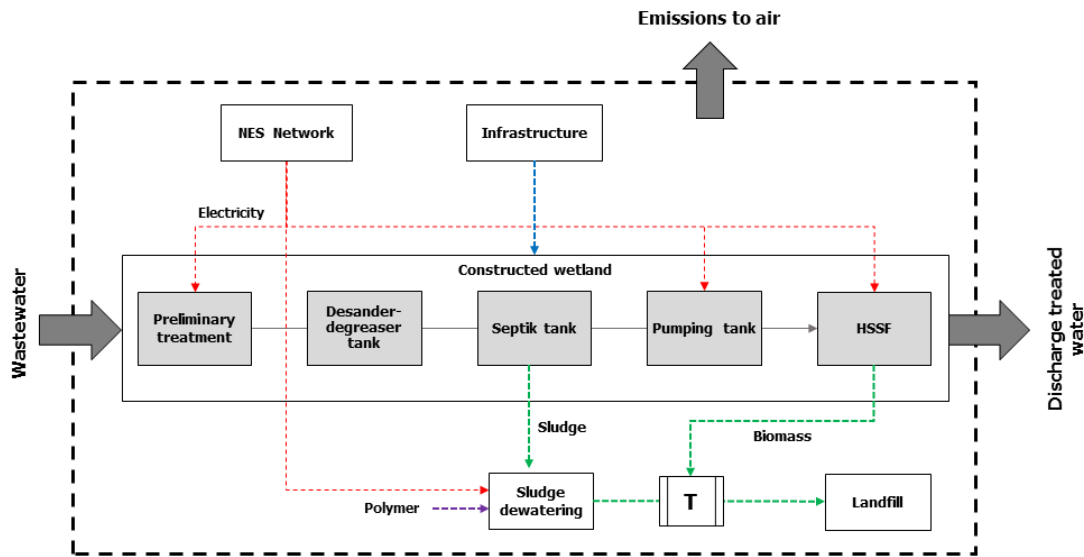


Figure 6.1. System boundary of wastewater treatment using constructed wetland technology. HSSF: horizontal subsurface flow; T: transport; NES: National electric system.

2.4. Life cycle inventory analysis (LCA)

The inventory data of the CW system for the investigated scenarios are shown in Tables 6.2 and 6.3 for infrastructure and operation, respectively. The CW pilot plant inventory data on infrastructure materials, energy consumption, water quality parameters, transport distances, sludge generation and biomass were obtained in situ from the monitoring of eight years of operation, carried out by the same research group (Rojas et al., 2012; Ledon et al., 2017; Carrillo et al., 2021). However, some secondary data were supplemented with *Ecoinvent* 3.6 database or bibliographic references (Weidema et al., 2013). The main sources of information for the infrastructure and operation stages are described as follows:

Infrastructure: The land used for the construction of the CW was an area of 120.9 m². The data base of the materials for the infrastructure was compiled according to the design of the pilot system, which was carried out by the same research group, see Table 6.2. The weight of each material used was considered, which was referred to the functional unit.

HSSF operation: As previously mentioned, the entire treatment process based on the HSSF system consists of a preliminary treatment, a primary treatment, and a secondary treatment.

-Preliminary treatment: Wastewater is separated from solids and transported to the primary treatment by a submersible pump that requires 0.10 kWh/m³ of electricity. All pump energy consumption in this study is estimated by pump power and operating time.

Table 6.2. Summary of the materials inventory for the infrastructure of constructed wetland systems for wastewater treatment. The values are referred to the functional unit (1 m³ of treated water).

Materials	Unit	Values
<i>Inputs</i>		
High density polyethylene	kg	1.42E-02
Polyvinyl chloride (PVC)	kg	1.82E-02
Metal	kg	2.64E-04
Polyethylene	kg	3.68E-02
Polypropylene	kg	6.82E-03
Gravel	kg	2.90E+00
Steel	kg	1.71E-02
Wood	kg	6.13E-03
Concrete	m ³	1.07E-05
Sand	kg	8.52E-02

-Primary treatment: The settleable solids were 0.027 kg/m³ which were removed from the septic tank in the form of sludge. This value was estimated based on a sludge generation rate of 0.040 m³/PE/year by Novelo et al. (2007). The wastewater was pumped to an elevated tank, where the wastewater flowed by gravity to the four cells of the HSSF. The pump electricity consumption was 0.18 kWh/m³.

-Secondary treatment (HSSF): The physicochemical characterization of the influent and effluents were obtained from measurements made by Carrillo et al. (2021). The system was started up in July 2011. The stabilization time was 85 days during the winter season, and the HSSF ran from 2011 to 2019, for 2833 days in total. Monitoring consisted of collecting samples by season (spring, summer, fall and winter) during the entire period of operation. Direct GHG emissions of CO₂, CH₄ and N₂O were considered for the HSSF. The CH₄ emissions were calculated based on the specific methanogenic activity by plant species and season of the study HSSF systems, reported by López et al. (2019), see Table 6.3. The CO₂ and N₂O emissions were estimated by literature

from CW systems with similar characteristics, such as water type, configuration, temperature, scale and plant type (Sovik et al., 2006; Liikanen et al., 2006; Gui et al., 2007; Picek et al., 2007; Inamori et al., 2008; Liu et al., 2009; Maltais-Landry et al., 2009; Barbera et al., 2014; Mander et al., 2014; De la Varga et al., 2015; Jahangir et al., 2016; Maucieri et al., 2017). The HSSF treatment system does not include the sludge accumulated on the support medium which may be negligible (Lopsik et al., 2013; Corbella et al., 2017). According to Lopez et al. (2019) the attached biomass in HSSF, represents only a minor fraction (0.15 gVSS/m²) corresponding to 1.2E-06 kg/m³. The inventory included the removal of biomass collected in the HSSF cells. Due to lack of information, there is no estimate of how much and when the HSSF should be harvested. However, a 15% harvest was estimated for *Phragmites* resulting in a biomass of 0.006 kg/m³ for the Phr_warm and 0.010 kg/m³ for Phr_cold. On the other hand, for *Schoenoplectus*, a 25% harvest was estimated which represented 0.028 kg/m³ for Sch_warm and 0.025 kg/m³ for Sch_cold. The effluent from the pilot plant is pumped out of the system. For effluent pumping, energy of 0.025 kWh/m³ was consumed.

Sludge dewatering: Sludge dewatering was based on literature data. Polyacrylamide polymer was used at 0.01 kg/ton dry sludge (Roskosch and Otto 2014). The dry sludge index was 0.21 kg DS/kg sludge (Piao et al., 2015). The energy consumed by the press band was 0.20 kWh/m³ sludge (Roskosch and Otto, 2014).

Transportation: The solid waste transportation, represented by dry sludge and dry biomass collected in the HSSF cells, was considered. The solid waste was transported to a sanitary landfill located in the locality of Copiulemu (commune of Florida), located at 20 km from the CW (commune of Hualqui). The distances traveled were estimated using information provided by Google Earth and considered diesel trucks of 3.5 to 7.5 metric tons (EURO 5) capacity.

Landfill: Final disposal is carried out in a landfill of 28 ha that currently receives 18,000 m³/year of waste (SEIA, 2018). The plant has a gas collection and recovery system, a biogas flaring plant and a leachate treatment plant.

Electricity network: The CW electricity requirements were provided by the Chilean national electricity system (NES). For 2021, the mix consisting of 25% hydropower, 17% coal, 16% solar, 15% diesel, 14% gas, 11% wind and 2% biomass (CNE, 2021).

Table 6.3. Summary of the inventory of wastewater treatment by constructed wetlands for each scenario according to the season and plants considered. Values are referred to the functional unit (1 m³ of treated water).

Inputs	Unit	Scenarios			
		Phr_Warm	Phr_Cold	Sch_warm	Sch_cold
Transport of waste	tkm	1.30E-03	1.48E-03	2.20E-03	2.08E-03
Polyacrylamide	kg	3.75E-03	3.75E-03	3.75E-03	3.75E-03
Electricity	kWh	3.12E-01	2.93E-01	3.12E-01	2.93E-01
Land use	m ² a	2418	2418	2418	2418
Outputs					
<i>Emissions to air</i>					
CO ₂	kg	1.35E-01	6.49E-02	1.57E-01	5.97E-02
CH ₄	kg	2.71E-02	2.46E-02	5.62E-02	3.09E-02
NO ₂	kg	8.35E-05	2.62E-05	1.04E-04	2.60E-05
<i>Emissions to water</i>					
COD	kg	1.20E-01	1.26E-01	1.28E-01	1.27E-01
BOD	kg	6.59E-02	6.03E-02	6.48E-02	6.08E-02
TSS	kg	2.63E-02	1.82E-02	2.57E-02	1.76E-02
TN	kg	7.13E-02	6.77E-02	7.52E-02	6.37E-02
TP	kg	1.29E-02	1.19E-02	1.28E-02	1.15E-02
N-NH ₄	kg	5.60E-02	6.31E-02	5.97E-02	6.31E-02
P-PO ₄	kg	1.02E-02	1.06E-02	9.90E-03	9.95E-03
<i>Waste for treatment</i>					
Landfill of waste	kg	3.24E-02	3.70E-02	5.49E-02	5.20E-02

CH₄ Methane; NO₂: Nitrous oxide; COD: chemical oxygen demand; BOD: biological oxygen demand; TSS: total suspended solids; TN: total nitrogen; TP: total phosphorus; NH₄⁺-N: ammonium nitrogen; PO₄³⁻-P: phosphate phosphorus; Waste: sludge and biomass.

2.5. Life cycle impact assessment (LCIA)

Potential environmental impacts were calculated using SimaPro v 8.5.2.0 software (Pré, 2016). The method used was the ReCiPe midpoint methodology, in his hierarchist version (Goedkoop et al., 2009). Among the categories of environmental impacts considered were: climate change (CC); terrestrial acidification (TA); Freshwater eutrophication (FE); Marine eutrophication (ME);

Photochemical oxidation formation (POF); Particulate matter formation (PMF), that have primary data from the inventory and related to direct aspects of the HSSF. The categories climate change; terrestrial acidification; Freshwater eutrophication; Marine eutrophication are considered the most relevant in most articles on wastewater treatment (Zang et al., 2015; Corominas et al., 2020). Although categories such as photochemical oxidation formation and particulate matter formation have gained less attention than the others discussed above, they are becoming a standard in LCA studies (Zang et al., 2015). In addition, for the analysis of infrastructure impacts, the following categories were added: human toxicity (HT); urban and agricultural land occupation (ALO) (ULO); natural land transformation (NLT); water depletion (WD); metal depletion (MD) and fossil depletion (FD) which have been highlighted in LCA in CW being relevant in the infrastructure phase (Garfi et al., 2017; Resende et al., 2019).

2.6. Life cycle interpretation

For the interpretation of the data, two analyses were performed; 1) An uncertainty analysis; 2) contribution analysis.

1) *Uncertainty analysis*: Since the values of the LCA parameters are not exact and are distributed according to their range, the comparison of results must be carried out in all possible combinations. For this purpose, the Monte Carlo method was used to evaluate the uncertainty of the results. To do so, the descriptive statistics of the data compiled from direct measurements was analyzed, using relevant parameters such as the distribution, mean, standard deviation mode, minimum and maximum values. In the case of the inventory data showing a normal distribution (determined based on a Shapiro-Wilks test with an alpha value of 0.05), the mean and standard deviation were used as parameters in the inventory. In the remaining cases, a triangular distribution was assumed, which was described by the mode, minimum and maximum values observed in the data. In the case of bibliographic data, the uncertainty was determined through the Pedigree Matrix method, as implemented in the SimaPro software. Monte Carlo simulations were run with 1,000 iterations and at a significance level of 95%.

2) *Contribution analysis*: The relative contribution was identified with the goal of identifying the critical points of the infrastructure life cycle and operation in each impact category, giving this approach to the interpretation of results.

2.7. Environmental Impact Assessment

Wastewater treatment LCAs do not usually consider influent water quality and WWTP efficiency (Corominas et al., 2020). It has been shown that this can be a key aspect in the definition of environmental profiles because the results do not really express the environmental performance associated with treatment efficiency (Rodríguez-García et al., 2011). Therefore, some indicators have been sought or adapted the FU to reflect pollutant loads recognizing the removal efficiency especially when comparing different scenarios. Godin et al. (2012) developed a parameter that they defined as the net environmental benefit (NEB). The goal of the NEB is to show the environmental trade-offs between the avoided impact due to wastewater treatment and the impact generated by the life cycle of the WWTP. So, this methodology relates the quality of the influent whereas for an LCA this the influent is not necessary. The NEB formula was determined using the following expressions (1):

$$\text{NEB (kg/m}^3\text{)} = [\text{PI}_{\text{NT}} - \text{PI}_{\text{T}}] - \text{PI}_{\text{IN}} \quad (1)$$

The induced impact (PI_{IN}) corresponds to the potential impact of extracted resources and emissions associated with treatment. The avoided environmental impact is the difference between the no treatment (PI_{NT}) and treatment (PI_{T}) scenarios. In addition, another option for understanding nutrient removal is to express UF in terms of kgPeq removed, associating the wastewater treatment performance with the associated environmental impact. Total phosphorus (TP) removed in treatment is considered, due to its relevance in eutrophication as the major environmental problem of wastewater treatment and also the category climate change. Finally, this potential environmental impact index (EP) gives rise to the following expression (2):

$$\text{Index EP} = \text{PI}_{\text{T}} (\text{kg eq/m}^3) / \text{Removed (kg removed/m}^3\text{)} \quad (2)$$

3. RESULTS AND DISCUSSION

3.1. Infrastructure life cycle assessment

Table 6.4 shows the relative contribution of the environmental impact of the infrastructure versus the operation of the CW for the four scenarios. When comparing between scenarios, there were no differences between species and season because the infrastructure was the same for each scenario. The results indicate that infrastructure is responsible for more than 70% of the total impact

for the categories human toxicity, land occupation, water, metal, and fossil depletion. While in impact categories such as climate change and particulate matter formation, the operation phase dominates with 70-75% and 100% in the case of marine and freshwater eutrophication. Categories such as terrestrial acidification and photochemical oxidant formation were relevant in both phases at approximately 50%. In the infrastructure phase were slightly higher in the cold season with 4 and 8% respectively for the mentioned categories. This is justified due to the lower emissions in the cold season, which lower the potential impact in the operation phase. The opposite is the case in the Sch_warm scenario, where emissions increase and are associated with the operation phase.

These results agree with previous reports that indicate that in smaller and less energy intensive plants, the infrastructure processes can account for up to 65-80% of the environmental impacts (Lutterbeck et al., 2017; Resende et al., 2019; Corominas et al., 2020). This indicates that conventional technologies with a high level of mechanization and energy consumption, the operation phase is more influential than non-conventional technologies that stand out for low energy expenditure and lower operational requirements (Zang et al., 2015). However, one of the disadvantages of CW is that they can require up to 10 times the surface area of conventional systems. This is reflected in the natural land transformation category, where infrastructure accounts for up to 70-71% of the environmental impact. In terms of land use categories, the contribution of infrastructure is higher at 86% for urban land than agricultural 56-58% in all scenarios. It is worth considering that urban land is more valuable nowadays due to its scarcity. In general, this category is not very well considered and there is little information.

Among the most influential materials were steel contributing 77% in the metal depletion and 42% in the human toxicity category. Polyethylene 43% and 39% in the fossil depletion and human toxic categories respectively. Polyvinyl chloride with 51% in the water depletion category. Similar results have been found by Garfí et al. (2017), Resende et al. (2019) and Morera et al. (2020) in pilot-scale HSSF, who highlighted the substantial contribution of steel to the metal depletion (60-65%). Polyethylene is one of the most common plastics, a subproduct of oil. It has been identified that plastics generate risks to human health and possible endocrine problems which is why they present high degrees of toxicity due to carcinogenic or dioxin emissions during their manufacture (Gongora

et al., 2021; Phillips et al., 2021). Finally, polyvinyl chloride affects the water depletion category due to high water consumption (6,931.4 liters) in its lifetime (Shi et al., 2019).

Table 6.4. Relative contribution to the environmental impact of the infrastructure and operation of the constructed wetland for each scenario according to the season and plants considered.

Impact Category (ReCiPe)	Unit	Scenarios			
		Phr_warm	Phr_cold	Sch_warm	Sch_cold
CC	kgCO ₂ eq	1.02E+00 Op=73%; Inf=27%	9.55E-01 Op=71%; Inf=29%	1.66E+00 Op=83%; Inf=17%	1.08E+00 Op=74%; Inf=26%
TA	kg SO ₂ eq	2.14E-03 Op=51%; Inf=49%	2.04E-03 Op=48%; Inf=52%	2.14E-03 Op=51%; Inf=49%	2.04E-03 Op=48%; Inf=52%
FE	kgP _{eq}	1.63E-02 Op=100%; Inf=0%	1.55E-02 Op=100%; Inf=0%	1.60E-02 Op=100%; Inf=0%	1.48E-02 Op=100%; Inf=0%
ME	kgNeq	1.15E-01 Op=100%; Inf=0%	1.17E-01 Op=100%; Inf=0%	1.22E-01 Op=100%; Inf=0%	1.13E-01 Op=100%; Inf=0%
HT	Kg1.4DBeq	4.34E-02 Op=29%; Inf=71%	4.27E-02 Op=28%; Inf=72%	4.34E-02 Op=29%; Inf=71%	4.27E-02 Op=28%; Inf=72%
POF	kg MVOC	2.16E-03 Op=48%; Inf=52%	2.03E-03 Op=44%; Inf=56%	2.46E-03 Op=54%; Inf=46%	2.09E-03 Op=46%; Inf=54%
PMF	kgPM ₁₀ eq	1.85E-03 Op=69%; Inf=31%	1.76E-03 Op=68%; Inf=32%	1.85E-03 Op=69%; Inf=31%	1.75E-03 Op=68%; Inf=32%
ALO	m ² a	2.84E-02 Op=44%; Inf=56%	2.77E-02 Op=42%; Inf=58%	2.85E-02 Op=44%; Inf=56%	2.77E-02 Op=42%; Inf=58%
ULO	m ² a	5.15E-03 Op=14%; Inf=86%	5.12E-03 Op=14%; Inf=86%	5.17E-03 Op=14%; Inf=86%	5.13E-03 Op=14%; Inf=86%
NLT	m ²	1.03E-04 Op=30%; Inf=70%	1.01E-04 Op=29%; Inf=71%	1.03E-04 Op=30%; Inf=70%	1.01E-04 Op=29%; Inf=71%
WD	m ³	8.31E-03 Op=21%; Inf=79%	8.21E-03 Op=20%; Inf=80%	8.31E-03 Op=21%; Inf=79%	8.21E-03 Op=20%; Inf=80%
MD	kgFeeq	6.03E-02 Op=6%; Inf=94%	6.02E-02 Op=5%; Inf=96%	6.04E-02 Op=6%; Inf=94%	6.02E-02 Op=5%; Inf=96%
FD	kgoileq	1.89E-01 Op=27%; Inf=73%	1.86E-01 Op=27%; Inf=74%	1.89E-01 Op=27%; Inf=73%	1.86E-01 Op=27%; Inf=74%

Op: operation; Inf: infrastructure; CC: climate change; FE: Freshwater eutrophication; ME: Marine eutrophication; HT: Human toxicity; PMF: Particulate matter formation; ALO: Agricultural land occupation; ULO: Urban land occupation; NLT: Natural land transformation; WD: Water depletion; MD: Metal depletion; FD: Fossil depletion.

3.2. Operation phase life cycle assessment

Figure 6.2 shows the potential environmental impact for the treatment of CW in operational phase in the different scenarios. In the climate change category, plant species, *Schoenoplectus* (0.69-1.25 kg CO₂eq/m³) had a higher impact than *Phragmites* (0.55-0.61 kg CO₂eq/m³). In terms of contribution, the critical point was the direct GHG emissions in the HSSF operation, responsible in all scenarios with an average of 64%. The Sch_warm scenario had the highest impact with 76% compared to Phr_cold which was the lowest with 57%. Likewise, HSSF GHGs were also responsible in the photochemical oxidant formation category, contributing between 14-27% following the same trend Sch_Warm >Phr_warm >Sch_cold >Phr_cold. Therefore, this showed that the *Schoenoplectus* species and the warm season were more influential in terms of direct CW emissions.

This rise in the Sch_warm scenario is due to the high methane production of 1,799-3,070 mg/m²d for the *Schoenoplectus* species with a seasonal variation of 42% being higher in the warm season than in the cold season (López et al., 2019). Maucieri et al. (2017) in a review found that the presence of plants and species types directly influence GHG emissions. In this study this was related to CH₄ being the main source of emissions generation in the HSSF. The CH₄ has been shown to have a more significant impact on climate change for HSSF wetlands than vertical flow wetlands (VSSF) according to Fuchs et al. (2011). In addition, environmental conditions such as temperature have a positive correlation with C, meaning that the higher the temperature (20-31°C) the higher the emissions, as shown by our results.

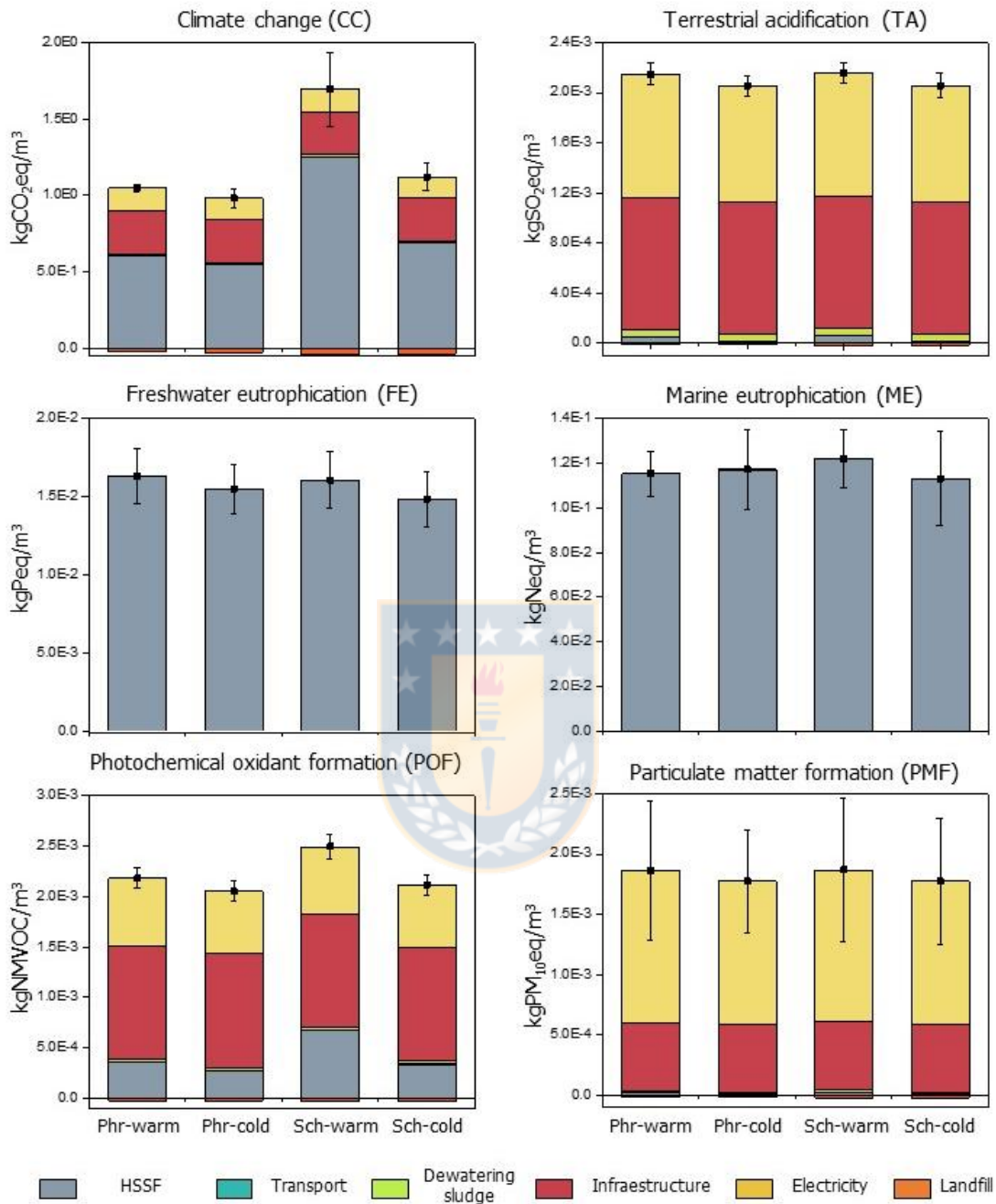


Figure 6.2. Potential environmental impact for each scenario according to the season and plants considered. Values are referred to the functional unit (1 m³ of treated water). Using Monte Carlo simulation, the mean (black point), and the 95% confidence interval (error bars) were obtained.

Generally, CO₂ emissions are not included in the LCA analysis since it is considered a biogenic source (Corbella et al., 2017; Resende et al., 2019). However, some studies show that CO₂ released

to the atmosphere can be considerable (Mander et al., 2014; Maucieri et al., 2017; Barbera et al., 2014). Our results indicate that CO₂ emissions were similar between species, with a mean of 5,969±2,429 mg/m²d, and higher in the warm season with 7,998±788 mg/m²d. The N₂O emissions also contribute to the environmental impact of climate change. The N₂O was higher for the Sch_warm scenario being 25% higher than Phr_warm. This agrees with Maucieri et al. (2017) where they observed in the growing season (Summer), the average N₂O flux values were 2 to 6 times higher than those of the senescence period (Winter).

The use of electricity it is associated with categories such as climate change, terrestrial acidification, formation of photochemical oxidants and formation of particulate matter. Its highest contribution was for the particle formation category for the warm season scenarios with 68%, while in the cold season it was 67% for both species. Followed, electricity had an influence of 46% in the warm scenarios versus 45% for the cold season in the terrestrial acidification category—however, slightly less (5%) than the impact of infrastructure. In contrast, in categories such as photochemical oxidant formation and climate change, electricity contributed 31% and 15% for the *Phragmites* scenarios which were higher than the *Schoenoplectus* scenarios respectively. Electricity is associated with emissions such as carbon monoxide, nitrogen dioxide, sulfur oxides and dioxides, coming from fossil fuel involved in Chilean energy matrix, which corresponds to 43%. Nevertheless, the electricity contribution could vary in life cycle wastewater treatment due to differences in energy matrix by countries and treatment technologies (Zang et al., 2015). For example, the use of renewable energies could improve environmental performance. Resende et al. (2019) in a VSSF study with aeration highlighted that Brazil's energy matrix use comprises 46% of hydropower, showing a contribution of 8% in the climate change category.

In this sense, the electricity consumed in CW remains low (0.30 kWh/m³) concerning the activated sludge treatments (1.05-1.26 kWh/m³), reaches 3 to 4 times lower (capacity 10-1000 P.E.). This performance is justified by higher energy requirement during aeration in wastewater treatments), which could be more energy intensity if activated sludge treatment is combined with extended aeration (2.0 to 2.25 kWh/m³) (Flores et al., 2019). Therefore nature-based systems for treatment are low technology and low energy consumption.

The transport and sludge dewatering had a minor impact (< 3% of total impact) for all impact categories, regardless scenarios. Sludge dewatering achieved a 3% contribution to the land acidification category due to the chemical polymer used in the process. The sanitary landfill had negative values ranging from -3 to -1% due to avoided electricity coming from biogas produced in the sanitary landfill (CNE, 2021). The implementation of energy recovery strategies in WWTPs could help mitigate the negative influence of energy use, decreasing the impact on climate change, land acidification, formation of photochemical oxidants and formation of particulate matter. Some of these strategies are the coupling of CW to microbial fuel cells (MFC) in order to harvest energy to make a net energy producer system (Kataki et al., 2021; González et al., 2021). González et al. (2021) conducted a study of a CW-integrated MFC achieving a power density of 8.6 mW/m² planted with *S. californicus*. Likewise, Corbella et al. (2017) performed an LCA to compare a conventional constructed wetland system (without MFC) coupled with a gravel-based anode MFC, and one coupled with a graphite-based anode MFC. Their results showed power densities of 288 and 346 mW/m² respectively, with an electricity produced of 1.4E-02 kWh/m³. In terms of LCA, the results were positive and similar for the wetlands with the MFC where the electricity production could be reduced by 3% in all impact categories (climate change, ozone depletion, acidification, eutrophication, photochemical oxidant) except abiotic depletion.

For the freshwater and marine eutrophication categories, the CW contributed 100% of the total impact, see Figure 6.2. This is due to the concentrations of water treated by CW treatment, which contains phosphorus, nitrogen and to a lesser extent. Pollutant removal was slightly better (2 and 4%) in the cold season for both species (*Phragmites* and *Schoenoplectus*) than in the warm season. It was observed that in the warm season the summers were hotter with high levels of evapotranspiration, decreasing the flow and increasing the concentration of phosphorus (Carrillo et al. 2021). However, there was no variation between species with an average pollutant removal efficiency of 41%. It has been reported that, due to high lignin contents and better adaptability, plants such as *Phragmites*, *Typha* and *Scirpus*, the latter of the *Schoenoplectus* family, are more efficient in cold seasons (Kataki et al., 2021).

In the case of freshwater eutrophication, the characteristic limiting nutrient is phosphorus, whereas in the case of marine eutrophication, nitrogen is the most common limiting nutrient in marine waters

(Zang et al., 2015). The average treated water concentrations were 70 mg/L for nitrogen and 12 mg/L for phosphorus. This does not comply with the undiluted wastewater discharge limits of the Chilean standard (TN:50 mg/L; TP:10 mg/L) (Carrillo et al., 2021). It should be noted that WWTPs without nutrient removal or that do not discharge in areas sensitive to eutrophication are associated with relatively low removal efficiencies, and therefore a high environmental impact in the eutrophication category. While WWTPs that need to comply with standard requirements or that discharge in sensitive areas require nutrient removal, with longer aeration periods or chemical treatments, which increases the environmental impact in categories such as climate change or ecotoxicity (Rodríguez-García et al., 2011).

Figure 6.3 shows the main categories normalized for the four scenarios considered. The impact of freshwater eutrophication can be between 300 to 1500 times higher than the other impact categories, except for marine eutrophication, whose impact is up to 4 times higher. Eutrophication potential is the most relevant category in wastewater treatment where discharge of treated CW water generally accounts for 85 to 100% of the category (Zang et al. 2015; Flores et al., 2019; Resende et al., 2019; Gongora et al., 2021). To a lesser extent was the impact of GHG emissions, between 0.2 to 0.3% of the impact of eutrophication. However, the ratio between eutrophication and GHG emissions can be decreased. It has been reported that an optimal C/N ratio (~ 5) in CW input wastewater can determine relatively high nutrient removal efficiency and, at the same time, low GHG emission (Maucieri et al., 2017). The C/N ratio in the warm season was 2.5 compared to the cold season of 3, justifying a lower impact potential in the cold season independent of plant species.

Regarding the uncertainty of the data, the Monte Carlo simulation reported that the largest uncertainty are the values of particulate matter formation and eutrophication of fresh and marine water. In the case of particle formation, it can be associated with N₂O emissions, which were secondary data corresponding to a literature-based compilation. However, these emissions can be influenced by different aspects such as local environmental conditions, climate, wind, temperature and rainfall (which were not considered). For eutrophication, there is a direct relationship with the dispersion of the data obtained for effluent concentrations (TP, TN, PO₄-P and NH₄-N). The variability of these data may be due to the amount of data (approximately 60 data) in eight years of pilot plant operation. Despite the lack of country-specific databases (geographic or temporal

variability) and of each method to be evaluated, the uncertainty was reduced and there was no representative difference in uncertainty between scenarios and in the selected categories.

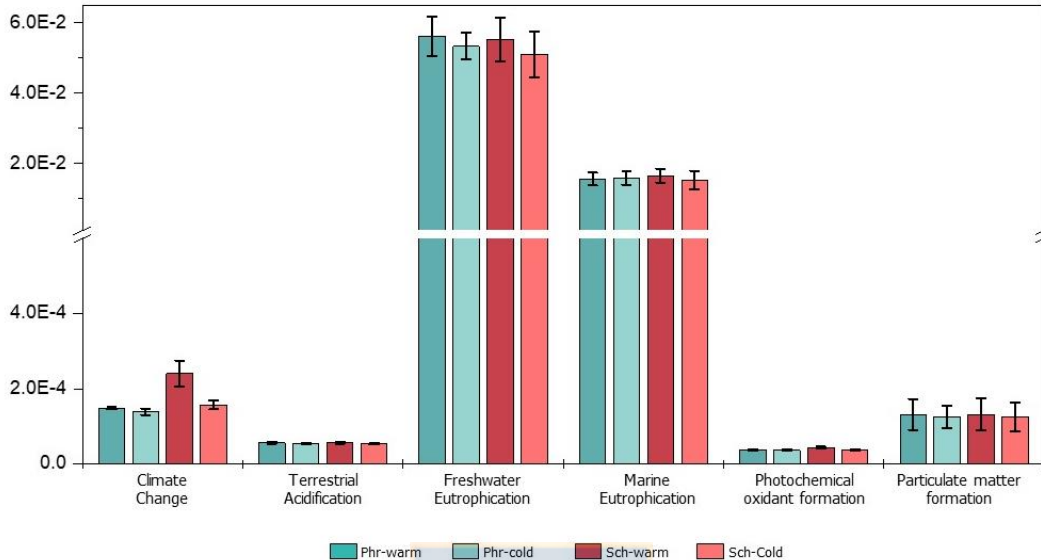


Figure 6.3. Normalization of the main categories for each scenario according to the season and plants considered. Using Monte Carlo simulation, the mean (black point), and the 95% confidence interval (error bars) were obtained.

Considering that freshwater eutrophication and climate change are the categories of greatest impact, a comprehensive analysis is performed between phosphorus removal efficiencies and potential environmental impact (Rodriguez-Garcia et al., 2011; Zang et al., 2015). Figure 6.4 shows a comparative analysis between the results of the LCA, the ϵP index and the NEB. Considering the LCA problem of not considering efficiencies and that everything is expressed in $FU\ m^3$, these approximations show that the scenarios have different efficiencies that are observed in both the ϵP index and the NEB. It should be noted that the ϵP index shows the potential impact generated while the NEB shows the treatment benefit. The values of the freshwater eutrophication potential wastewater non-treatment were $1.73E-02\ kgP_{eq}/m^3$ for the warm season and $1.79E-02\ kgP_{eq}/m^3$ for the cold season. In contrast, the results with CW treatment (LCA) indicate that the potential impact of freshwater eutrophication ($1.48E-02$ - $1.64E-02\ kgP_{eq}/m^3$) was lower, reducing by 5-20% concerning wastewater without treatment. The NEB results show positive impacts for eutrophication potential due to phosphorus removal.

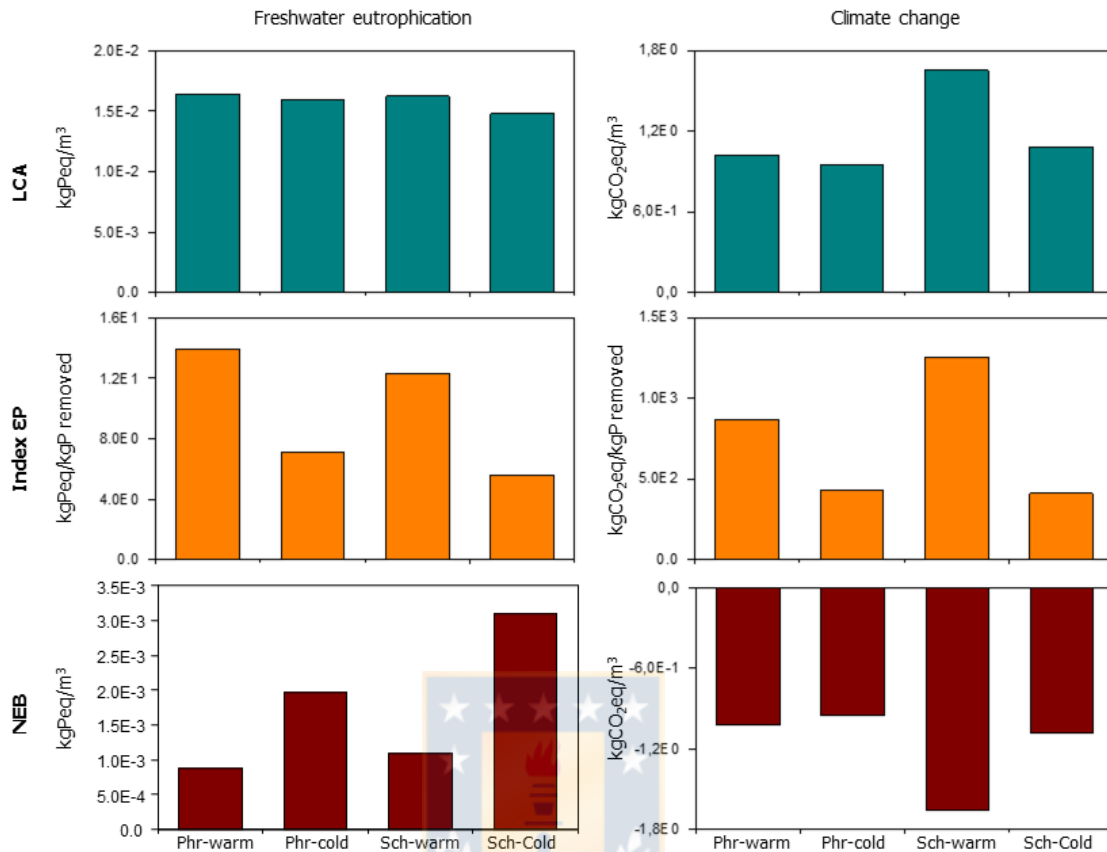


Figure 6.4. Comparative analysis between the LCA, potential environmental impact Index (EP) and net environmental benefit (NEB) for the categories of freshwater eutrophication and climate change for the four scenarios studied.

Furthermore, they show that the induced impact on CW is negligible ($-3E-06$ to $9E-06$) due to the low consumption of energy, chemicals and solid waste generation. This means that CW treatment does not exceed the impacts generated by the life cycle of the pilot plant. Therefore, CW presented positive impacts due to the improvement of water quality without any compensation, which makes it a reasonable technology for rural areas. When comparing between scenarios the NEB agrees with what was obtained in the LCA (higher impact Phr_warm and Sch_warm) where the highest benefit was seen in the Phr_cold scenarios with $2.0E-03$ and Sch_warm $3.1E-03$.

On the other hand, the index EP reflects the potential eutrophication impact per 1 kg of phosphorus removed in the CW. Based on this, the results show the same impact trend as the LCA but establishing clear differences between one scenario and the other. The highest values were for Phr_warm and Sch_warm with 13.9 and 12.3 kgPeq/kgP removed, while they were lower with 7.1

and 5.6 kgPeq/kgP removed for Phr_cold and Sch_cold respectively. Thus, it is possible to appreciate the CW performance consistent with higher phosphorus removal efficiency of 16% Phr_cold and 19% for Sch_cold, compared to 8% for Phr_warm and 9% Sch_warm.

With respect to the climate change category, the assumption was made that the emissions without treatment are the same as those with treatment, so only the induced impact of the CW treatment plant is considered. The index represents the climate change potential per 1 kg of phosphorus removed in the CW. It showed a similar tendency to LCA, however with evident differences between scenarios, those that had better efficiency such as Phr_cold and Sch_cold expressed less potential impact. On the other hand, the NEB showed a negative benefit, being greater for the *schoenoplectus* species, as well as the LCA. This means that there is an impact caused by the life cycle of wastewater treatment, which is associated with CW emissions, electricity, infrastructure, transportation and sludge dewatering. According to the above, Phr_warm is the least optimal scenario for CW treatment. It is because it presented the highest impacts. Although Sch_warm showed a large environmental impact in the climate change category, it compensates with phosphorus removal by reducing eutrophication. Therefore, the *schoenoplectus* species was shown to be the most optimal option and is recommended for use in CW located in southern Latin America, being a sustainable native species in CW.

It should be considered that the low phosphorus removal obtained here could also be related to the fact that the pilot-scale HSSF does not have as its main function and was not designed for phosphorus removal. In this sense, CW configuration improvement could be a feasible alternative for achieving better effluent quality, in particular higher phosphorus removal, reducing the potential environmental impacts. For example, Resende et al. (2019) found that hybrid CW (28%) and aerated CW (47%) achieves higher phosphorus removal efficiency compared conventional CW. This agrees with Carrillo et al. (2020) who reported that combining mechanisms with CW, such as the addition of tertiary treatment or combined technologies, improves phosphorus removal performance reaching efficiencies of 50-75% at low input concentrations (< 10 mgTP/L). However, the application of such systems to our case study could imply an increase in the induced impacts. For example, an increase in electricity demand implies a higher load in categories such as particle formation and terrestrial acidification to a greater extent, due to the contribution of the Chilean

energy matrix. Therefore, a trade-off between electricity consumption and pollutant removal efficiency could have arisen.

One way of compensation is the implementation of energy recovery strategies (discussed above), macrophyte harvesting, effluent reuse biogas production and nutrient recovery (Kataki et al., 2021; Zang et al., 2015; Corominas et al., 2020). In this sense, in rural areas, these types of strategies take on greater strength due to the limitations that may exist in technologies and electricity use. For example, from the point of view of technical design, it would be more feasible to use zeolite as a support medium in CW, which increases phosphorus removal efficiency by 60% and adsorbs >50% that can be used as fertilizer in rural areas (Andrés et al., 2018). This implementation would reduce the impact on eutrophication to 0.34 kgP eq/kgP removed with no induced impact (data not shown). On the other hand, macrophyte biomass can be used as soil amendment, livestock feed, for biogas production or in case of ornamental plants with aesthetic and commercial value (Ingrao et al., 2020; Kataki et al., 2021). *Schoenoplectus* species showed a high biomass production of 5.4 kgDW/m², higher environmental impact in the climate change category, so its collection in the summer season could decrease the potential environmental impact. In addition, the induced impact of this species was negative due to a higher biomass that was disposed of in the landfill, which generates the production of biogas.

4. CONCLUSION

Based on the results obtained, it can be stated that the CW is an attractive solution for rural areas and environmentally friendly for wastewater treatment. As for the infrastructure, it was responsible for 70 % of the environmental impact in categories such as human toxicity, land occupation, water, metal, and fossil depletion. However, most of the potential impacts are related to the operation phase with 70-75 % for the category climate change and 100% for eutrophication. It could be deduced that the cold season obtained a better environmental performance compared to the warm season, being the high temperature a variable to be considered especially in the direct GHG emissions of the plants. No significant differences were observed between species. The uncertainty analysis supported the empirical data which were directly related to the distribution of the statistical data. Finally, the use of indicators such as EP and NEB is recommended to consider the removal efficiencies of wastewater treatment which is more representative. Future research should focus on

better alternatives associated with treatment disposal efficiency, such as environmental offsets to obtain an assessment of net environmental performance.

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CAPÍTULO VII

DISCUSIÓN



1. DESEMPEÑO Y ELIMINACIÓN DE FÓSFORO EN HUMEDALES CONSTRUIDOS PLANTADOS CON MONOCULTIVO Y POLICULTIVOS PARA EL TRATAMIENTO DE AGUAS RESIDUALES

Considerando el primer objetivo específico, para poder identificar los mecanismos de eliminación de fósforo en un HSSF a escala piloto. Primero, se caracterizaron las aguas residuales a la entrada y de salidas de los HSSF por estación cálida (Primavera/Verano) y fría (Otoño/Invierno) para los monocultivos de plantas *Phragmites australis* (Phr) y *Schoenoplectus californicus* (Sch); los cuáles se presentan en el capítulo IV de la presente tesis. Mientras que en el capítulo V se presentaron los resultados del monocultivo con planta ornamental *Cyperus papyrus* (Cyp) y el policultivo de planta ornamentales *Cyperus papyrus/Zantedeschia aethiopica* (Cyp/Zant).

El afluente fue el mismo para todos los tratamientos con una concentración de fósforo $14,1 \pm 2,1$ mg/L en un rango de 11 a 20 mg/L, sin variaciones entre estaciones. Las cuáles concuerdan con concentraciones típicas de agua residuales descritas en la Tabla 3.1 del Capítulo III que van desde 5-30 mg/L (Carrillo et al., 2020). En cuanto a las concentraciones de fósforo medidos en los efluentes de los HSSF estos fueron decreciendo de 12,9, 11,5, 10,3 y 9,7 mg/L para las plantas Phr, Sch, seguido por las plantas ornamentales (Cyp) y para el policultivo (Cyp/Zant). Siendo Cyp/Zant el de mayor eliminación de fósforo de los efluentes. Los valores obtenidos en esta tesis fueron superiores a las concentraciones de fósforo en efluentes encontrados en literatura sobre HSSF con un rango de 1-9 mg/L. Cabe destacar que estas concentraciones se encuentran en el rango de la norma chilena de emisión de descargas residuos líquidos a aguas marinas y Continentales Superficiales (D.S. MINSEGPRES N°90/2000), la cual establece la descarga de fósforo total permitida varía de 2 a 15 mg/L, dependiendo de la capacidad de dilución del cuerpo de agua receptor. Por lo tanto, el impacto ambiental si cumple la norma puede ser variable según el área de descarga.

En cuanto el desempeño de cada tratamiento de HSSF, la Tabla 7.1 muestra una comparación entre el desempeño de HSSF de este estudio y lo reportado en literatura, que varían por tipo de plantas, sistemas de cultivo y distintas estaciones. En comparación nuestros resultados varían entre 9-33%, los cuáles son bajos a los observados por literatura que varían entre 13-99%. Sin embargo, siguen la misma tendencia, de que los HSSF con policultivos (30-33%) y plantas

ornamentales (22-27%) tienen un mejor rendimiento frente a los HSSF monocultivos plantados con plantas comunes (9-18%). En general las eficiencias de remoción de fósforo varían entre un 40-60% dependiendo del tipo de humedal construido o carga de entrada (Vymazal, 2007). Otros autores informan eliminaciones de fósforo entre 20-30% en humedales construidos sin algún diseño para la remoción de fósforo (Brix y Arias, 2005; Vohla et al., 2005). En cuanto a los sistemas de cultivos, los sistemas policultivos han demostrado un gran potencial destacando una eliminación de fósforo entre un rango de 56-81% (Abou-Elela et al., 2013; Rai et al., 2015; Marín-Muñiz et al., 2020). Mientras que los monocultivos en un rango de 13-78% (Akratos y Tsihrintzis, 2007; Konnerup et al., 2009; Zurita et al., 2009; Leto et al., 2013).

El impacto ambiental de las plantas en humedales construidos respecto a la eliminación de fósforo ha alcanzado hasta un 24-80%. Sin embargo, también han reportado eliminaciones en un rango de 10-34% (Gorgoglione y Torretta, 2018). Esto demuestra resultados similares en nuestro estudio, donde las plantas fueron un factor fundamental en el rendimiento de HSSF. Las plantas ornamentales como Cyp y Zant mostrando entre un 22-33% de desempeño en la eliminación de fósforo. Estas eficiencias concuerdan con lo encontrado en literatura donde las plantas ornamentales tienen eficiencias de eliminación entre 13-69% (Zurita et al., 2009; Konnerup et al., 2009; Leto et al., 2013; Marín-Muñiz et al., 2020). En general las plantas ornamentales se destacan por desarrollar flores lo cual, al mismo tiempo de eliminar contaminantes, tiende a mejorar el paisaje del sistema de tratamiento, donde pueden brindar beneficios económicos a la comunidad a través de la producción de flores (Zurita et al., 2009). Machado et al. (2017) evaluó el uso de humedales construidos en Brasil, incluidos los sistemas con plantas ornamentales, y concluyó que las climas tropicales y subtropicales, y las horas de luz solar extensas son características importantes para fomentar el crecimiento y la proliferación de este tipo de plantas. Esta puede ser una de las razones de porque las plantas ornamentales no alcanzaron valores de 68-79% de eliminación de fósforo (Marín-Muñiz et al. 2020). Pues, Marín-Muñiz et al. (2020) evaluó un humedal construido en Veracruz, México con un clima tropical y temperaturas de 18-32°C. En cuanto al rendimiento observado por Phr y Sch estas no superando el 20% de eficiencia de eliminación de fósforo, lo cual llega a ser un valor común cuando las condiciones de operación del HSSF no son las óptimas.

Tabla 7.1. Concentraciones de fósforo en efluentes y eficiencias de eliminación de fósforo en HSSF para el tratamiento de aguas residuales comparados con los resultados del estudio.

Escala	Especie planta	Sistema	T °C	Influente (mg/L)	Efluente (mg/L)	Eficiencia (%)	Referencias	
Piloto	<i>P. australis</i>	Monocultivo	15-22	14,1±2,1	12,9±2,9	9±18	Este estudio (Capítulo IV)	
			10-15		11,9±3,2	15±12		
	15-22		12,8±3,3		10±19			
	10-15		11,5±3,4		18±17			
	<i>C. papyrus</i>		Policultivo	15-22	14±2,1	10,6±4,0	22±25	Este estudio (Capítulo V)
				10-15		10,3±2,9	27±18	
	15-22			9,3±3,5		30±29		
	10-15			9,7±4,2		33±19		
Industrial	<i>T. latifolia</i>	Policultivo	35	7,4±0,05 ^b	1,7±0,03	75±2,8	Rai et al., 2015	
	<i>P. australis</i>		21	6,8±0,04 ^b	2,9±0,09	56±2,1		
	<i>C. esculenta</i>							
Piloto	<i>C. papyrus</i>	Policultivo	15-37	3,2±1,1	1,3±0,5	63±14	Abou-Elela et al., 2013	
	<i>C. indica</i>							
	<i>P. australis</i>							
Piloto	<i>S. reginae</i>	Policultivo	10-29	8,3±1,2	4,9±0,4	35±3	Zurita et al., 2009	
	<i>A. andreaum</i>							
	<i>A. africanus</i>							
Piloto	<i>Z. aethiopica</i>	Monocultivo			4,2±0,4	44±3		
	<i>P. australis</i>	Monocultivo	>15	9,1±1,0	6,5±1,5	29±26	Akratos y Tsihrintzis, 2007	
	<i>T. latifolia</i>				2,72,1±	70±34		
	<i>P. australis</i>				7,3±2,8	20±28		
	<i>T. latifolia</i>				5,2±1,5	42±37		
Laboratorio	<i>C. elata</i>	Monocultivo	14-28	9,1±2,5	0,3±2,0	98±3,1	Borin y Salvato, 2012	

	<i>J. effusus</i>				0,6±2,1	97±5,3	
	<i>P. arundinacea</i>				1,9±3,8	94±9,0	
	<i>P. australis</i>				0,7±3,4	97±5,0	
	<i>T. latifolia</i>				0,5±2,4	98±4,8	
Piloto	<i>C. indica</i>	Monocultivo	28	9,8±1,9	6,4±2,1	35±9	Konnerup et al., 2009
	<i>H. psittacorum</i>				8,5±0,8	13±9	
Piloto	<i>S. viminalis</i>	Monocultivo	19 -2	24,8±8,8	6,2±3,8 5,5±2,8	75±18 77±10	Józwiakowski et al., 2020
Piloto	<i>T. latifolia</i>	Monocultivo	20-22	8,0±0,2	4,2±0,2	48±16	Leto et al., 2013
	<i>C. alternifolius</i>				5,6±0,3	32±20	
Laboratorio	<i>A. purpurata</i>	Monocultivo	18-32	4,9±1,9	1,1±0,5	78±10	Marín-Muñiz et al., 2020
	<i>C. hybrid</i>				1,5±0,4	69±11	
	<i>H. coronarium</i>				1,6±0,4	68±11	
	<i>C. hibrido</i>	Policultivo	1,0±0,3	81±17			
	<i>A. purpurata</i>						
	<i>H. coronarium</i>						

b: Fosfato (P-PO₄); T: Temperatura

En particular, los parámetros de diseño y manejo de factores como parámetros operacionales e *insitu*, fueron fundamentales para lograr una mejor optimización del HSSF y así obtener un mejor rendimiento ambiental. El análisis de componentes principales (PCA, siglas en inglés) demostró que factores como la carga de entrada de fósforo (PLR, siglas en inglés), tasa de carga hidráulica (HLR, siglas en inglés) y el oxígeno disuelto (DO, siglas en inglés) fueron parámetros importantes para el buen desempeño de la eliminación de fósforo. Así también en menor medida el tiempo de retención hidráulico (HRT, siglas en inglés) y temperatura.

En este estudio el PLR varió entre 0,3-0,5 gP/m²d sin diferencias entre especies y estaciones. Estas cargas son similares a las cargas de fósforo aplicada a HSSF que van entre 0,04-0,6 gP/m²d como se describe en la Tabla 1.3 (características de operación, diseño y de los humedales construidos. Capítulo I, sección 4.1). Mientras que el HLR vario entre 20-30 mm/d lo cual también está dentro del rango en literatura con un máximo de 50 mm/d (Konnerup et al., 2009). La carga de fósforo en el influente debe estar regulariza por el HLR. Se ha visto que las alteraciones en las cargas afectan la remoción de fósforo y tienen una correlación significativa (Stefanakis y Tsihrintzis 2012; Oliver et al., 2017). Stefanakis y Tsihrintzis (2012) estudió los efectos de carga en VSSF donde la concentración inicial disminuyó de 10 a 8 mg/L y aumento el HLR de 190 a 440 mm/d. Por lo tanto, una PLR de 2,0 a 3,8 gP/m²d observando una disminución en la eficiencia de 33% a 26%.

La eficiencia de eliminación de fósforo tiene una correlación negativa con el HLR. Se ha demostrado una eficiencia de remoción de fósforo de 13-37% a HLR como 110-400 mm/d (Konnerup et al., 2009; Stefanakis y Tsihrintzis, 2012; Abou-Elela et al., 2017). Konnerup et al. (2009) evaluó el efecto del aumento del HLR que varió de 50 a 400 mm/d en HSSF con plantas ornamentales, donde la eficiencia de eliminación de fósforo disminuyó de 13-35% a 10-6%. Asimismo, Abou-Elela et al. (2017) observaron en un HSSF con aguas residuales que el mejor rendimiento fue lineal al disminuir el HLR (180 a 70 mm/d) y al aumentar el HRT. Un mayor HLR promueve un paso más rápido de las aguas residuales a través de los medios, lo que reduce el tiempo de contacto óptimo. Es sabido, (al igual que en estudio) que hay una correlación positiva entre el HRT y la eficiencia de eliminación (Gorgoglione yTorretta, 2018). Para eficiencias de eliminación de fósforo se recomienda un HRT prolongado entre 6-10 días (Akratos y Tsihrintzis,

2007; Wu et al., 2013). Esto se debe a que un HRT de 6-10 días genera el contacto e interacciones de fósforo con el medio y las raíces. Lo que a su vez promueve la adsorción, transformación (mineralización e inmovilización) y asimilación. Sin embargo, a veces el tiempo de contacto es suficiente debido a la saturación del medio soporte y asimilación de plantas y bacterias.

Finalmente, el DO es uno de los factores principales en la eliminación de fósforo. Los resultados de esta tesis mostraron valores entre 0-0,7 mgO₂/L sin variaciones entre especies, pero con diferencias significativas entre estaciones siendo en promedio 0,2 mgO₂/L la estación cálida y 0,4 en la estación fría. El DO y la temperatura (que son inversamente proporcionales) pueden influir en la eficiencia de los humedales construidos, ya que afectan varios procesos biogeoquímicos del fósforo. Oliver et al. (2017) midió una concentración de oxígeno disuelto de 15,43 mgO₂/L en HSSF en invierno, lo que resultó en una eliminación de fósforo de 88-92% durante esa temporada. Asimismo, Ilyas y Masih (2018), informaron que las estrategias de aireación podrían ser responsables de la eliminación de fósforo al mejorar los niveles de oxígeno para beneficiar la precipitación y la absorción de fósforo. Además, las concentraciones de oxígeno determinan las condiciones aeróbicas o anaeróbicas del humedal, por ende, a los microorganismos asociados y a su vez a la rizosfera de las plantas (Ilyas y Masih, 2018; López et al., 2019). Esto justifica que las plantas ornamentales y policultivos hayan logrado mejores eficiencias debido a que desarrollan más raíces lo que crea mejores condiciones hidráulicas y la oxigenación del sistema. En cuanto a un sistema radicular profundo entre 40-60 cm, más oxígeno se suele proporcionar a los sustratos más profundos.

En cuanto a la temperatura no hubo diferencias significativas. Sin embargo, fueron más óptimas en las estaciones fría para todos los tratamientos. La literatura mostró resultados similares donde la estación fría y cálida mostraron eficiencias de eliminación de fósforo de 19-77% y 13-81% respectivamente (ver Tabla 7.1). O'Neill et al. (2011) informaron que a temperaturas extremas en los HSSF; es decir un verano caluroso con niveles elevados de evapotranspiración o un invierno con heladas daría como resultado una liberación de fósforo en la columna de agua (efluentes). Aun así, se ha reportado que, debido a los altos contenidos de lignina y su adaptabilidad, plantas como *Phragmites*, *Typha* y *Scirpus* spp. esta última de la familia Sch, son más eficientes en estaciones

frías (Kataki et al., 2021). Además, en general los policultivos son menos susceptibles a los cambios climáticos.

Considerando lo anteriormente descrito, se realizó el balance de masa de fósforo para los cuatro sistemas evaluados con la finalidad de determinar los mecanismos de eliminación de fósforo. La Figura 7.1 muestra el balance de masa de fósforo para a) estación cálida y b) estación fría. En este estudio se consideraron los mecanismos de eliminación de fósforo por la asimilación por plantas, retención de fósforo en el HSSF el cual considera la adsorción/precipitación por el medio de soporte y la asimilación por microorganismos. Finalmente, el fósforo que no queda retenido es eliminado en el efluente.

La carga de entrada vario entre 60-63 gP/m² entre estaciones. En cuanto a los valores expresados anualmente, la carga media de fósforo fue de 140±30 g/m²año con un mínimo de 90 g/m²año y un máximo de 216 g/m²año. De manera similar, Vymazal (2007) informó que las cargas de fósforo de entrada varían según el tipo de humedal de 120-200 g/m²año, siendo 141 g/m²año para los HSSF. Estas cargas son altas por lo que la cantidad de fósforo eliminada a través de las plantas puede < 5%, pero podría ser importante en los humedales que tienen una carga de entrada menor de 10–20 g/m²año (Vymazal, 2011). Por lo tanto, las diferentes tasas de carga de fósforo son responsables de la diferencia en la asimilación por parte de las plantas.

El fósforo en el efluente mostró una descarga de 36,6-49,7 gP/m². La retención de fósforo en los HSSF de este estudio varió entre 8,7 y 17,4 gP/m² los cuáles fueron superiores a los encontrados en la literatura. Estudios de Shan et al. (2011) desarrollados en un HSSF a escala piloto sembrado con *P. australis*, mostraron una retención de fósforo de 8,4 gP/m². Aún más, estudios de Maucieri et al. (2020) en un HSSF de laboratorio evaluaron 5 tipos de especies de planta obteniendo una retención de -4-4 a 7,8 gP/m². Siendo la retención del HSSF plantado con *P. australis* un 64% con una masa de 5,3 gP/m². Debido a que Maucieri et al. (2020) utilizó como medio de soporte grava, se estima que entre un 20-60% del fósforo retenido en el humedal quedo en la biomasa microbiana.

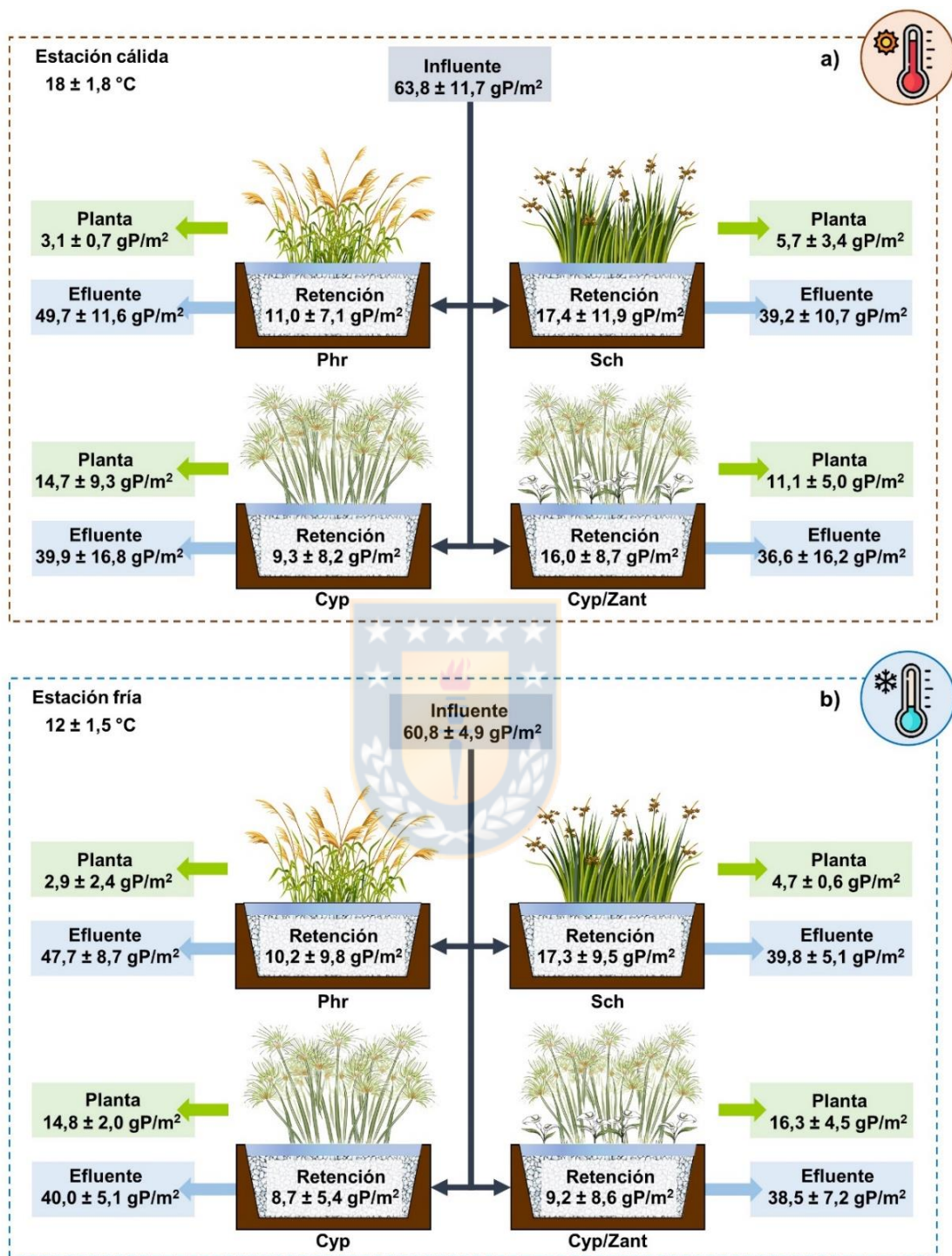


Figura 7.1. Balance de masa de fósforo para los tratamientos de HSSF en la a) estación cálida y b) estación fría. Phr: *P. australis*; Sch: *S. californicus*; Cyp: *C. papyrus*; Cyp/Zant: *C. papyrus*; *Z. aethiopica*.

La retención de fósforo en los HSSF es compleja y se basa en ciclos biogeoquímicos, que involucran los tres tipos de mecanismos: biológico a través de la asimilación por microorganismos, y fisicoquímico a través de la precipitación y adsorción de fósforo por el medio de soporte (Vymazal y Kröpfelová, 2008). El Capítulo III, explica en mayor detalle la eliminación de fósforo por mecanismos físico, químico y biológico, donde se pudo deducir que el mecanismo químico es el más relevante en la eliminación de fósforo. En general el potencial de eliminación de fósforo está asociado a las propiedades fisicoquímicas e hidrológicas del medio de soporte. La adsorción/precipitación de fósforo está dada por distintos elementos como Fe, Al, Ca y Mg formando parte de diversos componentes (DeLaune y Reddy, 2008). El fósforo, es eliminado hasta un 90% por adsorción (Brix y Arias, 2005). En esta tesis el medio de soporte utilizado fue la grava que presenta una capacidad de adsorción de fósforo entre 0,02-0,05 gP/kg (Vera et al., 2014), la cual no fue objeto de estudio en esta tesis. La mayoría de los estudios de humedales construidos utilizan como medio soporte la grava (Konnerup et al., 2009; Borin y Salvato, 2012; Leto et al., 2013; Abou-Elala et al., 2013; Rai et al., 2015; Akratos y Tsihrintzis, 2007). Sin embargo, la capacidad de eliminación de fósforo por este medio de soporte es la más desfavorable.

En el Capítulo III, Sección 3.1.2 se realizó una revisión de los distintos materiales de soporte evaluados para la eliminación de fósforo. Donde se destacan otros medios de soporte como la arena, zeolita, madera orgánica, roca volcánica, caliza que han demostrado eficiencia de eliminación de un 15 a un 60%. La zeolita es un recurso abundante, económico y de gran área superficial y porosidad, se ha presentado como una alternativa óptima, con una capacidad de retención de 0,30 a 0,93 mgP/g. Además, la zeolita adsorbe >50% de fósforo que puede ser utilizado posteriormente como fertilizante en zonas rurales (Andrés et al., 2018). Una de las limitaciones puede ser la acumulación de metales pesados o productos farmacéuticos que posteriormente pueden ser bioacumulados en los cultivos (De Boer et al., 2018).

Otro mecanismo incluido en la retención de fósforo es la asimilación de fósforo a través de los microorganismos en la biomasa bacteriana que se encuentra adherida al medio de soporte como a las raíces de las plantas (Vymazal, 2007). La biomasa microbiana cumple un rol fundamental en la transformación; mineralización e inmovilización del fósforo orgánico a fósforo soluble inorgánico el cual es asimilado por los microorganismos y plantas. De hecho, en este estudio la relación PT/PO_4^-

³ del influente fue de 77% mientras que en los efluentes fueron de 80% para Phr y Sch y 84% para Cyp y 89% en Cyp/Zant. Por lo tanto, queda demuestra que dentro del humedal hubo mayor transformación de fósforo orgánico a inorgánico sobre todo en el sistema de policultivo. Cabe destacar que el fósforo inorgánico, es biodisponible el cual es más fácil de asimilar por plantas o microorganismos. En el Capítulo III, Sección 3.3.1 se describió que la asimilación depende de los microorganismos, específicamente de un grupo conocido como organismos acumuladores de polifosfato (PAO) capaces de asimilar el fósforo intracelular como polifosfatos (Poly-P). En fase anaeróbica los PAO toman los ácidos grasos volátiles almacenándolos. En cambio, en la fase aeróbica se metabolizan para proporcionar la energía necesaria para que los microorganismos PAO acumulen el fósforo. Se ha demostrado que el fósforo puede formar entre 15 al 20% del peso seco de la célula. Sin embargo, en procesos sin la influencia de eliminación de fósforo y con una limitada abundancia de microorganismos como en el tratamiento de aguas residuales el contenido puede ser de 1 a 2% (Yuan et al., 2012).

Las plantas jugaron un papel fundamental en la eliminación de fósforo si bien se ha demostrado que la su asimilación es finita, puede ser importante según las especies, el sistema de cultivo y las condiciones óptimas a largo plazo. La cantidad de fósforo eliminada en el HSSF aumentó del 10% al 42% a medida que la capacidad de absorción del sustrato disminuía en la operación a largo plazo (Kadlec y Wallace, 2009). Asimismo, Zhang et al. (2008) observó en un humedal construido con medio de soporte como arena la eliminación de fósforo disminuyo a 40% y la asimilación de la planta aumentó de 4% a 50% durante el curso de 10 semanas. Cabe destacar que la asimilación por plantas y la adsorción por medio de soporte son procesos que tienen una capacidad finita para la eliminación sostenible de fósforo a largo plazo en humedales construidos.

Se calculo la contribución de los mecanismos de eliminación de fósforo en el HSSF. La Figura 7.2. muestra la proporción de fósforo total eliminada por el efluente, la retención y las plantas. Los resultados del presente estudio mostraron que del fósforo total que ingresa en el influente (100%), entre un 57-79% es eliminado en el efluente o descarga de aguas tratadas, entre un 13-31% queda retenido en el HSSF y finalmente entre un 4-26% es asimilado por los distintos tipos de plantas. Estos resultados concuerdan con la literatura donde la retención en el HSSF que generalmente es el medio de soporte, que es la ruta principal de eliminación de fósforo. En este estudio, debido al

tipo de medio de soporte utilizado como la grava no se determinó el fósforo acumulado. Sin embargo, mediante el balance se obtuvo la retención que es la precipitación/adsorción por medio de soporte o asimilación por microorganismos. En general, dependiendo del medio de soporte la contribución a la retención de fósforo es 28-51% (Wu et al., 2013; Yang et al., 2019; Maucieri et al., 2020). Se estima que la eliminación de fósforo por microorganismos va desde 0,2 a 6,8% del fósforo que ingresa en el influente, siendo la menor contribución en la eliminación de fósforo (Wu et al., 2013; Yang et al., 2019).

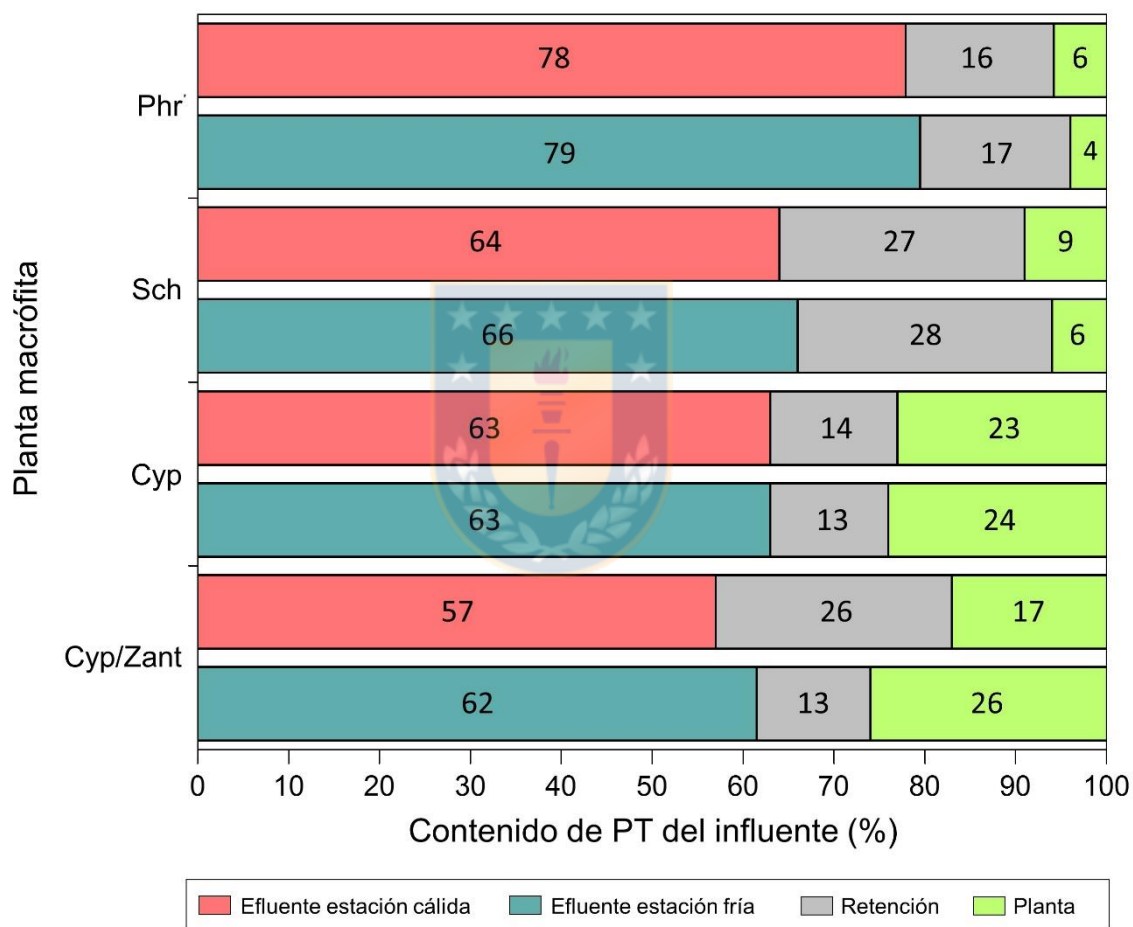


Figura 7.2. Proporción de fósforo total del influente eliminada en el efluente, la retención y la asimilación por las plantas para los tratamientos de HSSF en la estación cálida y estación fría. Phr: *P. australis*; Sch: *S. californicus*; Cyp: *C. papyrus*; Cyp/Zant: *C. papyrus*; *Z. aethiopica*.

Las plantas ornamentales en el policultivo Cyp/Zant alcanzaron una contribución de asimilación de fósforo del 26%. Estos resultados fueron inferiores en comparación con Zheng et al. (2020) en un policultivo de HSSF a escala piloto donde alcanzaron una tasa de absorción de fósforo a largo plazo por las plantas del 41,9%. Asimismo, Zhang et al. (2007) también lograron una absorción de la planta del 49% del fósforo de entrada en un policultivo con una concentración de entrada de 10 mg/L. Wu et al. (2013) evaluaron los mecanismos de eliminación de fósforo en un humedal construido a escala laboratorio plantado con *I. pseudacorus* (Ornamental) y una carga de entrada de fósforo 9,4 g/m²año (1,6 mg/L), obteniendo una contribución hasta el 22% por asimilación de planta. Por lo tanto, las diferentes tasas de carga de fósforo son responsables de la diferencia en la asimilación por parte de las plantas en los diferentes estudios. En cuanto a la contribución de las plantas en la retención total se estima que es más del 20% y en el caso de la especie Cyp alcanzó un 70% de la retención total. Kyambadde et al. (2004) informaron que la absorción de fósforo por parte de la planta *C. papyrus*, fue del 88,8%.

En cuanto a las plantas comunes con Phr y Sch se obtuvo una contribución del 4-10% en la eliminación de fósforo. Sin embargo, estos pueden ser muy variados con rangos que van desde el 1% hasta 39% (Vohla et al., 2005; Zhang et al., 2007; Shan et al., 2011; Vymazal, 2011; Wu et al., 2013; Yang et al., 2019; Dell'Osbel et al., 2020). Wu et al. (2013) compararon 4 plantas *T. orientalis*, *P. australis*, *S. validus* y *I. pseudacorus* donde la eliminación de fósforo por las plantas contribuyó en un 10%, 6%, 18% y 22% respectivamente. Yang et al., (2019) indicaron que humedales de laboratorio plantados con *P. australis* contribuyeron entre 8-9% a la eliminación de fósforo. Por lo tanto, nuestros resultados sugieren que la presencia de plantas no es suficiente para maximizar la eficiencia de eliminación de fósforo de los humedales construidos.

En cuanto a la estacionalidad se observa que la contribución por parte de las plantas fue mejor durante la estación cálida entre un 2-9%. Se debe considerar que la eliminación de fósforo por parte de las plantas es mejor en la estación cálida debido a su etapa de desarrollo y crecimiento. Sin embargo, se excluyó el policultivo HSSF-Cyp/Zant que alcanzó valores de 13% para la estación cálida y 26% para la estación fría en la asimilación de fósforo. Se justifica en que el policultivo sembrado con la especie *Z. aethiopica* presenta latencia estival y su floración es desde finales de invierno hasta la primavera (Morales et al., 2013). Zhou et al. (2017) destacaron que los

monocultivos tienden a disminuir la asimilación de nutrientes a temperatura de 8,9 °C. Sin embargo, en los sistemas de policultivo no se observaron cambios a esa misma temperatura. Por lo tanto, los sistemas de policultivo son más resistentes a la variación estacional que un sistema de monocultivo (Licata et al., 2021).

2. ASIMILACIÓN DE FÓSFORO POR PLANTAS MACRÓFITAS EN HUMEDALES CONSTRUIDOS PLANTADOS CON MONOCULTIVO Y POLICULTIVOS PARA EL TRATAMIENTO DE AGUAS RESIDUALES

El segundo objetivo específico fue evaluar la asimilación de fósforo por plantas en sistemas de monocultivo y policultivo en HSSF. En el capítulo V de la presente tesis se presentó la producción de biomasa, cobertura, densidad, contenido de fósforo en tejido y asimilación de plantas para Phr, Sch, Cyp y Cyp/Zant en HSSF.

El desarrollo de las plantas en HSSF no presentó diferencias significativas entre las estaciones cálida y fría. Mientras que la especie Sch presentó el desarrollo óptimo mostrando diferencias entre las otras especies de plantas. El sistema de monocultivo de Sch tuvo una buena adaptación, lo cual se refleja en una abundancia de 1192-1298 individuos/m², cobertura de 85-93% y biomasa de 4,5-5,4 kg PS/m². Una de las razones de la elección de la especie Sch fue principalmente porque es una de las especies de macrófitas más abundante en la región, es decir especie nativa. La especie Sch, se distribuye a lo largo de las costas del Atlántico y el Pacífico de las Américas, desde California hasta Chile (Macía y Balslev, 2000). Por otro lado, la especie Cyp en monocultivo mostró un menor desarrollo con una abundancia de 461-742 individuos/m², cobertura de 60-68% y una biomasa de 1,6-2,1 kg PS/m². Estos resultados son inferiores a los informados por Abou-Elela et al. (2013) donde Cyp desarrollaron una biomasa de 5,6 kgPS/m² en un HSSF piloto en Egipto a una temperatura entre 15 y 37°C el cual es su origen. Esto puede explicar la mala adaptación de Cyp en el HSSF, ya que, Perbangkhem y Polprasert (2010) con abundante luz solar y un área de clima tropical con bastante humedad, el Cyp generó una biomasa de alrededor de 3,1 kgPS/m² durante el período de dos meses.

El policultivo Cyp/Zant presentó una densidad de 435-620 individuos/m² y una biomasa de fósforo acumulado de 1,9-3,1 kgPS/m². En general los policultivos se destacan por ser inestables debido a la competencia y/o interacciones entre especies de plantas a lo largo del tiempo. Liang et al.

(2011) al comparar un sistema de monocultivo con policultivo observaron que el primer año el policultivo tenía una densidad de 123 individuos/m², luego el segundo año el desempeño de ambos cultivos era similar con 86 y 83 individuos/m² respectivamente. Sin embargo, al finalizar los 4 años de operación el monocultivo obtuvo una densidad de 74 individuos/m². Esto sucede ya que los primeros años son de adaptación y hay más espacio para propagarse. Zheng et al. (2020) en un HSSF de policultivo con *P. australis* y *T. orientalis* obtuvieron una densidad de plantas durante el primer año que aumentó alrededor de 13,2 veces y se estabilizó en alrededor de 210 individuos/m² del cuarto año en adelante. En este estudio de tesis se mostró que el policultivo Cyp/Zant tuvo un aumento de 2,3 veces al año. Sin embargo, una disminución al tercer año de 1,5 veces. La interrupción de la densidad de plantas se debe a la tasa de propagación de plantas. Cuando ya no hay espacio disponible, se genera una especie dominante, disminuyendo o extinguiendo a las otras especies. En este caso la dominancia fue de Cyp que tiene una tasa de propagación de 5,4 m/año. Mientras Zant tiene una tasa lenta (0,05-0,1 m/año), por lo que a largo plazo tiende a ser un monocultivo (Morales et al., 2013).

En cuanto a la especie Phr es una de las especies más utilizadas en humedales construidos, presenta una distribución cosmopolita y una tasa de propagación de 10 m/año (Vymazal, 2011). En este estudio Phr demostró rangos de biomasa de 1,5-2,9 kgPS/m², con una buena adaptación en los primeros años de estudio alcanzando una biomasa de 4,2 kgPS/m². Zheng et al. (2020) demostraron que la biomasa de Phr aumentó anualmente en 116,5%, 36,6%, 9,4% y 7,8% por lo que el primer año tuvo una gran adaptación la que luego fue disminuyendo. Estos resultados son conocidos ya que varios estudios datan sobre este tipo de especies donde la biomasa está dentro del rango por literatura de 1,0-3,2 kgPS/m² (Liu et al., 2012, Abou-Elala et al., 2013; Maucieri et al., 2020; Zheng et al., 2020).

La Figura 7.3 muestra la asimilación total de fósforo separadas en la raíz, tallo y flor para las especies macrófitas estudiadas en esta tesis. La absorción de fósforo por las plantas contribuyó al tratamiento con HSSF en función de la especie y el sistema de cultivo. Se pudo observar que los valores de asimilación de Phr fueron de 3,0 gP/m² y para Sch de 5,2 gP/m². Mientras que la asimilación de fósforo promedio entre el monocultivo Cyp y el policultivo Cyp/Zant fue similar con 30 gP/m² esto se puede justificar pues el Cyp creció más y Zant fue excluido en los últimos años.

Estos resultados son cercanos a los observados por Vymazal, (2007) en plantas ornamentales estaban en un rango de 1,4 a 37,5 gP/m². Sin embargo, fueron inferiores a los obtenidos por Abou-Elela et al. (2017), quienes informaron una absorción de fósforo de 70,2 gP/m² por Cyp en un HSSF a escala real (área de superficie 185,5 m²). En comparación con las especies típicamente utilizadas en HSSF como *P. australis*, *T. orientalis*, *P. arundinacea*, *S. validus* entre otras, la asimilación de fósforo en el presente estudio fue menor entre un rango de 1,0-19 gP/m². Por el lado del policultivo Cyp/Zant nuestros resultados fueron superiores a Zhang et al. (2007) y Zheng et al. (2020) quienes en HSSF con sistemas de policultivo obtuvieron una asimilación de fósforo de 7,6 y 15 gP/m² respectivamente. No obstante, ellos utilizaron plantas típicas como *C. indica* y *S. validus*; y *P. australis* and *T. orientalis*.

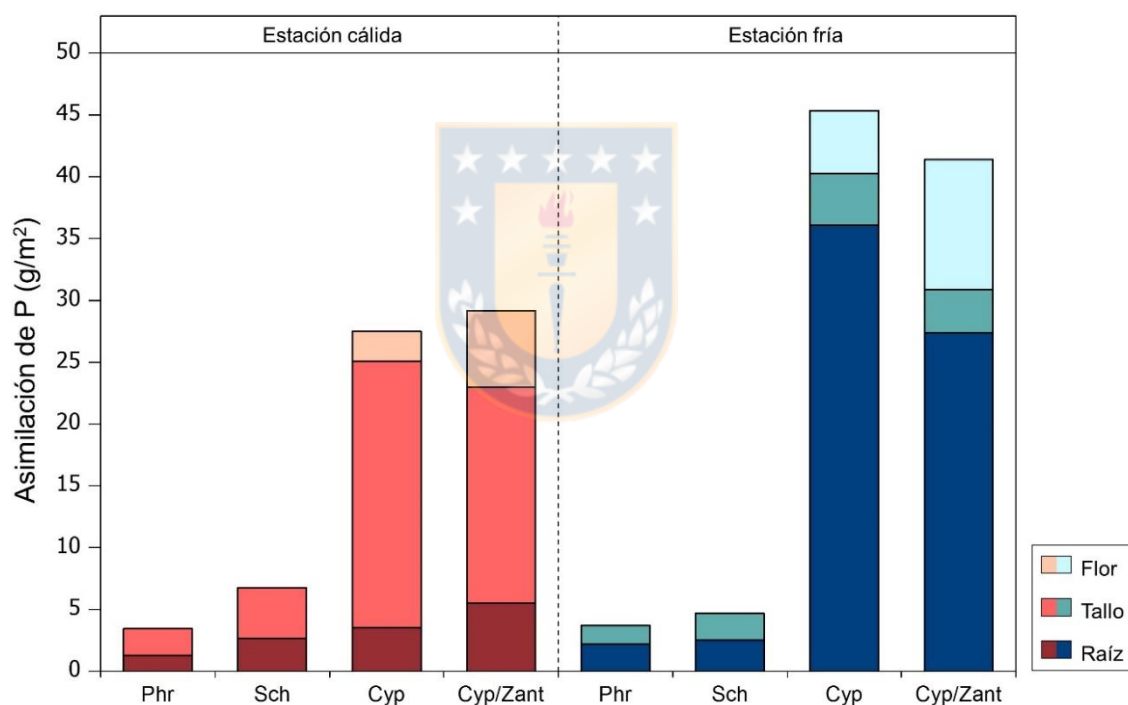


Figura 7.3. Asimilación de fósforo total por tipo de plantas en los tratamientos de HSSF por sistemas de cultivo en la estación cálida y estación fría. Phr: *P. australis*; Sch: *S. californicus* Cyp: *C. papyrus* Cyp/Zant: *C. papyrus*; *Z. aethiopica*.

Como se vio en el Capítulo III, Sección 3.3.3, la asimilación de fósforo y otros nutrientes principalmente por las plantas es a través de la epidermis y los haces vasculares de las raíces, y luego son transportados hasta el tallo, las hojas y flores. Generalmente, en la estación cálida se genera la fase de crecimiento de las plantas, donde el contenido de fósforo se moviliza desde las

raíces hacia los tallos, lo cual se observa en la Figura 7.3. La asimilación de fósforo en los tallos fue 1,5 a 6 veces mayor que las raíces en la estación cálida, donde Cyp alcanzó hasta 6 veces más. Se ha informado que la acumulación de fósforo sobre suelo (es decir en los tallos, hojas o flor dependiendo de la especie) está dentro del rango de 0,2 a 11 gP/m². Lo cual concuerda con este estudio donde los resultados mostraron que vario de 1,27-5,5 gP/m². Liu et al. (2012) compararon la acumulación de fósforo de tres especies *P. communis*; *S. stoloniferum* y *T. orientalis* en HSSF donde observaron valores entre 0,3-3,4 gP/m² en tallos y 5,1-23,1 gP/m² en raíces. Por el contrario, se ha reportado que la acumulación de fósforo en la raíz en la estación de invierno ocurre la fase de latencia, donde los nutrientes se translocan desde los tallos a las raíces y los rizomas (Liu et al., 2012; Zheng et al., 2020). La razón entre el fósforo en raíces y tallos fue de 1,5 a 7,5, lo cual concuerda con que más del 50% de fósforo se almacena bajo tierra (Vymazal, 2007; Zhang et al., 2007; Liu et al., 2012; Maucieri et al., 2020; Zheng et al., 2020).

En los policultivos se generan más raíces cuando hay una mezcla de especies de plantas en un humedal construido debido al desarrollo de raíces y forma vertical (15-30 cm) en la competencia generada por las especies de plantas (Liang et al., 2011). Rodríguez y Brisson (2016) plantearon la hipótesis de que “*la combinación de diferentes especies de plantas en un humedal construido podría mejorar la eficiencia del tratamiento mediante complementariedades funcionales*”. Asimismo, Zheng et al. (2020) indicaron que la competencia interespecífica y la contribución de las plantas intensifica la asimilación de fósforo, es debido a que albergan diversas comunidades bacterianas que podrían mejorar el rendimiento de los humedales a través de la degradación de la materia orgánica, el reciclaje de nutrientes y el apoyo al crecimiento de las plantas. Otra manera de mejorar la eficiencia de eliminación de fósforo es a través de plantas con una gran biomasa de raíces. La especie Cyp puede clasificarse como una planta de raíces fibrosas favoreciendo las tasas de asimilación de fósforo (Lai et al. 2011). En conclusión, raíces más grandes y red entre ellas son favorables para la asimilación de nutrientes, además sirven como hábitat para comunidades que a la vez descomponen el fósforo orgánico haciéndolo disponibles para su eliminación.

La cosecha de las plantas también ha demostrado como ser una buena práctica de humedales construidos contribuyendo a un buen manejo ambiental. Como demostramos anteriormente la

mayor concentración de fósforo se almacena en los tallos en la temporada de crecimiento que es primavera - verano. Por lo tanto, para ser más eficiente, la cosecha debería ser antes de otoño para eliminar el fósforo y evitar así la translocación debido a la senescencia en invierno. Zheng et al. (2018) destacó que la cosecha anual mejoraba hasta 3 veces la eliminación general de nutrientes y además observó un aumento de la densidad y biomasa de las plantas.

3. EVALUACIÓN AMBIENTAL EN HUMEDALES CONSTRUIDOS PLANTADOS CON MONOCULTIVO Y POLICULTIVOS PARA EL TRATAMIENTO DE AGUAS RESIDUALES

Después de comprender el tipo de agua residual, los mecanismos de eliminaciones, el comportamiento de las plantas y los posibles factores que contribuyen a mejorar el rendimiento de los humedales construidos, es necesario estudiar el impacto ambiental de su tratamiento. El tercer objetivo específico de la presente tesis fue evaluar el desempeño ambiental de la eliminación de fósforo por plantas en sistemas de monocultivo y policultivos. En el capítulo VI se presenta la evaluación ambiental mediante la herramienta de ACV para los sistemas de monocultivo de Phr y Sch. Mientras que en la siguiente sección se presenta el análisis del monocultivo Cyp y el policultivo Cyp/Zant. Por lo tanto, se evaluaron 8 escenarios los cuáles se diferencian en términos de plantas y por estación cálida y fría.

Para los escenarios del monocultivo Cyp y el policultivo Cyp/Zant se consideró la misma metodología que se describe en el capítulo VI para el ACV. Es decir, el mismo límite y alcance del sistema (planta piloto Hualqui), unidad funcional, inventario y evaluación del impacto del ciclo de vida. Se identificaron las emisiones de gases GEI en el sistema HSSF para cada tratamiento. En este estudio las emisiones de CH₄ fueron calculadas en base a la actividad metanogénica para Phr, Sch, Cyp y Cyp/Zant. Mientras que las emisiones de CO₂ y N₂O fueron estimadas por datos obtenidos de la literatura sobre sistemas de humedales construidos (capítulo VI, sección 2.4). Los cuales también fueron considerados en la evaluación de impacto ambiental.

La Tabla 7.2 muestra las emisiones de gases GEI en HSSF para el tratamiento de aguas residuales según tipo de cultivo, planta y estación para este estudio y literatura. En este estudio se puede observar que hubo una clara diferencia en las emisiones de CH₄ por tipo de especies y por sistema de cultivo. Las emisiones de CH₄ para los monocultivos fueron de 1110-1631 mg/m²d para Phr,

1457-4358 mg/m²d para Sch, 4900-7078 mg/m²d para Cyp mientras que para el policultivo Cyp/Zant alcanzó hasta los 11718-11930 mg/m²d.

En cuanto a la estacionalidad, en todos los tratamientos las emisiones fueron entre un 9-20% más en la estación cálida que en la estación fría. Asimismo, muestra la literatura (Tabla 7.2) que las emisiones son superiores en la estación cálida comparado con la fría. Sovik et al. (2006) y Picek et al. (2007) demostraron emisiones de CH₄ de 340-1716 mg/m²d y de CO₂ correspondientes a 2845-3800 mg/m²d en humedales construidos HSSF en la estación cálida, mientras que en la estación fría las emisiones de CH₄ alcanzaron los 15-756 mg/m²d y emisiones de CO₂ 895-960 mg/m²d. Además, lo correlacionaron positivamente con la densidad de la vegetación. Esto concuerda con los resultados obtenidos para Sch que mostró una densidad de biomasa (vegetal) de 5,4 kgPS/m² y alcanzó valores de emisión de CH₄ de 4358 mg/m²d en la estación cálida. Maucieri et al. (2017), demostraron que las condiciones ambientales afectaban en gran medida la emisión de los GEI, donde la temperatura se correlacionaba positivamente con las emisiones de GEI y la radiación solar con las emisiones de CO₂ y CH₄. Aun así, Mander et al. (2014) en una revisión no encontró una relación significativa con las emisiones de CH₄ y N₂O y la zona climática. Se ha informado que las emisiones GEI pueden variar por una serie de factores, entre ellos, la condición de oxido-reducción, la carga orgánica aplicada, la especie de planta, la temperatura ambiental, las características espaciales y estacionales, entre otros (Wang et al., 2013; Maucieri et al., 2017; Chen et al., 2020). Los datos de literatura extraídos de la Tabla 7.2 muestran que las emisiones de CO₂, CH₄ y N₂O en HSSF monocultivos van desde 42-3000 mg/m²d, 17-1716 mg/m²d y -3,0 a 150 mg/m²d respectivamente. Mientras que para los policultivos las emisiones de dichos gases varían en un rango de 380-3800 mg/m²d, 11-11000 mg/m²d y 0,5-37 mg/m²d respectivamente.

Se ha observado que el efecto de la riqueza de plantas ha sido debatible con resultados no únicos y además es poco informado (Maucieri et al., 2017). Wang et al. (2013) compararon sistemas de monocultivos de *Z. latifolia* con policultivos (*T. latifolia*, *Z. latifolia* y *P. australis*), donde concluyeron que el policultivo emitió casi el doble de CH₄ (2208 mg/m²d) que el monocultivo (1142 mg/m²d). Además, pudieron notar un 50% más de cantidad de bacterias metanógenas asociadas a la profundidad de la raíz de plantas, lo que contribuye a la generación de CH₄. Esto concuerda con el

estudio de Hernández et al. (2018) quienes investigaron las emisiones de CH₄ en un policultivo con plantas ornamentales como *Z. aethiopica*, *C. papyrus* y planta típica como *T. latifolia* donde las emisiones de CH₄ fueron 11000, 5500 y 4500 mg/m²d respectivamente. Se puede deducir que los policultivos generan más redes entre raíces creando zonas anóxicas, generando CH₄. Esto justifica las emisiones del policultivo Cyp/Zant en nuestro estudio, donde se observó una concentración de DO de 0,1-0,2 mgO₂/L y un potencial redox (-230 mV) lo cual indica una condición aeróbica o anaeróbica.

Por otra parte, con respecto a las emisiones de N₂O no hubo diferencia entre monocultivo y policultivos. Hernández et al. (2018) observaron en la especie *Z. aethiopica* que las emisiones de N₂O oscilaron en -3 y 150 mg/m²d con un pico de emisión en épocas de senescencia, lo cual concuerda con que esta especie desarrolla una flor en esta época. Además, pudieron concluir que las emisiones de N₂O se correlacionaron positivamente con la eliminación de nitrógeno por parte del HSSF. Asimismo, Wang et al. (2008) compararon sistemas HSSF plantados con policultivos con 3 especies distintas *T. latifolia*; *Z. latifolia*; *P. australis* donde revelaron que las emisiones de N₂O alcanzaron entre 20-32 mg/m²d y estaban asociadas a un rendimiento del 80% en la eliminación de nitrógeno. Además, también observaron que hubo entre 10 y 30 veces más actividad de bacterias oxidantes de amoníaco en los humedales construidos durante las estaciones de crecimiento donde los valores medios de flujo de N₂O fueron entre 2 a 6 veces más altos que los del período de senescencia. Por lo tanto, el efecto de diversidad de plantas en policultivos no era factor, sino más bien la disponibilidad de nitrógeno en las aguas residuales y las estaciones de crecimiento (Maucieri et al., 2017).

Tabla 7.2. Emisiones de gases de efecto invernadero (GEI) en HSSF para el tratamiento de aguas residuales.

Cultivo	Estación	T °C	Especie	Emisiones (mg/m ² d)			Referencias	
				CO ₂	CH ₄	N ₂ O		
Monocultivo	Cálida	15-22	<i>P. australis</i>		1408-1578		[1]	
	Fría	10-15			1110-1631			
	Cálida	15-22	<i>S. californicus</i>		2139-4358			
	Fría	10-15			1457-2306			
	Policultivo	Cálida	15-22	<i>C. papyrus</i>		5421-7078		
		Fría	10-15			4900-6100		
Cálida		15-22	<i>C. papyrus</i>		7074-11718			
Fría		10-15	<i>Z. aethiopica</i>		4850-11930			
Monocultivo	Cálida	13-21	<i>P. australis</i>	790-15100	340-1716	2,4-8,5	[2, 3, 4, 5, 6]	
	Fría	0-12		260-11500	15-756	0,8-2,4	[2, 3, 5, 6, 7]	
Policultivo	Cálida	10-15	<i>T. latifolia</i>	2100-3800	160-4500	2,4-17	[1, 8, 9, 10]	
	Fría	0-12	<i>P. australis</i>	380-1200	11-1214	0,5-2,3	[1, 8, 9]	
Policultivo	Cálida	18-27	<i>T. latifolia</i>		1920-5976	2,43-37	[8, 9]	
	Fría	6-17	<i>Z. latifolia</i>		480-2400	0,5-9,8		
			<i>P. australis</i>					
Monocultivo	Cálida	21	<i>T. angustifolia</i>	5880-10200		1,3-2,0	[4]	
	Fría	5		2400-8400		0,6-2,7		
	Fría	4-12		5047-30000	90-520	0,5-1,0		
Monocultivo	Cálida	20-30	<i>C. papyrus</i>	146-795	17-231	14-42	[11]	
	Fría	1-20		42-200	23-64	5,8-12		
Policultivo	Cálida	20-25	<i>T. latifolia</i> <i>C. papyrus</i> <i>Z. aethiopica</i>		4500-11000		[10]	
Monocultivo	Cálida	> 18	<i>Z. aethiopica</i>		407-1575	0,8 -10	[10]	
	Fría	< 18			75-550	-3,0 -150		

T: Temperatura; Cálida: Primavera/Verano; Fría: Otoño/Invierno. [1] Este estudio; [2] Sovik et al., 2006; [3] Picek et al., 2007; [4] Maltais-Landry et al., 2009; [5] Barbera et al., 2014; [6] Maucieri et al., 2014; [7] Mander et al. 2014; [8] Wang et al., 2008a; [9] Wang et al., 2013; [10] Hernández et al., 2018; [11] Chuersuwana et al., 2014

La Figura 7.4 muestra los resultados del ACV para los distintos escenarios. Se vieron 3 resultados distintos según las categorías de impactos. Para las categorías de cambio climático y formación de oxidantes fotoquímicos. Los escenarios Cyp y Cyp/Zant presentaron un impacto ambiental entre 3 a 9 veces mayor para cambio climático y entre 2-3 veces para formación de oxidantes fotoquímicos que Phr y Sch. Wang et al. (2013) reportaron que un humedal construido de policultivo tiene mayor potencial de cambio climático que un monocultivo. Esto se atribuye a las emisiones GEI directas del HSSF, que representa entre un 58% para Phr, 63-76% para Sch y entre un 92-95% para Cyp y Cyp/Zant. Como se describió anteriormente (Tabla 7.2) las emisiones de las plantas ornamentales como Cyp y Zant alcanzaron emisiones de CH₄ entre 4850-11930 mg/m²d. El CH₄ tiene efecto directo en la categoría cambio climático, debido a que el impacto es 25:1 con el CO₂ y es responsable de alrededor del 20% del calentamiento previsto (Mander et al., 2014). De hecho, se ha encontrado que esta categoría es sensible a las emisiones de CH₄ y un aumento del 10% en las emisiones aumenta el impacto ambiental en un 3,5% en cambio climático (Grafi et al., 2017). En cambio, para formación de oxidantes fotoquímicos el factor de caracterización más importante fue el N₂O. La contribución en esta categoría fue representada mayormente por las emisiones directas del HSSF con un 58-70%. Mientras que en los escenarios de Phr y Sch fue mayor la contribución de la infraestructura con un 46-56% y en menor medida por las emisiones de la electricidad con un 27-31%.

Para las categorías de formación de material particulado y acidificación terrestre los escenarios mostraron resultados muy similares con una media de 2,16E-03 kgSO₂eq/m³ y 1,83E-03 kgPM₁₀eq/m³ respectivamente. A excepción del escenario Cyp-cálida que mostró valores de 2,58E-03 kgSO₂eq/m³ y 2,03E-03 kgPM₁₀eq/m³. Este aumento observado se debió a las emisiones de N₂O del HSSF que fueron 24,7 mg/m²d. En cuanto a la contribución la etapa de infraestructura represento un 44-52% para acidificación terrestre contribuyendo por igual a todos los escenarios. Mientras que en la categoría formación de material particulado la contribución de la electricidad fue de 62-68%. Esto se debe principalmente al uso de combustibles fósiles y a las emisiones de gases (es decir, NO_x y SO₂) procedentes de la matriz energética chilena que se compone en un 46% de energías no renovables. El aumento del uso de energías renovables en el mix energético, podría reducir el impacto de la electricidad en categorías como cambio climático, la acidificación terrestre,

formación de oxidantes fotoquímicos y la formación de partículas. Resende et al. (2019) estudió un VSSF con aireación destacando que el uso de la matriz energética de Brasil comprende el 46% de la energía hidroeléctrica, mostrando una contribución del 8% en la categoría de cambio climático.

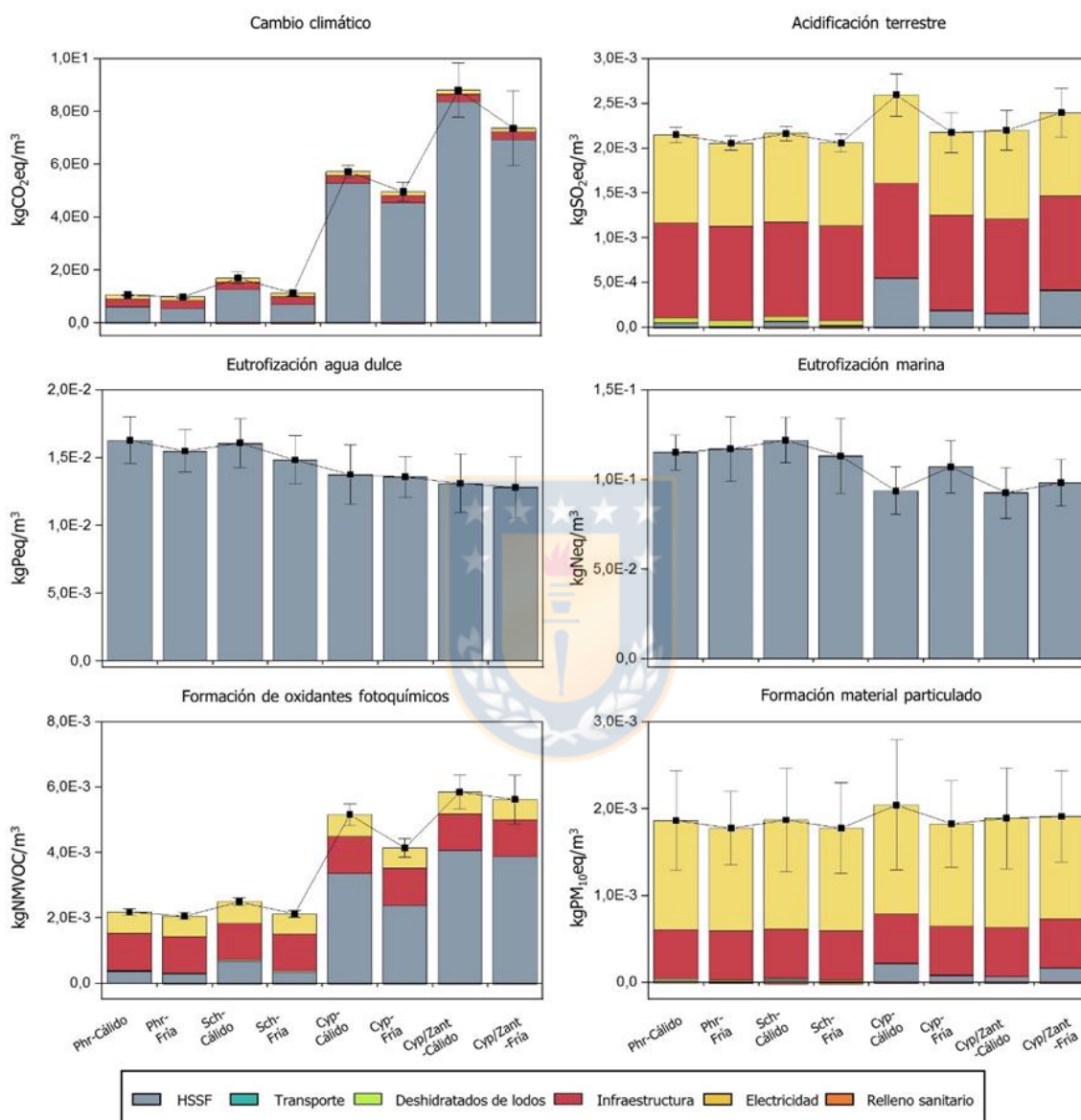


Figura 7.4. Potencial de impacto ambiental para los tratamientos de HSSF en la estación cálida y estación fría, según la categoría seleccionada. Los valores están referidos a la unidad funcional (1 m³ de agua tratada). Mediante simulación de Monte Carlo, se ha obtenido la media (punto negro), y el intervalo de confianza del 95% (barras de error). Phr: *P. australis*; Sch: *S. californicus* Cyp: *C. papyrus* Cyp/Zant: *C. papyrus*; *Z. aethiopica*.

Otra manera, de mitigar la influencia negativa del uso de la energía, es con el acoplamiento de pilas de combustible microbianas (MFC) a humedales construidos con el fin de recolectar energía para hacer un sistema productor neto de energía (Kataki et al., 2021; González et al., 2021). González et al. (2021) realizaron un estudio de una MFC integrada en humedal construido que alcanzó una densidad de potencia de 8,6 mW/m² plantada con Sch. Asimismo, Corbella et al. (2017) realizaron un ACV para comparar un sistema de humedal construido convencional (sin MFC) acoplado a una MFC con ánodo de grava, y otro acoplado a una MFC con ánodo de grafito. Sus resultados mostraron densidades de potencia de 288 y 346 mW/m² respectivamente, con una electricidad producida de 1,4E-02 kWh/m³. La instalación de las celdas microbianas acoplados a humedales construidos donde logro reducir la huella del sistema en un 20%.

Para las categorías de eutrofización de agua dulce y marina la tendencia fue decreciente con un potencial de impacto de 1,59E-02 kgPeq/m³ y 1,16E-01 kgNeq/m³ para el monocultivo Phr respectivamente, disminuyendo en un 3,1% y 1% para Sch, 14% para Cyp y 18% en el policultivo (Cyp/Zant). Todos los escenarios representaron un 100% de contribución que está asociada directamente con las aguas residuales del tratamiento de HSSF. Para la eutrofización de agua dulce el impacto es generado por las concentraciones de fósforo mientras que para la eutrofización de marina por las concentraciones de nitrógeno. Se pudo observar un impacto de 9,37E-02 kgNeq/m³ para el escenario Cyp-cálida en la categoría eutrofización marina. Lo cual tiene estrecha relación con que la eliminación de un 40% de nitrógeno aumenta las emisiones de N₂O alcanzando 24,7 mg/m²d. Esto se ve reflejado en la categoría de acidificación terrestre. Finalmente, en todos los escenarios, el transporte y la deshidratación de lodos tuvieron un impacto leve (0-3% % del impacto total) en todas las categorías consideradas. La disposición de solidos en relleno sanitario, y su recuperación de energía eléctrica a partir del gas generado en el relleno resultó en una disminución de un 3-2% en el potencial de cambio climático y 1% en las categorías acidificación terrestre, formación de oxidantes fotoquímicos y formación de material particulado.

La magnitud y relación del impacto ambiental de las categorías seleccionadas normalizadas se resume en la Figura 7.5. La eutrofización de agua dulce y marina mostró ser el impacto más relevante en el tratamiento de aguas residuales por el humedal construido. Dependiendo del escenario el impacto de la eutrofización de agua dulce llegó a ser cerca de 328 y 277 veces mayor

que cambio climático para Phr y Sch respectivamente. Mientras que 60 y 38 veces más para los escenarios Cyp y Cyp/Zant. En menor medida se encuentra el impacto de cambio climático que corresponde a 0,2% para Phr y Sch, y entre 1-2% para Cyp y Cyp/Zant. Esto lleva a la reflexión que, aun siendo el objetivo de reducir los contaminantes de las aguas residuales, las aguas ya tratadas sigan siendo el mayor responsable del impacto ambiental por la categoría eutrofización en comparación cambio climático.

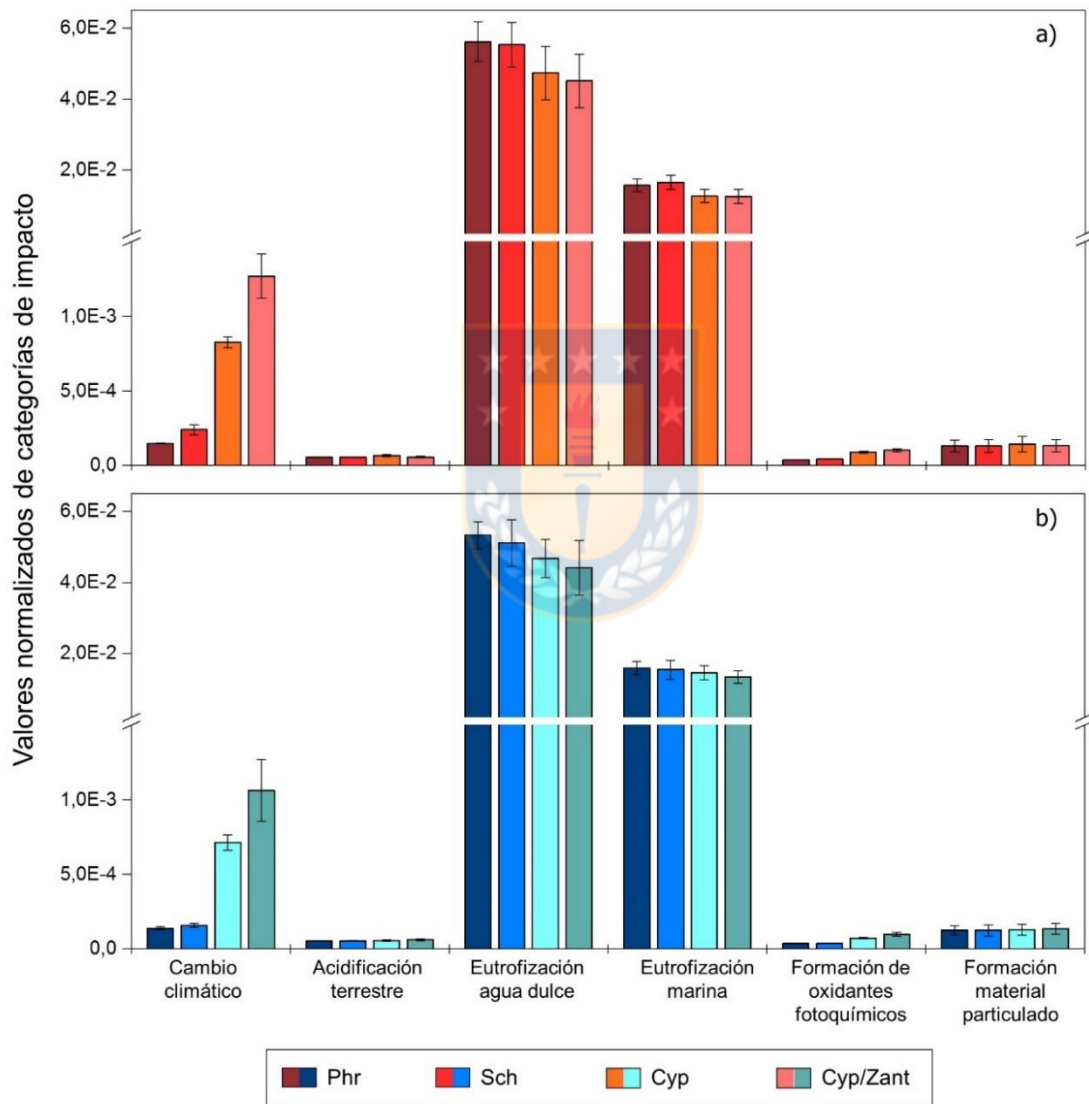


Figura 7.5. Normalización de las categorías seleccionadas para los tratamientos de HSSF en la estación cálida a) y estación fría b). Mediante simulación de Monte Carlo, se ha obtenido la media (punto negro), y el intervalo de confianza del 95% (barras de error). Phr: *P. australis*; Sch: *S. californicus* Cyp: *C. papyrus* Cyp/Zant: *C. papyrus*; *Z. aethiopia*.

En su mayoría de los estudios de ACV de los humedales construidos muestran un impacto negativo en la categoría cambio climático lo que se atribuye a las emisiones directas GEI. Las emisiones de agua tratada en humedales construidos reportada en literatura muestran valores de 0,5 a 4,5 kg CO₂eq/ m³ (Chen et al., 2011; Corbella et al., 2017; Garfí et al., 2017; Flores et al., 2019; Resende et al., 2019). Al compararlo con los sistemas convencionales, que se utilizan para el tratamiento de agua residuales, han demostrado ser una opción favorable desde el punto de vista ambiental. Se ha reportado que para eliminar 1kg de DBO de las aguas residuales, el sistema de humedales construidos emitió (3,18 kg CO₂eq) alrededor del 50% de CO₂eq respecto al sistema convencional (7,26 kg CO₂eq) (Pan et al., 2011). Chen et al. (2011) al comparar un humedal construido versus un sistema convencional de lodos activados, encontraron que para tratar 1 m³ de aguas residuales, la emisión de GEI de humedal fue solo una cuarta parte que el sistema convencional. Asimismo, Flores et al. (2019) consideraron el tratamiento de aguas residuales por humedales construidos y lodos activados, donde los humedales construidos ayudaron a reducir las emisiones en un 70-98% en comparación con las tecnologías convencionales.

Si bien nuestros resultados para los escenarios de Phr, Sch y Cyp de los humedales construidos en la categoría cambio climático concuerdan con la literatura; para el escenario de Cyp/Zant el impacto en cambio climático fue 8,0 kg CO₂eq/m³ debido a las emisiones de GEI (95% de contribución). Por lo tanto, pueden ser similares a tratamientos convencionales terciarios en esta categoría. Especialmente en la etapa de operación del tratamiento, donde las emisiones de los sistemas convencionales son 7 veces más que las de los humedales construidos (Pan et al., 2011). Sin embargo, en general los sistemas convencionales aumentan su potencial de impacto ambiental debido al impacto inducido por las plantas de tratamiento más que por las emisiones directas del tratamiento. En una planta de lodos activados, las emisiones directas representaron el 24% del total de emisiones de GEI, mientras que el resto (76%) se asocia a la energía eléctrica y químicos que utilizan. En cambio, las emisiones directas de un humedal construidos representan un 41%, por lo tanto, estos valores debieran siempre ser considerados con la finalidad de no sobreestimar los valores (Chen et al., 2011). En este estudio las emisiones directas representaron 64% para Phr y Sch y 94% para Cyp/Zant. Además, el escenario Cyp/Zant en la categoría cambio climático mostro una mayor incertidumbre en comparación con los demás escenarios. Esto se asocia a una

mayor varianza en los datos (emisiones de CH₄) y la estimación de emisiones (N₂O y CO₂) lo cual representa una menor calidad de los datos.

La Figura 7.6 muestra el potencial de impacto expresado por 1 kg de fósforo eliminado en el humedal construido para las categorías de eutrofización de agua dulce y cambio climático siendo las más relevantes. Como se observa en la categoría cambio climático el policultivo Cyp/Zant tiene una eliminación de fósforo del 32%, un potencial impacto en eutrofización de 3,34 kgP_{eq}/kgP eliminado que mostró valores de 2080 kgCO_{2eq}/kgP eliminado. Mientras que Phr tiene un impacto de 649 kg CO_{2eq}/kgP eliminado. Sin embargo, una eliminación de fósforo de 12% tiene un potencial de impacto de 10,37 kgP_{eq}/kgP eliminado. Estos resultados muestran que, la eliminación de fósforo en el humedal construido requiere de mayor actividad microbiana y asimilación de la planta, lo cual se refleja en las emisiones generadas por las plantas en el policultivo Cyp/Zant. Esto se ha visto en plantas de tratamiento convencionales, pero de manera mecanizada, donde la instalación y operación de tratamientos terciarios para la eliminación de fósforo lleva consigo periodos de aireación más largos o tratamientos de adición de químicos, lo que aumenta el impacto ambiental en la categoría cambio climático entre 1,7-2,5 veces (Rodríguez-García et al., 2011; Remy et al., 2014).

Como se discute en el Capítulo III, la principal vía de eliminación de fósforo es el mecanismo químico, sobre todo la precipitación logrado eficiencias de retención del 62 al 67%. Sin embargo, es necesario algún químico (coagulante), el cual puede contribuir entre un 15-23% en cambio climático. En Chile en general no se cuenta con tratamiento terciario o de eliminación de nutrientes lo cual genera un impacto ambiental en términos de eutrofización y daño ambiental a los ecosistemas acuáticos. Una mejora en el diseño de los sistemas de policultivo se asemejaría a un tratamiento terciario el cual beneficiaría la eliminación de nutrientes. Sin embargo, algunas limitantes serían la carga de fósforo de las aguas residuales, el tamaño de la población; para pequeñas comunidades y zonas rurales, y los terrenos disponibles para abarcar las cargas. Por lo tanto, no sería la solución definitiva.

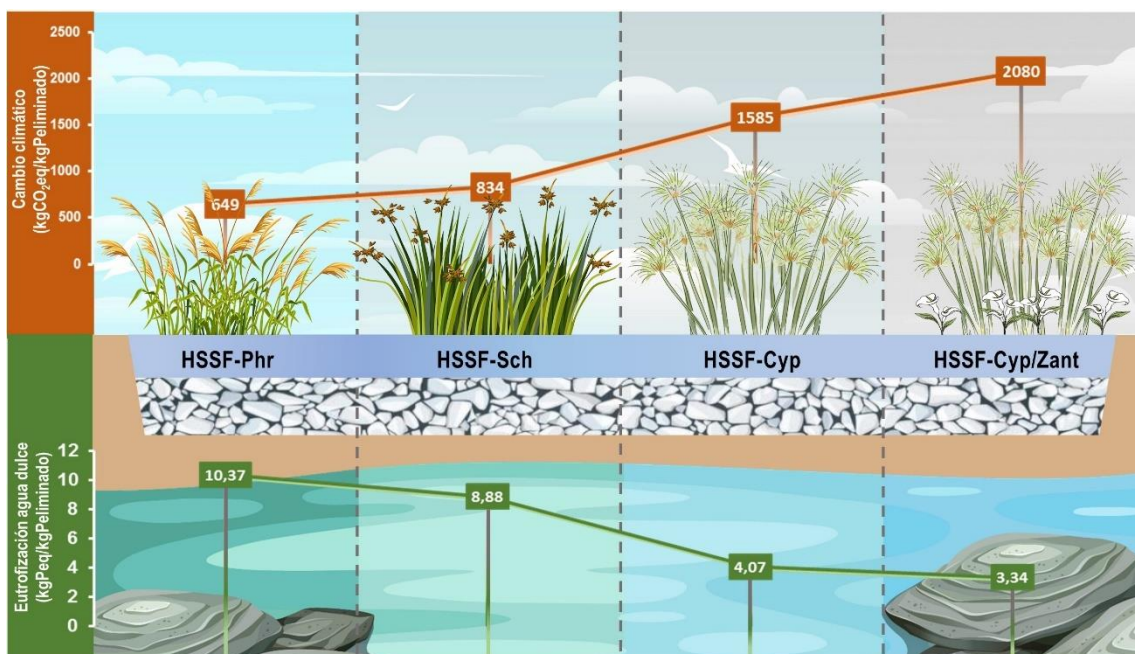


Figura 7.6. Resumen del potencial impacto ambiental por kg de fósforo removido por los tratamientos de HSSF en las categorías más influyentes como eutrofización de agua dulce y cambio climático. Phr: *P. australis*; Sch: *S. californicus* Cyp: *C. papyrus* Cyp/Zant: *C. papyrus*; *Z. aethiopica*.

Sin bien el HSSF no fue construido directamente para la eliminación de fósforo esta brecha en los impactos podría acotarse a través de modificaciones para mejorar el rendimiento ambiental. Un cambio en el medio de soporte podría aumentar la eliminación de fósforo como a la vez regular las emisiones GEI. Desde el punto de vista del diseño técnico, sería más factible utilizar zeolita como medio de soporte, con una eficiencia de eliminación de fósforo de 60% y adsorción >50% que puede ser utilizado como fertilizante en zonas rurales (Andrés et al., 2018). Además, su gran área superficial 243 m²/g y porosidad 40% mejoraría la oxigenación del sistema entregando condiciones aerobias, reduciendo la emisión de CH₄. Asimismo, como vimos en este estudio el tipo de planta es un factor importante que considerar. El uso de especies nativas siempre será la mejor opción para los humedales construidos, lo cual debe ser evaluado considerando las estaciones del año. Otra opción puede ser las plantas ornamentales pero acorde a la región. Chen et al. (2020) recomendó la utilización de *C. indica* la cual exhibió un potencial cambio climático de 74 mg/m²d y un rendimiento de eliminación de 87% en un humedal construido a escala laboratorio.

Finalmente, una forma de compensación ambiental es la implementación de estrategias de recuperación de energía, recolección de macrófitas, producción de biogás, reutilización de

efluentes y recuperación de nutrientes (Kataki et al., 2021; Zang et al., 2015; Corominas et al., 2020). En este sentido, en las zonas rurales, este tipo de estrategias cobran mayor fuerza debido a las limitaciones que pueden existir en el uso de tecnologías y el uso de la electricidad. Las tecnologías combinadas utilizan los mecanismos de eliminación de fósforo (físico, químico y biológico) (Capítulo III, Sección 3.4) que surgen como una alternativa para la eliminación y recuperación de fósforo. Estos sistemas integran la remoción de todas las formas de fósforo maximizando las eficiencias hasta un 99%. Una combinación de precipitación química, por ejemplo, el uso de magnesio, y humedales construidos podría disminuir las concentraciones del efluente ($< 10 \text{ mgP/L}$) y recuperar el fósforo en forma de estruvita el cual puede ser utilizado como fertilizante. Teniendo en cuenta el diseño, operación e implementación eficiente de los humedales construidos, los estudios futuros deben centrarse en la evaluación técnica e integral de nuevas tecnologías.



CAPÍTULO VIII

CONCLUSIÓN Y RECOMENDACIONES



1. CONCLUSIONES

- Se obtuvieron mejores resultados para la eliminación de fósforo en el sistema de policultivo plantado con especies ornamentales Cyp/Zant con una eficiencia de eliminación de 30-33%. Seguido por el monocultivo ornamental Cyp con una eficiencia de eliminación de un 22-27% y finalmente los monocultivos de Phr y Sch entre un 9-18%. No se observó un efecto significativo en el rendimiento entre las estaciones cálida y fría. La mayor parte del fósforo fue retenida por el medio de soporte y microorganismos en el HSSF con 13-31%. Las plantas representaron entre un 4-26% de asimilación de fósforo, mientras que el fósforo en los efluentes fue de 57-79%. El rendimiento de eliminación de fósforo estuvo influenciado por factores de operación como la carga de entrada de fósforo, la tasa de carga hidráulica y el oxígeno disuelto.
- El desarrollo de las plantas fue superior para el monocultivo Sch con una cobertura de 89% y una biomasa de 4,9 kgPS/m², su adaptabilidad se debe a que es una especie nativa. De manera contraria las plantas ornamentales mostraron una biomasa en el monocultivo Cyp de 1,8 kgPS/m² y el policultivo Cyp/Zant de 2,5 kgPS/m² mostrando una baja adaptabilidad, sobre todo la especie *Z. aethiopica*. La asimilación de fósforo promedio por las plantas fue 3 gP/m², 6 gP/m² para los monocultivos Phr y Sch y 30 gP/m² el monocultivo Cyp y el policultivo Cyp/Zant. Además, la asimilación de fósforo en la estación cálida fue hasta 6 veces mayor en los tallos debido a su etapa de crecimiento. Mientras que en la estación fría hasta 7,5 veces en las raíces en la etapa de senescencia. Sin embargo, a pesar de que la presencia y características de las plantas son importantes, nuestros resultados indican que no es suficiente para maximizar la eficiencia de eliminación de fósforo en los humedales construidos.
- El desempeño ambiental del sistema del policultivo (Cyp/Zant) presentó un impacto ambiental 14% menor que los monocultivos para la categoría eutrofización de agua dulce, reduciendo la eutrofización de aguas continentales. En cambio, en la categoría de cambio climático el policultivo Cyp/Zant mostró el mayor potencial de impacto con 8,05 kgCO₂eq/m³, principalmente debido al efecto directo de las emisiones GEI. Dependiendo del escenario el impacto de la eutrofización de agua dulce llegó a ser cerca de 328 y 277 veces mayor que el impacto de cambio climático para Phr y Sch respectivamente. Mientras que 60 y 38 veces más para los escenarios Cyp y Cyp/Zant.

- En base a todos los resultados reportados, se rechaza la hipótesis planteada, pues los resultados del ACV muestran que el policultivo en humedales construidos favoreció la eficiencia de eliminación de fósforo en un 10% en comparación con el sistema de monocultivo. Sin embargo, incrementó las emisiones GEI hasta 3 veces más. Por lo tanto, no mejora el desempeño ambiental de los humedales construidos plantados con monocultivo, siendo el sistema de cultivo y tipo de planta un factor de diseño considerable en humedales construidos.

2. RECOMENDACIONES FINALES

- Considerando las bajas eficiencias reportadas en este estudio, se recomienda una optimización del diseño y parámetros de operación de sistema de humedales construidos. Se recomienda tratar los humedales construidos con una baja carga de entrada de fósforo ($< 10\text{--}20\text{ g/m}^2\text{año}$). Lo cual hará que los componentes del sistema asimilen sólo el fósforo que necesitan. Mas aún se recomienda mantener una buena oxigenación de humedal construidos entregando condiciones aerobias. Un cambio en el medio de soporte con mayor capacidad de adsorción de fósforo o una mezcla de materiales, como por ejemplo la zeolita optimizaría la eliminación de fósforo, entregando mayor oxigenación, y sobre todo alargaría la vida útil.
- En cuanto a la especie vegetal probadas en este estudio, la planta ornamental *Z. aethiopica* no es una buena opción para el tratamiento debido a sus altas emisiones y adaptación. En cambio, la especie ornamental *C. papyrus* puede ser una planta alternativa para lograr el estado de operación ideal, es decir, una buena asimilación de fósforo, y a la vez aumentar el valor ambiental y paisajístico del tratamiento de aguas residuales. La selección de la planta debe ser considerada en cuanto a su raíz y su difusión radial, las raíces más superficiales y raíces delgadas entregan mayor oxigenación. Además, se recomienda una mezcla en sistema policultivo con la especie nativa, *S. californicus* y *C. papyrus* podría mostrar un buen desempeño ambiental. Otra opción es la especie *C. indica*.
- Finalmente, respecto a la generación de emisiones una relación C/N óptima de 5:1 pueden lograr una buena eficiencia de eliminación de nutrientes biológicos y disminuir en un 15% la emisión de CO_2 y CH_4 . Por otro lado, se ha observado que algunos estudios de ACV han ampliado los alcances del sistema agregando procesos posteriores con la finalidad de obtener

un beneficio o compensar los impactos ambientales. Algunos tratamientos serían la producción de biogás, incineración de lodos o la producción de fertilizantes en tecnologías combinadas. Estas recomendaciones podrían disminuir los impactos ambientales generales del tratamiento de aguas residuales, a través de una buena toma de decisiones en diseño, operación y tecnología.



CAPÍTULO IX

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(Introducción-discusión)



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ANEXO I

PORTADA DE LOS ARTÍCULOS PUBLICADOS





Characterization and recovery of phosphorus from wastewater by combined technologies

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Abstract Phosphorus is a critical element in agriculture because of its role in fertilizing fields. Thus, and due to sewage discharges, phosphorus is also present in aquatic ecosystems, causing eutrophication. Phosphorus can be found in inorganic and organic forms. One solution to phosphorus-related conflicts is the application of technologies for the recovery of phosphorus from wastewater and its possible reuse. However, existing technologies are focused on the elimination/recovery of inorganic phosphorus, while technologies based on combined mechanisms have demonstrated greater efficiency in the treatment of different forms of phosphorus and its recovery. This article reviews the operational factors of the different technologies based on the physical, chemical and biological mechanisms of phosphorus recovery. Emerging combined technologies that have been able to maximize the recovery of organic and inorganic phosphorus from different wastewater streams are also reviewed. Thus, the forms of phosphorus must be understood for the appropriate technology for the recovery different forms of P in wastewater discharges

to be chosen, providing environmental protection to aquatic ecosystems.

Keywords Phosphorus recovery · Combined technologies · Wastewater · Organic phosphorus · Inorganic phosphorus

1 Introduction

Phosphorus (P) is an essential chemical element for living beings that has no substitute and is a non-renewable resource (Tarayre et al. 2016). It is naturally found in geological deposits of phosphate rock or phosphorite, which are unevenly distributed throughout the world (Desmidt et al. 2015). In recent years, P has taken on great importance due to the depletion of this mineral, with approximately 95% extracted P used in agriculture, mainly as fertilizer (Jasinski 2018). Globally, apart from the mineral reservoir of phosphorite rock, P is found in surface water and oceans. The greatest P flows to aquatic ecosystems are from soil erosion, runoff and point source discharges. The discharge of high concentrations of P into wastewater encourages excessive proliferation of algae and floating plants, resulting in eutrophication of aquatic systems (Mekonnen and Hoekstra 2018).

A long-term sustainable solution to address the dual problems of P mineral shortages and P-based

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Evaluation of long-term phosphorus uptake by *Schoenoplectus californicus* and *Phragmites australis* plants in pilot-scale constructed wetlands

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ABSTRACT

The aim of this study was to evaluate long-term phosphorus (P) retention in a pilot-scale system made of four horizontal subsurface flow (HSSF) constructed wetlands for wastewater treatment. Each wetland had an area of 4.5 m² and was operated for nearly 8 years (2833 days). Two wetlands with *Schoenoplectus californicus* (HSSF-Sch) and the other two with *Phragmites australis* (HSSF-Phr) were planted. The P removal efficiency was 18% for both types of HSSF wetlands. The primary factors that correlated with long-term P retention efficiency in HSSF were phosphorus loading rate (PLR), hydraulic loading rate (HLR) and dissolved oxygen (DO). Average biomass production of HSSF-Phr and HSSF-Sch was 4.8 and 12.1 kg dry weight (DW)/m², respectively. The P uptake by the plant increased over the years of operation from 1.8 gP/m² to 7.1 gP/m² for *Phragmites* and from 3.2 to 7.4 gP/m² for *Schoenoplectus* over the same periods. Moreover, the warm season (S/Sm) was more efficient reaching 14% P uptake than the cold season (F/W) with 9%. These results suggest that both plants' P retention capacity in HSSF systems represents a sustainable treatment in the long term.

Novelty statement

Long-term (8 years) phosphorus uptake by *Schoenoplectus californicus* and *Phragmites australis* and retention in pilot-scale constructed wetlands are evaluated. *Schoenoplectus californicus* is an uncommon species that has been less studied for phosphorus uptake compared to *Phragmites australis*, a globally known species in constructed wetlands. Moreover, some studies evaluating the performance of constructed wetland systems for domestic wastewater treatment are usually limited in time (1–3 years). Therefore, this long-term study demonstrates that the plant plays an important role in phosphorus retention, especially the species *Schoenoplectus californicus*. So, the phosphorus uptake by plants can contribute between 9 and 14% of the phosphorus load of constructed wetland systems in early years of operation.

KEYWORDS



Constructed wetlands; phosphorus removal; *Phragmites australis*; plant uptake; *Schoenoplectus californicus*

Introduction

Constructed wetlands (CW) are a technology for natural, environmental and sustainable wastewater treatment. In terms of P treatment, they have shown removal efficiencies ranging from 10 to 80%, depending on the type of wetland, plant species or supporting media (Vymazal 2007; López *et al.* 2016; Józwiakowski *et al.* 2018; Maucieri *et al.* 2020). The P removal mechanisms occur through interactions between supporting media, plants, and microorganisms (Vera *et al.* 2013; Vymazal 2007). The plants play an important role in P reduction in HSSF through their effect on P transformations (Cheng *et al.* 2009). Key functions are associated with physicochemical effects such as oxygen release to the rhizosphere, regulation of hydraulic conditions, and stimulation of productivity, diversity, and microbial activity in the rhizosphere (Burgos *et al.* 2017; Leiva *et al.* 2018; Zheng *et al.* 2020).

The commonly used plants in CW are *Phragmites australis*, *Typha* spp. and *Scirpus* spp. (Vymazal 2020). To the contrary, *Schoenoplectus californicus* this is a common species in some parts of its range as along the Atlantic and Pacific coasts of the Americas from California to Chile (Macía and Balslev 2000). Similar to *Schoenoplectus californicus* is *Schoenoplectus validus* which is distributed in northern America and has been less widely used in CW (Greenway and Woolley 2001; Zhang *et al.* 2008). However, the effect of this plant species on P uptake in CW has not been thoroughly investigated.

The P uptake by plants has shown contradictory results on CW treatment efficiency. Lee *et al.* (2012) found that P uptake by plants was less than 1% in a six-cell surface flow CW planted with three species (*Phragmites australis*, *Miscanthus sacchariflorus*, *Typha orientalis*). Wu *et al.* (2013) treated river water in a microcosmic CW and demonstrated a P uptake of 4–22% by four types of plants

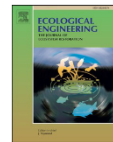
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Phosphorus uptake by macrophyte plants in monocultures and polycultures in constructed wetlands for wastewater treatment

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ABSTRACT

Phosphorus uptake by common and ornamental plants was studied in pilot-scale horizontal subsurface flow (HSSF) constructed wetlands (CWs) with monocultures and polycultures. Three HSSF CWs were planted with monocultures of *Phragmites australis* (HSSF-Phr), *Schoenoplectus californicus* (HSSF-Sch) and *Cyperus papyrus* (HSSF-Cyp), and one polyculture was planted with *C. papyrus* and *Zantedeschia aethiopica* (HSSF-Cyp/Zant). During the experimental period, removal efficiency, growth characteristics, biomass production and phosphorus uptake were evaluated in the cold season (fall/winter) and warm season (spring/summer). In general, the cold season showed better performance with an order of HSSF-Cyp/Zant > HSSF-Cyp > HSSF-Sch > HSSF-Phr in the evaluated parameters. The removal efficiencies were 33%, 27%, 23% and 12%, respectively. The biomass production and density of the HSSF treatments ranged from 1.5 to 5.4 kg dry weight (DW)/m², and 435 to 1298 individuals/m² with higher values for HSSF-Sch. The tissue phosphorus content was 5 to 20% higher below ground in all plants, including ornamentals. Phosphorus uptake was higher for polyculture (HSSF-Cyp/Zant) and monoculture (HSSF-Cyp) planted with ornamentals, with a mean of 30 g P/m². Also, the polyculture was not affected by the seasons, reaching up to 27% phosphorus uptake by the plants. According to our results, the ornamental species of the polyculture contribute to the phosphorus uptake.

1. Introduction

Human intervention in the global phosphorus cycle has generated anthropogenic sources, such as municipal wastewater, runoff from agricultural areas and terrestrial leachates in lakes, rivers and coastal areas, constitute a risk for water quality reduction and eutrophication (Rittmann et al., 2011; Vera et al., 2013). Constructed wetlands (CWs) have been widely used as a promising advanced technology for the treatment of these types of wastewater due to their advantageous characteristics, such as low cost, high efficiency and easy operation (Vymazal and Kröpfelová, 2008; Vera et al., 2014; López et al., 2015). Subsurface CW systems are known to be poor in phosphorus removal (Arias et al., 2003). According to Vymazal (2020) nutrient (nitrogen and phosphorus) removal does not exceed 50% for municipal wastewater. Generally, phosphorus removal in a CW is attributed to substrate adsorption, plant uptake, and microbe assimilation (Vera et al., 2014). Substrates and plants are the main removal pathways of phosphorus compounds in a CW, with 4 to 22% assimilation and uptake by plants, while substrates accumulate approximately 36 to 50% (Wu et al., 2013).

Therefore, mainly different substrates that can increase phosphorus removal have been studied (Vohla et al., 2011). However, only a few studies have focused on the effect of plants on phosphorus removal in CW (Abbasi et al., 2019; Shan et al., 2011).

Common plants include *Phragmites* spp., *Typha* spp. and *Scirpus* spp., which are the most commonly used species in horizontal subsurface flow (HSSF) CWs (Sandoval-Herazo et al., 2018; Vymazal and Kröpfelová, 2008). *Phragmites australis* have shown its benefits, such as its great capacity for long term invasion, its vertical root development increasing hydraulic conductivity in a CW, its rhizomes and the great variety of life it harbors, which enhances the complete treatment of CW scrubbing (Uddin and Robinson, 2018; Zheng et al., 2020). An uncommon and lesser known species is *Schoenoplectus californicus*, which is distributed along the Atlantic and Pacific coasts of the Americas, from California to Chile (Macía and Balslev, 2000). Similar to *S. californicus* is *Schoenoplectus validus*, which is distributed in northern America and has been less commonly used in CWs (Greenaway and Woolley, 2001; Zhang et al., 2007b).

On the other hand, an emerging alternative is the use of ornamental

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