Carbon fluxes in a Mediterranean reservoir under a scenario of changing hydrology

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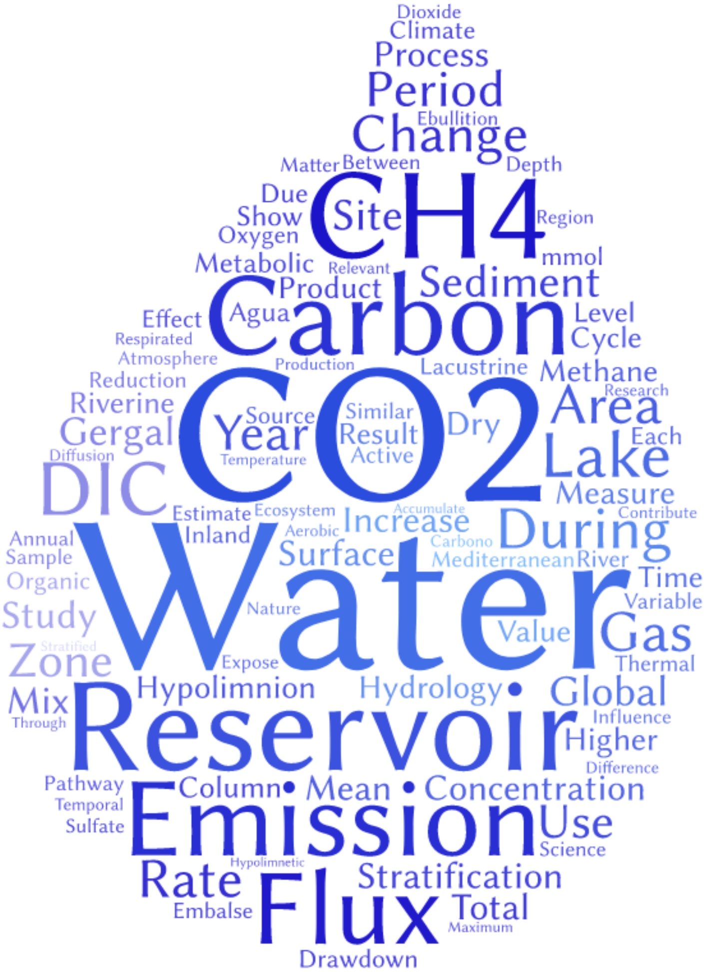

”Cambia,
todo cambia.”

– *Mercedes Sosa.*

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Resumen

En la presente tesis doctoral se estudia el efecto que tienen los cambios hidrológicos sobre los flujos de carbono (CO_2 y CH_4) en un embalse mediterráneo, El Gergal (Guillena, Sevilla).

Las aguas continentales, como los ríos, lagos o embalses, han jugado y juegan un papel fundamental en el desarrollo humano. La humanidad ha estado ligada a estos sistemas desde tiempos remotos y se beneficia de múltiples servicios ecosistémicos como el aprovisionamiento de agua, alimento o el uso recreacional y cultural. Entre estos servicios ecosistémicos, recientemente se ha puesto de manifiesto la función clave que desempeñan estos sistemas como reguladores del ciclo global de carbono y, por lo tanto, la necesidad de incluirlos dentro de las estrategias para mitigar el cambio climático.

Tradicionalmente, la aguas continentales han sido consideradas como sistemas con un impacto limitado sobre los ciclos biogeoquímicos con un efecto a escala local o regional. Esto, junto con la pequeña superficie que ocupan a nivel global ($< 3\%$ de la superficie de los continentes), explica la poca atención que han recibido en los estudios sobre el ciclo del carbono a escala global. Sin embargo, recientemente se ha puesto de manifiesto el papel que estos sistemas juegan a escala global y, actualmente, se estima que el flujo de carbono desde las aguas continentales hacia la atmósfera es del mismo orden de magnitud que el flujo neto de los océanos.

Las aguas continentales reciben carbono desde los ecosistemas terrestres y transportan este carbono hacia lo océanos. Sin embargo, pese a lo que tradicionalmente se ha pensado, estos sistemas no actúan simplemente como “tuberías” que transportan el carbono de un compartimento a otro, si no que participan activamente en su procesado, absorbiendo, emitiendo y enterrando

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carbono a lo largo del continuo continente-océano. De hecho, se estima que aproximadamente la mitad del que carbono que reciben las aguas continentales es emitido directamente a la atmósfera (en forma de CO_2 y CH_4) o enterrado en el sedimento. Es por esto que las aguas continentales han sido recientemente integradas en el ciclo global del carbono, incluyéndose en los últimos informes del IPCC. Además, las agua continentales están consideradas como sistemas clave dentro de las estrategias para mitigar los efectos del cambio climático.

Dentro de las masas de agua continentales, los embalses han sido señalados como uno de los componentes más activos en la biogeoquímica del carbono. Estos sistemas entierran entorno al 40% del carbono orgánico almacenado por las aguas continentales y, solo la centrales hidroeléctricas, producen alrededor del 4% de las emisiones que tienen lugar desde estos ecosistemas. Además, durante el último siglo, la construcción de embalses ha experimentado un gran aumento y, debido a la necesidad de cubrir las demandas de energía y el abastecimiento de agua de una sociedad en crecimiento, se prevé que su número seguirá en aumento en las próximas décadas. Por lo tanto, el estudio de los flujos de carbono que tienen lugar en los embalses se torna de crucial relevancia a la hora de comprender y evaluar una fracción importante del ciclo global del carbono.

En este sentido, ya es conocido que los flujos, tanto de CO_2 como de CH_4, desde la superficie del agua de los embalses son importantes y tienen una relevancia a escala global. Estos flujos son el resultado del procesado de carbono, tanto en la columna de agua como en los sedimentos. Por un lado, estos procesos pueden conducir a una situación de desequilibrio entre la concentración de CO_2 y CH_4 en la masa de agua y la atmósfera y, por ende, provocar la retirada o liberación de carbono desde/hacia la atmósfera a través de procesos de difusión molecular. Por otro lado, en el caso del CH_4, debido a su baja solubilidad y la presión hidroestática a la que puede llegar a estar sometido el sedimento, se puede producir la acumulación de gases que sean liberados repentinamente a la atmósfera mediante procesos de burbujeo o ebullitivos. Sin embargo, estos flujos presentan una gran variabilidad tanto espacial como temporal que depende de diversos factores como el estado trófico del sistema o las características de la cuenca. Entre estos factores, la variaciones hidrológicas (cambios en el nivel del agua, tiempo de residencia, escorrentía, etc) pueden promover cambios en la magnitud y la dirección de estos flujos. Aunque en los últimos años ha incrementado el número de estudios sobre los flujos de CO_2 y CH_4 desde la lámina de agua de los embalses, la información con respecto al efecto de la hidrología sobre estos flujos, especialmente en el mediterráneo, es aún escasa.

Por otro lado, una fracción del carbono que entra en los embalses es depositado y enterrado en los sedimentos. Sin embargo, una de las particularidades de la mayoría de los embalses es que sufren importantes fluctuaciones del nivel de agua debido a su gestión, como es, por ejemplo, la extracción de agua. Estas fluctuaciones del

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nivel del agua exponen los sedimentos a la atmósfera y potencian la actividad microbiana, promoviendo la respiración de la materia orgánica y aumentando la producción y liberación de CO_2. Esta liberación del carbono que se encontraba enterrado en los sedimentos y que podría permanecer secuestrado ahí durante un largo periodo de tiempo pueden provocar un desequilibrio sobre el balance global de carbono en el embalse, incrementando las emisiones y disminuyendo el secuestro de carbono. Tradicionalmente, las emisiones desde estos sedimentos expuestos no se han considerado dentro del balance de carbono de los embalses. Sin embargo, recientemente se ha puesto de manifiesto que estas emisiones pueden llegar a ser hasta un orden de magnitud superior a las emisiones desde la lámina de agua. Por lo tanto, es necesario cuantificar estos flujos e incluirlos dentro del balance de los embalses con el fin de aportar una visión más completa del papel que desempeñan en la biogeoquímica del carbono a nivel global.

Además de lo expuesto anteriormente, en la región mediterránea, los embalses experimentan generalmente un periodo de estratificación al año. Durante la estratificación, debido al fuerte gradiente de densidad (termoclina) que se establece, la columna de agua se encuentra estratificada, aislando las aguas profundas del hipolimnion del contacto con la atmósfera. En el hipolimnion, los procesos heterotróficos de respiración producen y acumulan sustancias reducidas (como HS^- o ${NH_4}^+$), que perjudican la calidad del agua, así como CO_2 y CH_4, que contribuye a las emisiones de carbono del embalse. La mayor parte del CO_2 y CH_4 acumulado en el hipolimnion, podrá ser liberado a través de la extracción de agua del hipolimnion, a través de un proceso conocido como degasificación, o por difusión, una vez se produzca el proceso de mezcla y esta masa de agua vuelva a entrar en contacto con la atmósfera. Alteraciones que influyan sobre el metabolismo en el hipolimnion pueden afectar a la producción de CO_2 y CH_4 pudiendo tener un efecto directo sobre el balance de carbono en el embalse.

El cambio climático junto con las actividades antrópicas, tales como la extracción de agua para riego o la gestión de los embalses, tienen un impacto directo sobre la hidrología. Estos impactos modifican el régimen hídrico de los ríos, influyen sobre el tiempo de residencia del agua en los embalses y incrementan los oscilaciones en el nivel del agua debido a las sequías y a las inundaciones, cada vez más intensas y recurrentes. Estos impactos son especialmente acuciados en la región mediterránea convirtiéndola en una de las más vulnerables al déficit hídrico y en la que se espera que la situación empeore en los próximos años. Además, estos cambios hidrológicos pueden tener un efecto sobre los flujos de carbono que tienen lugar en los embalses, tanto desde la lámina de agua, desde los sedimentos expuestos así como dentro del hipolimnion.

Por tanto, bajo este escenario de cambio hidrológico, la intensidad y la distribución (tanto espacial como temporal) de los flujos de carbono desde la lámina de agua, los sedimentos expuestos así como el ciclado de carbono en el

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hipolimnion podrían sufrir modificaciones significativas. Sin embargo, a pesar de que la región mediterránea es una de las más vulnerables al cambio climático y a las presiones humanas, el efecto de lo cambios hidrológicos sobre los flujos de carbono en embalses mediterráneos ha recibido poca atención. De hecho, la mayoría de los estudios se han llevado a cabo en regiones templadas y la proporción de estudios relacionando cambios hidrológicos y flujos de carbono en embalses mediterráneos es escasa. Por lo tanto, el objetivo general de esta tesis es contribuir al conocimiento sobre el efecto de los cambios hidrológicos sobre la dinámica del carbono en los embalses mediterráneos.

Los objetivos particulares de esta tesis, que se abordan en cada uno de los capítulos, son:

1. En el capítulo 4, el objetivo es analizar la variabilidad espacial y temporal de los flujos de CO_2 y CH_4 desde la lámina de agua de un embalse mediterráneo y explorar la relación existente entre la magnitud y signo de esos flujos y los factores hidrológicos (tiempo de residencia y fluctuaciones del nivel del agua) y limnológicos (clorofila *a* y pH).

2. En el capitulo 5, el objetivo se centra en cuantificar los flujos de CO_2 desde los sedimentos expuestos de un embalse mediterráneo y explorar su relación con las propiedades fisico-químicas del suelo con el fin de completar la información disponible sobre flujos de carbono desde sedimentos expuestos en embalses, especialmente para la región mediterránea.

3. El objetivo en el capítulo 6 es cuantificar el flujo de carbono a través de diversas rutas metabólicas heterotróficas (respiración aeróbica, desnitrificación, sulfato reducción, reducción de Fe y Mn y metanogénesis) y su contribución a la producción total de carbono inorgánico disuelto (DIC) en el hipolimnion de un embalse mediterráneo durante dos periodos de estratificación con condiciones hidrológicas muy contrastadas.

4. En el capítulo 7, los resultados obtenidos en los capítulos anteriores son combinados con el fin de estimar un balance anual de carbono y obtener un visión general de los flujos de carbono en un embalse mediterráneo.

Para alcanzar estos objetivos, el lugar de estudio escogido donde se realizaron todos los muestreos y mediciones de la presente tesis es el embalse de El Gergal (Guillena, Sevilla). El embalse de El Gergal es un embalse mediterráneo situado en el sur-oeste de la península ibérica y que cuenta con un amplio historial de investigación.

Como se ha expuesto anteriormente, debido a la importancia de los embalses en las emisiones CO_2 y CH_4 a la atmósfera, existe la necesidad de evaluar la magnitud de estos flujos y su variabilidad tanto espacial como temporal, especialmente en

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la región mediterránea. Para ello, en el capítulo 4, se realizaron mediciones simultáneas de CO_2 y CH_4 en el embalse de El Gergal a lo largo de un ciclo anual. Con una frecuencia mensual o inferior, se midieron los flujos difusivos de CO_2 y CH_4, así como el flujo ebullitivo de CH_4 en dos zonas del embalse: la zona fluvial, cercana a la entrada del río, y la zona limnética, la más profunda del embalse y cercana a la presa. El flujo difusivo de CO_2 se midió mediante un analizador de gases infrarrojo conectado a una campana flotante. Sin embargo, el flujo difusivo de CH_4 se estimó en base a la diferencia entre la concentración en el agua de superficie y la concentración en agua equilibrada con la concentración atmosférica multiplicado por el coeficiente de intercambio gaseoso para el CH_4. El flujo ebullitivo se midió mediante trampas de burbujeo colocadas durante 24 horas. Todas las concentraciones de CH_4 se midieron mediante cromatografía de gases. Además, también se registraron variables limnológicas e hidrológicas con el fin de estudiar su relación con los flujos medidos. Los principales resultados mostraron que durante el año de estudio la lámina de agua del embalse de El Gergal se comportó como un sumidero de CO_2 durante la estratificación, con un flujo medio de 9.04 ±11.8 mmol·m^{-2}·d^{-1} y 15.1 ± 11.5 mmol·m^{-2}·d^{-1} en la zona limnética y fluvial, respectivamente. Sin embargo, durante el periodo de mezcla la lámina de agua fue una fuente de CO_2 con un flujo medio de 65.1 ± 42.7 mmol·m^{-2}·d^{-1} y 34.9 ± 8.41 mmol·m^{-2}·d^{-1} la zona limnética y fluvial, respectivamente. En cuanto a las flujos de CH_4, ambas zonas fueron una fuente hacia la atmósfera durante todo el año, con flujos difusivos medios entre 0.05 y 0.6 mmol·m^{-2}·d^{-1} y flujos ebullitivos medios entre 0.008 y 1.5 mmol·m^{-2}·d^{-1}. En ambos casos existió una marcada variabilidad temporal con diferencias significativas entre el periodo de mezcla y el periodo de estratificación. De las variables estudiadas, pH y concentración de clorofila *a* fueron las variables que mostraron un efecto significativo sobre los flujos de CO_2, sugiriendo que la producción primaria juega un papel relevante sobre la dirección y magnitud de estos flujos. En cuanto a las emisiones de CH_4, la concentración de CH_4 en el hipolimnion junto con factores hidrológicos (tiempo de residencia del agua y la profundidad de la columna de agua) fueron los factores que más influyeron sobre las emisiones. Estos factores, potencialmente afectados por el cambio climático y la eutrofización, podrían alterar estos flujos en el futuro.

Las aguas continentales en general, y los embalses mediterráneos, en particular, experimentan fluctuaciones del nivel del agua dejando los sedimentos expuestos a la atmósfera. En el caso de los embalses, estas áreas de sedimento expuesto pueden ser especialmente importante debido a la gestión hidráulica necesaria para satisfacer la demanda de agua y energía. Recientemente se ha puesto de manifiesto que las emisiones desde los sedimentos expuestos pueden suponer un flujo muy importante de carbono hacia la atmósfera removilizando carbono que permanecía secuestrado en los sedimentos. Para cuantificar este fenómeno, en el capítulo 5, estudiamos las emisiones de CO_2 desde las sedimentos expuestos en el

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embalse de El Gergal. Las medidas de emisiones de CO_2 se realizaron durante una campaña llevada a cabo en septiembre de 2018 en un episodio de bajo nivel de agua (26 y 27 de septiembre). Con el fin de cubrir la mayor variabilidad espacial, se seleccionaron 4 zonas del embalse abarcando un área total de $\sim$ 6.4 ha. En cada zona, se efectuó un vuelo con drone para obtener una medición detallada de fotogrametría. A la par se llevaron a cabo una serie de medidas aleatoria georreferencidas de emisiones de CO_2. El flujo de CO2 se midió mediante una campana de respiración de suelo conectada a un analizador de gases infrarrojos. Además, para cada punto donde se midió el flujo de CO_2, también se midieron variables físico-químicas del suelo *in situ*, como temperatura y pH, y se estimó la distancia a la orilla y la granulometría, a partir de los modelos digitales del terreno obtenidos con la fotogrametría. Los resultados obtenidos mostraron que, durante la campaña, los sedimentos expuestos del embalse del Gergal fueron una fuente de CO_2 a la atmósfera con un flujo medio de 196.36 ± 207.27 mmol·m^{-2}·d^{-1}. Además, se puso de manifiesto una gran variabilidad espacial. Los flujos más altos fueron registrados en zonas influenciadas por el aporte del río o de arroyos intermitentes. La distancia a la orilla, la granulometría del sedimento, el pH y la temperatura mostraron una relación significativa con las emisiones de CO_2 desde los sedimentos expuestos del embalse. Debido al incremento en la frecuencia e intensidad de las sequías como resultado del cambio climático se espera un mayor superficie de sedimentos expuestos durante más tiempo. Esto podría potenciar e incrementar las emisiones de carbono desde los sedimentos expuestos en los embalses mediterráneos en un futuro cercano.

El cambio global está provocando alteraciones en los factores meteorológicos e hidrológicos con un efecto sobre el régimen térmico de los cuerpos de agua. Estas modificaciones están conduciendo a periodos de estratificación cada más largos con episodios de anoxia más recurrentes y prolongados. Estos periodos de estratificación asociados a anoxia favorecen los procesos heterotróficos anaeróbicos y alteran el ciclado del carbono en el embalse. Para evaluar el efecto de la hidrología y la estructura térmica sobre el ciclado del carbono, en el capítulo 6, se estudia la producción de DIC y CH_4 en el hipolimnion del embalse del Gergal durante dos años con condiciones hidrológicas muy distintas: un año húmedo y un año seco. Para ello, se monitorizaron los cambios en la concentración (acumulación o agotamiento), en el hipolimnion, de sustancias implicadas en las reacciones redox de las principales rutas metabólicas heterotróficas (respiración aeróbica, desnitrificación, reducción no asimilativa de metales, sulfato reducción y metanogénesis). En base a los cambios en la concentración y aplicando un balance de masas, se estimó la producción total de DIC a través de cada una de estas rutas metabólicas. Durante el año húmedo, las entradas de agua y las precipitaciones, con valores por encima de la media de los últimos 20 años, debilitaron la estabilidad de la columna de agua promoviendo una rotura de la

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termoclina más temprana. Por contra, en el año seco, las precipitaciones y las entradas de agua fueron más escasas permitiendo una mayor estabilidad térmica que condujo a un periodo de estratificación más largo. Durante el año húmedo la acumulación total de DIC en el hipolimnion fue menor, principalmente debido a una menor contribución de la sulfato reducción y de la metanogénesis. Sin embargo, durante el año seco, una estratificación más duradera permitió la acumulación de una mayor concentración de DIC en el hipolimnion, con un valor medio de producción de DIC para los dos años de estudio de 42.87 ± 2.06 $\mathrm{mmol{\cdot}m^{-2}{\cdot}d^{-1}}$, como resultado de una mayor actividad de la sulfato reducción y metanogénesis. Esta situación hidrológica de sequía y periodo de estratificación más largo condujo a su vez a una mayor producción de CH_4, con un valor medio para los dos años de estudios de 2.82 ± 1.96 $\mathrm{mmol{\cdot}m^{-2}{\cdot}d^{-1}}$, así como a un deterioro mayor de la calidad del agua, debido a la acumulación de sustancias reducidas como el HS^-. La contribución de la respiración aeróbica, la desnitrificación y la reducción de metales produjo una cantidad similar de DIC ambos años posiblemente como resultado de una limitación por disponibilidad de aceptor final de electrones (ej. O_2 o NO_3) para estos procesos metabólicos. En conjunto, los procesos biológicos (rutas metabólicas estudiadas) y geoquímicos (disolución de calcita) explicaron la mayor parte del DIC total acumulado durante la estratificación, independientemente de la condiciones hidrológicas reinantes. Sin embargo, existe aproximadamente un 30% del DIC acumulado el hipolimnion que no puede ser explicado por lo procesos contemplados en este estudio y merece más investigación al respecto.

En base a los resultados obtenidos en los capítulos 4, 5 y 6, toda esta información es puesta en común en el último capítulo (capítulo 6) para obtener un balance anual de carbono para el embalse de El Gergal. Además, para poder cerrar el balance total de carbono, en este capítulo, se estima la entrada y la salida total de carbono en el embalse a lo largo de un año. Para ello, aquí se asume que la entrada de carbono se produce principalmente por el aporte fluvial o a través del intercambio con la atmósfera (asimilación) y el carbono sale del embalse también, principalmente, a través del río (aguas abajo) o a través de las emisiones a la atmósfera.

El embalse de El Gergal es un embalse monomíctico mediterráneo. Esto implica que el embalse experimenta dos situaciones hidrodinámicas claremente diferenciadas: un periodo de mezcla y un periodo de estratificación. Durante el periodo de estratificación, la cota del embalse está más baja, las superficie de los sedimentos expuestos es mayor y la columna de agua se encuentra divida en dos capas principales: el epilimnion y el hipolimnion. Por otro lado, durante el periodo de mezcla, la cota del embalse está más alta, el área de sedimentos expuestos es menor y la columna de agua se encuentra completamente mezclada.

Durante el periodo de estratificación, la lámina de agua se comportó como un sumidero de carbono, tanto en la zona fluvial como en la zona limnética. Sin

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embargo, pese a que los flujos son similares en ambas zonas, la contribución de la zona fluvial es mucho menor debido a que la superficie que ocupa representa tan solo el ~18% de la superficie total del embalse. Sin embargo, durante este periodo, los procesos de respiración producen y acumulan CO_2 en el hipolimnion. Gran parte de este carbono acumulado será liberado cuando se produzca el proceso de mezcla de la columan de agua. Además, el papel de emisores de CO_2 que juegan los sedimentos expuestos se ve potenciado durante este periodo en el que el área de sedimentos expuestos es mayor, contrasrrestando la absorción realizada desde la lámina de agua. Por lo tanto, aunque durante el periodo de estratificación se está absorbiendo CO_2 desde la lámina de agua, tanto los sedimentos expuestos como el hipolimnion están produciendo CO_2 que será emitido a la atmósfera. En cuanto a las emisiones de CH_4, durante este periodo, fueron positivas tanto en la zona fluvial como limnética. El flujo ebullitivo dominó las emisiones debido posiblemente a una combinación de mayor producción de CH_4 en el sedimento, debido a las condiciones anóxicas en el hipolimnion, junto con un menor presión hidroestática, debio al menor nivel del agua, que favorece la liberación de burbujas. Además, la producción de CH_4 en el hipolimnion fue un orden de magnitud superior al emitido a la atmósfera durante este periodo reforzando la idea de que el hipolimnion juega un papel muy relevante del ciclo de carbono en el embalse.

Durante el periodo de mezcla, la lámina de agua se comportó como una fuente de carbono a la atmósfera tanto en la zona fluvial como en la zona limnetica. Esta emisión, en parte se debe a la producción de CO_2 que tuvo lugar en el hipolimnion durante la estratificación y que es liberada durante este periodo. Además, en el embalse de El Gergal, el nivel de la cota de agua en el embalse también fluctúa durante los meses de mezcla. Los sedimentos expuestos representan entorno a un 22% de la superficie total del embalse y, por tanto, las emisiones desde estas zonas son también relevantes, representando hasta un 50% de las emisiones de CO_2 que se producen durante el periodo de mezcla. En términos de emisiones de CH_4, las emisiones a través de procesos de difusión y de ebullición fueron similares pero, sin embargo, la difusión dominó las emisiones desde la zona limnetica mientras en la zona fluvial dominó la ebullición, debido posiblemente a la menor presión hidroestática (menor profundidad) en esta zona.

En el balance anual, la relevancia de la zona fluvial y limnética fue diferente para las emisiones de CO_2 que para las de CH_4 desde la lámina de agua. En el caso del CO_2, las tasas de emisiones en ambas zonas fueron similares por lo que la diferencia en el carbono total emitido se debió básicamente a la superficie relativa que ocupa cada una. Por contra, pese a la menor superficie que representa la zona fluvial (~20%), las emisiones de CH_4 fueron mayores que en la zona limnetica, principalmente debido a la diferencia en los procesos de ebullición. Por lo tanto, la cola del embalse de El Gergal conforma una zona muy activa en emisiones de CH_4.

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El hipolimnion también jugó un papel clave en ciclado de carbono en el embalse. La producción de CH_4 durante la estratificación fue un orden de magnitud mayor que las emisiones totales desde la lámina de agua, por lo tanto, aquí se estima que entorno al 80% del CH_4 producido en el hipolimnion debe ser oxidado antes de alcanzar la atmósfera. En cuanto a las emisiones de CO_2, la producción de DIC en el hipolimnion fue tan alta que puede ser comparada con las emisiones totales durante el periodo de mezcla. Si todo este CO_2 producido en el hipolimnion fuese emitido durante el periodo de mezcla podría llegar a representar hasta un 80% de las emisiones que tienen lugar durante este periodo desde la lámina de agua.

En un balance anual, el embalse de El Gergal se comportó como un emisor neto de carbono hacia la atmósfera. Además, en base a las entradas y salidas de carbono del embalse durante este año, el embalse de El Gergal parece emitir más carbono del que recibe a través de las entradas del río y de la absorción durante la estratificación. Una hipótesis planteada aquí es que el embalse alterne su rol de unos años a otros. De esta forma, algunos años se comportaría como sumidero, enterrando carbono en los sedimentos, y, otros años, se comportaría como fuente, emitiendo parte del carbono secuestrado en años anteriores.

En base a las proyecciones planteadas en el IPCC, se espera una disminución de las precipitaciones para la región del mediterráneo así como un incremento de las temperaturas. Esto conllevaría a mayores fluctuaciones en nivel del agua, dejando mayores áreas de sedimento expuestos, así como a periodos de estratificación cada vez más largos. Bajo estas circunstancias, un periodo de estratificación más largo podría conducir a una mayor producción de CH_4 así como a un deterioro de la calidad del agua debido a la acumulación de sustancias reducidas tales como HS^-. Además, aunque durante el periodo de estratificación existe una absorción de CO_2 desde la lámina de agua, la producción de DIC en el hipolimnon excede esa absorción. Por lo tanto, periodos más largos de estratificación favorecerían la producción y emisión de CO_2 desde el embalse. Por otro lado, la mayor superficie de sedimentos expuestos contribuiría aún más a agravar esta situación, incrementando las emisiones de carbono.

Las emisiones desde los sedimentos expuestos fueron un orden de magnitud superiores a las emisiones desde la lámina de agua, pudiendo llegar a representar hasta un 85% de las emisiones totales de carbono en el embalse de El Gergal. Cabe destacar que 2019 fue un año especialmente seco y la superficie de sedimentos emergidos llegó a suponer hasta un 60% de la superficie total del embalse. En este sentido, una gestión hidráulica del embalse, disminuyendo las fluctuaciones del nivel del agua podría contribuir a disminuir las emisiones de carbono desde estas áreas. Por lo tanto, si no se implementan las medidas propuestas por el IPCC para mitigar los efectos del cambio climático y se reduce la demanda de agua, es probable que en el futuro nos enfrentemos a un deterioro de la calidad del agua embalsada así como a un incremento de las emisiones de carbono desde

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los embalses que podrían retroalimentar los cambios hidrológicos.

El creciente interés, experimentado en las últimas décadas, por el papel que juegan los embalses en el ciclo global del carbono es reflejado en el incremento del número de publicaciones al respecto. Sin embargo, aún es necesaria más información sobre cómo el carbono es ciclado en los embalses y cómo este se verá afectado por futuros cambios en la hidrología. Con esta tesis, se contribuye a mejorar el conocimiento sobre los flujos de carbono en embalses y su relación con factores hidrológicos así como se contribuye a completar la visión global aportando información sobre los sistemas mediterráneos. por tanto, en base a los resultados obtenidos se puede concluir que:

1. Los flujos de CO_2 y CH_4 presentan una alta variabilidad espacial y temporal en embalses mediterráneos.

2. El flujo de CO_2 desde la superficie del agua es más alto durante el periodo de mezcla y el metabolismo, especialmente la producción primaria (clorofila-a y pH) parece influir sobre la magnitud y la dirección de este flujo.

3. El flujo de CH_4 es mayor en la zona fluvial y factores hidrológicos tales como el tiempo de residencia y la profundidad de la columna de agua están relacionados con las emisiones de CH_4.

4. La emisión de CO_2 desde los sedimentos expuestos a la atmósfera presenta una alta variabilidad espacial siendo el pH y la humedad los factores más importantes en relación con la magnitud de este flujo.

5. Los sedimentos expuestos a la desecación son áreas muy activas de emisiones de CO_2 y podrían tener un enorme impacto en el balance anual de carbono, incrementando la huella de carbono de estos sistemas artificiales.

6. La producción de CO_2 y CH_4 en el hipolimnion (mmol·m^{-2}·d^{-1}) están en el mismo orden de magnitud que los flujos desde la lámina de agua (difusión y difusión + ebullición, respectivamente) poniendo de manifiesto la relevancia de este compartimento en ciclo del carbono de los embalses mediterráneos.

7. El ciclado de carbono en el hipolimnion juega un papel clave en el balance anual de carbono en embalses mediterráneos.

8. Años secos, con baja precipitaciones y alto tiempo de residencia del agua podrían potenciar la producción de CH_4, metales reducidos, NH_4^+ y H_2S en el hipolimnion, deteriorando la calidad del agua e incrementando la huella de carbono del embalse.

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9. Periodos de estratificación más largos promueven la acumulación de carbono inorgánico disuelto, CH_4 y sustancias reducidas deteriorando la calidad del agua y actuando como una “bomba de relojería” emitiendo mayores cantidades de CO_2 y CH_4 durante el proceso de mezcla.

10. Durante el año 2019, el embalse de El Gergal fue una fuente neta de carbono a la atmósfera, emitiendo incluso más carbono del que se estima que entró en el sistema. Esto podría sugerir que el papel del embalse podría oscilar entre emisor o captador de carbono entre un año y otro dependiendo de las condiciones hidrológicas, resaltando la necesidad de más investigación sobre este aspecto.

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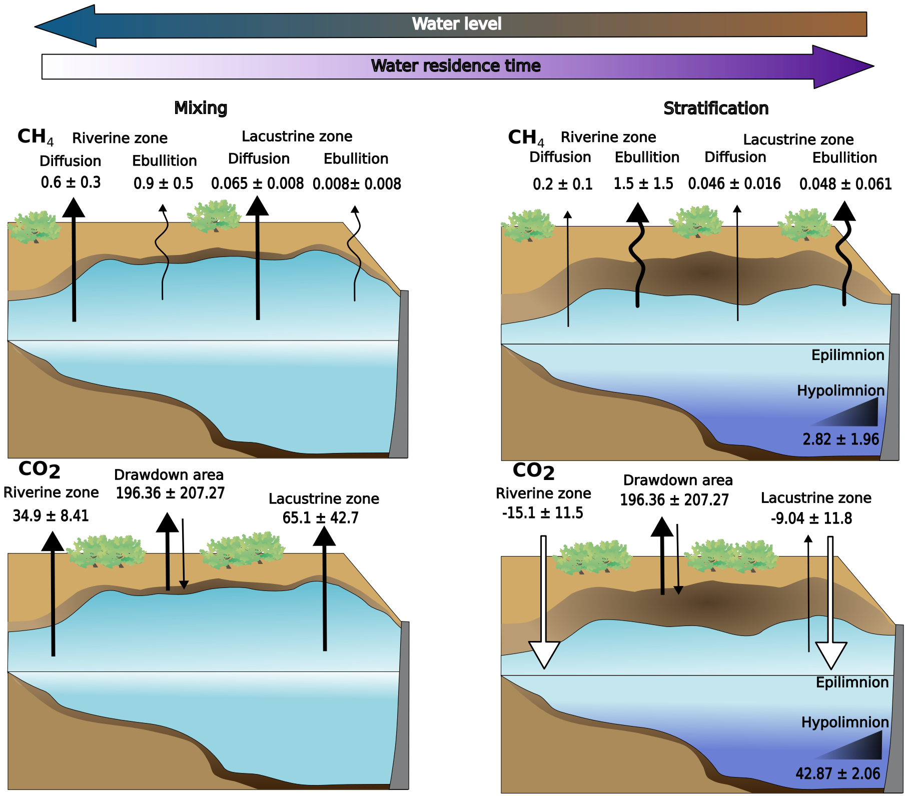

Figure 1.1: Graphical abstract showing main CO_2 and CH_4 fluxes, mmol·m^{-2}·d^{-1} measured in El Gergal reservoir during the stratification period (right) and mixing period (left) as well as main hydrological drivers

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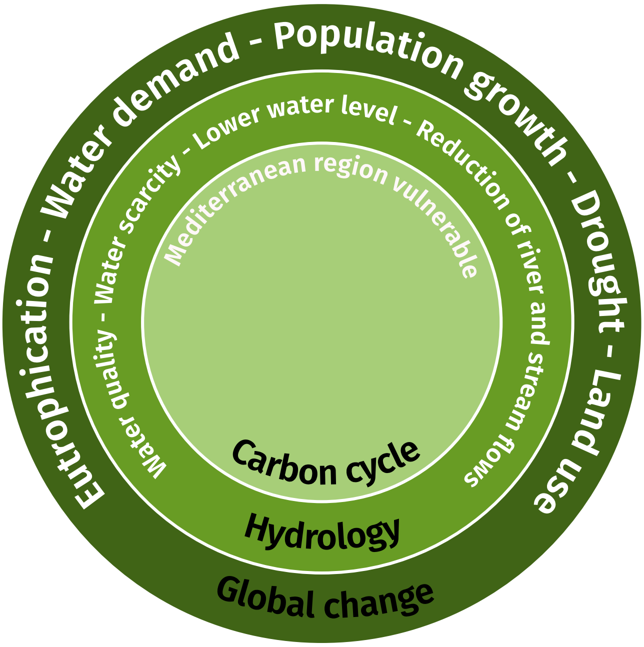
CHAPTER 2

General introduction



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2.1 The role of inland waters in the global carbon cycle

Inland waters, such as streams, rivers, ponds, lakes and reservoirs, can be permanently, seasonally or intermittently flooded, and have great relevance to biodiversity and ecosystem functioning. Humans have been ancestrally linked to inland waters since they provide a wide variety of ecosystem services including provisioning, regulating, cultural and supporting services, the four major categories proposed in the Millennium Ecosystem Assessment report (Rinke et al., 2019). Among these ecosystem services, over the past few decades, researchers have revealed the key role of inland waters in regulating the global carbon cycle (Cole et al., 2007; Tranvik et al., 2018) and the need to be considered in the strategies to mitigate climate change (Battin et al., 2009).

Traditionally, inland waters had been studied as semi-closed systems with a limited impact on local or regional scales. If we consider this view of inland waters and the small area of the global surface that they occupy (less than 3% of the Earth's landmass; Pekel et al. (2016)), it could explain why they have not been taken into account in global carbon cycle assessments until recently. However, now we know that their global relevance is remarkable. Actually, carbon flux from freshwaters to the atmosphere is of the same magnitude ($\sim$ 1.5 $\text{PgC}\cdot\text{yr}^{-1}$), although with the opposite sign, than net flux from oceans ($\sim$ -1.9 $\text{PgC}\cdot\text{yr}^{-1}$) (Raymond et al., 2013; IPCC, 2021). Freshwaters receive a large amount of carbon from terrestrial ecosystems (1.9 Pg C yr^{-1}; Cole et al. (2007)) that are transported to oceans. Nevertheless, as Cole et al. (2007) and Tranvik et al. (2018) highlighted, these ecosystems are not just closed pipes which transport carbon from the land to oceans. Their relevance in the global cycle is based on the fact that inland waters are bioreactors, contributing actively by processing the carbon in transport (Figure 2.1).

Inland waters receive carbon mainly from terrestrial ecosystems but also from in situ primary production. This carbon input has different fates, being transformed, stored, emitted or transported to the ocean (Cole et al., 2007; Tranvik et al., 2018, 2009). Approximately half of the carbon received by inland waters will be directly exported to the oceans, meanwhile, the other half will be transformed and emitted to the atmosphere (in the form of both CO_2 and CH_4) or buried in the sediments of depositional environments (e.g., lakes, reservoirs, floodplains). This defines a dual role in the global carbon cycling for inland waters, which may behave as net sources or sinks of carbon depending on an array of physiographic, hydrological, and ecological circumstances.

Because of these important emissions fluxes, during last years the relevance of emissions from freshwaters systems to atmosphere in the global carbon cycle have been highlighted, both as CO_2 (Battin et al., 2009; Tranvik et al., 2009)

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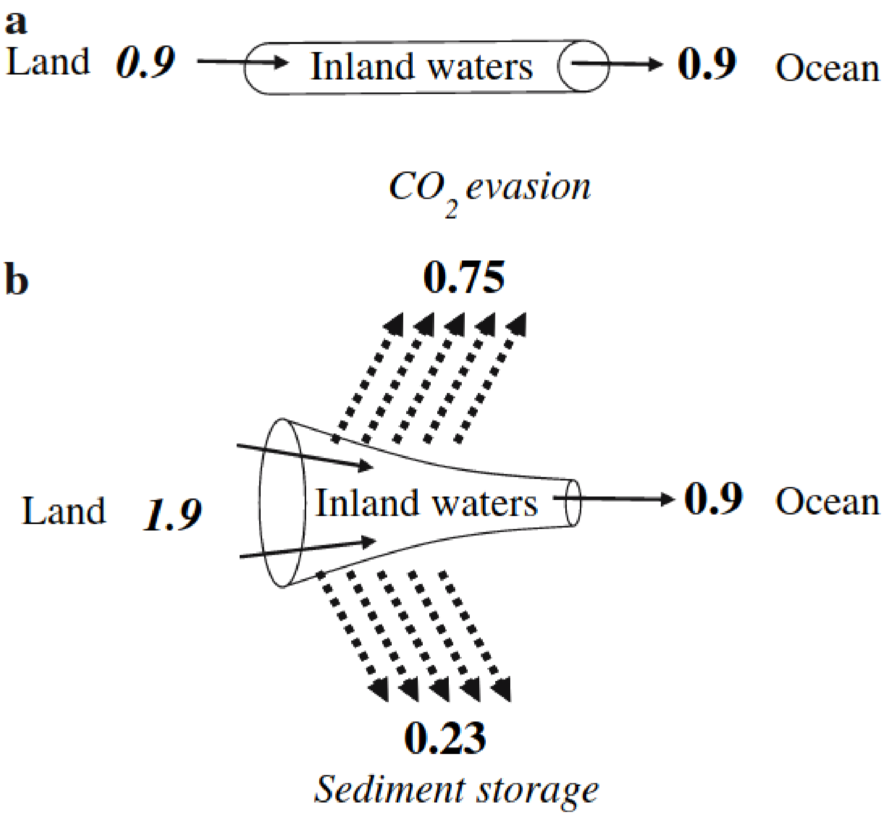

Figure 2.1: Change of paradigm proposed by Cole et al. (2007) whereby inland waters are considered as an "active pipe" (b) instead of systems which just transport the C from the land to the oceans (a)

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and CH_4 (Bastviken et al., 2004a; Tranvik et al., 2009). Actually, emissions from freshwater ecosystems were thought to potentially offset the once so-called continental residual carbon sink (Bastviken et al., 2011). Thus, freshwater systems are a net source of carbon to the atmosphere (Figure 2.2).

On the other hand, it has been widely disseminated that inland waters represent an important carbon sink (Dean and Gorham, 1998). Furthermore, lakes and reservoirs play a significant role offsetting anthropogenic CO_2 emission (Einsele et al., 2001). The principal reason for which lakes and reservoirs are considered a sink of carbon is because they accumulate large amounts of carbon in their sediments. Actually, mainly due to an increase in nutrient availability, freshwater carbon sequestration has increased during the last century, offsetting 20% (30% if reservoirs are included) of CO_2 global emission from freshwater (Anderson et al., 2020; Mendonça et al., 2017).

Therefore, while overall these ecosystems emit an important amount of carbon to the atmosphere, they are also responsible for the accumulation of a significant amount of carbon, and hence constitute a key element in this global biogeochemical cycle. The fate of this carbon (burial Vs mineralization) will be influenced by multiple environmental conditions (Sobek et al., 2009).

Considering these intense carbon fluxes, Battin et al. (2009) pointed out the need to include inland waters in the global carbon cycle and consider it in the strategies to mitigate climate change. However, despite this evident fact supported by scientific research it has not been until the previous fifth IPCC (2013) report when inland waters were included in the global carbon balance. Until that report, inland waters were considered as passive pipes with the only role in the global carbon cycle of transporting carbon from land to oceans.

2.2 Reservoirs relevance in the global carbon cycle

A particular feature of reservoirs is that they are artificial ecosystems. The construction of a dam in a river alter the natural flow of streams and rivers modifying the natural environment and changing flow regime, thermal stratification, depth, water-level fluctuation, land uses, etc (Tremblay et al., 2005). This changes nutrient transformation and impact on natural biogeochemical cycles modifying the timing, quantity, form and location of pre-impounded carbon fluxes (Prairie et al., 2018) and generating hotspots of carbon emissions (Maavara et al., 2020). Notwithstanding, impounded waters have great benefits for society, and therefore have been constructed since ancient times (the oldest known dam is Proserpina reservoir from 1st century BC , located in the Iberian Peninsula). Reservoirs provide a wide variety of services such as water supply, energy, food,

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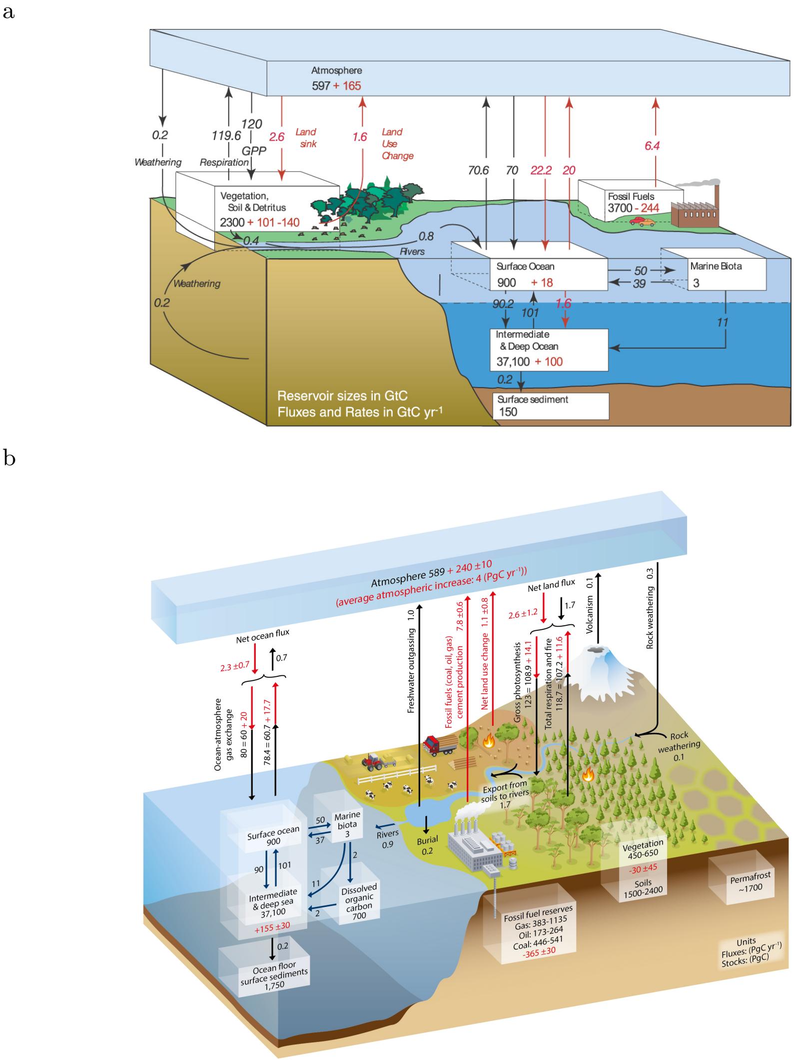

Figure 2.2: Global carbon cycle reported in IPCC's Fourth Assessment Report 2007 (a) without including inland waters role and global carbon cycle reported in IPCC's Fifth Assessment Report 2013 (b) including inland waters role

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recreation, etc (International Commission on Large Dams; https://www.icold-cigb.org) promoting economic activity in the region (Nilsson et al., 2005). At the beginning of this century, around half of the biggest rivers in the world were affected by damming (Nilsson et al., 2005). In addition, owing to population growth and a higher water demand, both energy (hydroelectric) and water supply (drinking water, irrigation), dam construction has been increasing and will probably continue to increase in the next decades (Zarfl et al., 2015; Mulligan et al., 2020).

Within inland waters, reservoirs have been pointed out as one of the most active components in the carbon cycle constituting both a source of carbon, emitting CO_2 and CH_4, and a sink, storing carbon in the sediments (Mendonça et al., 2017; Mendoça et al., 2012). Actually, reservoirs bury around 40% of the total organic carbon stored by inland waters (Mendonça et al., 2017) and only hydroelectric power plants contribute to around 4% of total carbon emissions from inland waters (Barros et al., 2011).

Already in the early 2000's, a study from St. Louis et al. (2000) revealed that greenhouse gas emissions (CO_2, CH_4, and NO_2) from reservoirs depict a relevant role at global scale, representing 7% of the anthropogenic global warming potential. At that moment, the number of studies assessing carbon emission from reservoirs was scarce and, most of them, was focused just on the evaluation the carbon footprint of hydroelectric energy (Rudd et al., 1993; Kelly et al., 1994; Duchemin et al., 1995) without paying attention to the impact of these emission on the global carbon cycle. St. Louis et al. (2000) pointed out that reservoirs are a net source of carbon because all organic carbon stored in the future flooded area (the wood forest or peatland soils) would be degraded and emitted to the atmosphere after the impoundment. In addition, in situ primary production, instead of counteracting this impact, seems to increase methane production enhancing total carbon emissions (St. Louis et al., 2000).

Nevertheless, the net effect of a dam construction on the whole river carbon balance is still not clear (Prairie et al., 2018). Dam construction implies a profound modification of the river course with the consequent displacement of carbon fluxes to or away from the flooded area. This changes the place where carbon is processed along the river land-ocean axis. For this reason, it is quite complex to unravel the "net" effect of a dam construction on the carbon balance in a whole basin scale (Prairie et al., 2018) and more research about carbon fluxes in reservoirs is necessary to shed light into this issue.

2.3 Emissions from the water surface

It is already known that CO_2 and CH_4 emissions from the water surface of inland waters are important and they have a global dimension contributing to

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anthropogenic greenhouse emissions (St. Louis et al., 2000; Deemer et al., 2016). These emissions are mainly a consequence of the transformation of an important fraction of organic and inorganic carbon entering the system, which ends up being released to the atmosphere as CO_2 and CH_4. Due to higher solubility, CO_2 is mainly released to the atmosphere through diffusive processes. Actually, most inland waters have their surface waters oversaturated with respect to the atmosphere (Cole et al., 1994; Raymond et al., 2013). CO_2 can be formed in sediments but the highest fraction of CO_2 exchange across the air-water interface came from CO_2 produced in the water column (Chmiel et al., 2016) and in many cases from inorganic carbon originated by weathering reactions in the watershed (Marcé et al., 2015). A fraction of the organic carbon input can also be processed in anaerobic environments (both anoxic hypolimnion or sediments) through methanogenesis. CH_4 produced in these zones can be released to the atmosphere through diffusion or bubbling (ebullitive flux). CH_4 production is usually higher and more intense in anoxic sediments (Grasset et al., 2018; Sobek et al., 2009). When CH_4 is produced in sediments, its low solubility together with the effect of hydrostatic pressure promote bubble formation and accumulation in the sediment (Liu et al., 2018). These bubbles can be suddenly released to the atmosphere diminishing the possibility of CH_4 oxidation in the water column and, therefore, constituting a shortcut from sediment to the atmosphere (Flury et al., 2015). On the other hand, CH_4 dissolved in the water column can be oxidated (Guérin and Abril, 2007; Yang et al., 2018) or released to the atmosphere through diffusive processes (Bastviken et al., 2004a).

However, these water surface emissions present a high variability (e.g. Bastviken et al. 2004a; McClure et al. 2020). Water surface emissions in reservoirs are influenced by several factors such as trophic state (Deemer et al., 2016), ecosystem age and latitude (St. Louis et al., 2000), and watershed characteristics (León-Palmero et al., 2020). In addition, emissions also depend on hydrological factors such as water level, residence time, runoff, etc (e.g. Yang et al. 2014; Kosten et al. 2018; Paranaíba et al. 2021). As an example, large inflows loaded with organic and inorganic carbon due to runoff and weathering can enhance heterotrophic metabolism and increase CO_2 water concentration promoting CO_2 emissions from water surface (Weyhenmeyer et al., 2015; Vachon et al., 2016). Also, water level drops can induce a hydrostatic pressure diminishing, and therefore promoting the release of CH_4 bubbles trapped into the sediment (Harrison et al., 2017). Furthermore, there is a high internal variability in carbon emission inside of each system implying changes in CH_4 fluxes and CO_2 fluxes over temporal and spatial scale (e.g. Natchimuthu et al. 2016; Yang 2019; Paranaíba et al. 2018; McClure et al. 2020; Yang et al. 2014; Gruca-Rokosz 2020).

Since St. Louis et al. (2000) pointed out the importance of evaluating and including these emissions into global estimations, studies about carbon fluxes in

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reservoirs have increased. However, more research has to be carried out in order to expand the knowledge on understudied geographical zones (e.g. Mediterranean region) and focusing on hydrological effects on spatial and temporal variability of carbon fluxes in reservoirs.

2.4 Emissions from drawdown areas

A fraction of the allochthonous (originated in terrestrial ecosystems), and the autochthonous carbon (derived from in situ primary production), entering water bodies is settled down and stored in the sediment. Organic carbon burial efficiency, the ratio between organic carbon sedimentation and organic carbon accumulation in sediments, is government by different environmental factors and will determine the fate of this carbon (Sobek et al., 2009, 2011; Mendonça et al., 2016). On the one hand, this carbon can be remineralized, and returned to the atmosphere as CO_2 or CH_4, by anaerobic or aerobic processes (Sobek et al., 2009). On the other hand, when electron acceptor availability is low (such as O2 or NO3), carbon remineralization is less efficient and may be unable to oxidase all the organic matter input (Fenchel et al., 2012). Thus, a fraction of this carbon could remain buried for a long time, at time scales of decades-centuries in reservoirs, to millennia in the case of lakes, constituting a significant carbon sink in the global carbon cycle (Mendonça et al., 2017; Cole et al., 2007).

However, when water level drops and sediments become exposed to the atmosphere, microbial activity is enhanced and organic matter aerobic respiration promotes the releasing of large amounts of CO_2 to the atmosphere (Fenner and Freeman, 2011; Jin et al., 2016). Also, an important amount of CH_4, produced under anoxic conditions, can be released when bubbles accumulated in sediments are relieved from hydrostatic pressure exerted by the water column (Kosten et al., 2018). Nonetheless, CH_4 emissions turn into minimal when drying progresses (Yang et al., 2014; Freeman et al., 1993). Therefore, these drawdown areas can remobilize an important amount of carbon that, potentially, could have remained buried in sediments (Marcé et al., 2019).

Traditionally, emissions from drawdown areas have not been taken into account in studies on inland waters contribution to the global carbon cycle (Prairie et al., 2018). Nevertheless, recent studies have revealed that drawdown areas can contribute significantly to the role played by inland waters in the global carbon cycle (Marcé et al., 2019; Keller et al., 2021). These areas can depict carbon fluxes up to one order of magnitude higher than those recorded in surrounding water surfaces (Almeida et al., 2019). Actually, it is estimated that emissions from drawdown areas can represent around 6-10% of total emissions from inland waters (Keller et al., 2020; Marcé et al., 2019) acting as carbon emission hotspots. In the case of reservoirs, considering emissions from drawdown areas could even

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offset the net carbon sink effect attributed to these systems (Keller et al., 2021). However, carbon emission (CO_2 and CH_4) from drawdown areas are still not included within inland water emissions (Marcé et al., 2019) and more research is needed to include reliable estimations of this system in order to achieve a more complete picture of the global carbon cycle.

2.5 Carbon cycling in the hypolimnion

In Mediterranean latitudes, most reservoirs undergo at least one thermal stratification per year. During the stratification period, the water column experiences an intense gradient of density which isolates the deepest and colder water layers of hypolimnion from the shallowest and warmer layers of epilimnion. Hypolimnetic water remains isolated from the surface, preventing contact with the atmosphere and the consequent gas exchange. Isolation of hypolimnion alters carbon transformation processes because of oxygen limitation and usually organic matter is mineralized through anaerobic metabolic pathways. Once the oxygen is depleted in the hypolimnion, organic matter respiration continues through anaerobic processes such as denitrification, dissimilatory metal reduction, sulfate reduction, and methanogenesis. All these metabolic processes generate inorganic carbon (Stumm and Morgan, 1996) which is accumulated in the deep water column. Therefore, changes in oxygen availability in the hypolimnion could alter the role of reservoirs as carbon sinks or sources (Carey et al., 2018). The dominance of some metabolic pathways determine how organic carbon is processed into gaseous, dissolved carbon compounds (CO_2 or CH_4), as well as water quality. In addition, dissolved inorganic carbon (DIC) in the water column and CH_4 accumulated along the stratification period could be released during fall turnover or through withdrawals (degassing). All these fluxes could modify the annual carbon balance in reservoirs. However, most of the studies about the metabolic processes involved in organic matter degradation in the hypolimnion have been carried out in natural systems (lakes) and little attention has been paid to this topic in relation with carbon cycling (Ingvorsen and Brock, 1982; Schindler et al., 1986; Schafran and Driscoll, 1987; Matthews et al., 2008).

2.6 Global change, hydrology and Mediterranean reservoirs

The major effects of climate change are characterised by an increase in temperatures as well as changes in precipitation patterns. At the present time, we already have experienced an increase in temperature and more frequent and intense heat waves (IPCC, 2021). Climate change will provoke changes

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in water quality and quantity with related effects on food supply, recreational and transport opportunities in lakes (Woolway et al., 2020). In addition, many regions in the world are suffering water stress that threatens their development and quality of life. These effects are especially pronounced in Mediterranean regions where there has already been an increase in temperature, hydrological drought frequency and severity in the past five decades in natural, regulated and highly regulated basins (Vicente-Serrano et al., 2014). In addition, it has been reported that global water surface temperature in lakes have increased during the last 50 years (Dokulil et al., 2021).

The Mediterranean region will experience an increase in drought periods (Schleussner et al., 2016; Kovats et al., 2014; Jiménez Cisneros et al., 2014, Figure 2.3). River and stream flows will be lower with a strong reduction of runoffs (Schleussner et al., 2016). These droughts will be more intense and persistent in many zones of Europe but, in particular, southern regions will suffer the sharpest flux reductions (Forzieri et al., 2014). Thus, water levels in lakes and reservoirs are expected to decrease (Cramer et al., 2018). In addition, flood risk associated with extreme rainfall events will increase due to climate change (Cramer et al., 2018). Actually, in the Mediterranean region, reduction of water availability is among the highest in the world (Jiménez Cisneros et al., 2014; Cramer et al., 2018). For this reason, this area is facing a huge water scarcity challenge: an increase in water demand, due to an increase in population and socioeconomic development, in combination with a decrease in availability of freshwater resources (Cramer et al., 2018). Climate change is also intensifying the effects of eutrophication in freshwater (Moss et al., 2011; Jeppesen et al., 2010). Hydrology patterns have been modified due to climate change, decreasing net inflows, wider water level fluctuations and influencing nutrient load and eutrophication (Meerhoff et al., 2022).

The anthropogenic effects on hydrology which alter hydrological cycles both on a regional and global scale are added to global climate change (Shiklomanov, 2009). At a local scale, land use changes modify streamflow flows and regimes (Brook et al., 2011; Stohlgren et al., 1998; Getu Engida et al., 2021) influencing water residence time and water levels. At a global scale, Fekete et al. (2010) showed that direct human impacts such as irrigation and reservoir operations have already altered hydrology in some regions with a similar or higher impact than climate change. Anthropogenic interventions have a negative effect on several river basins, reducing the runoff by 5% or even more (Haddeland et al., 2014). In particular, the negative impact of human-made reservoirs, water withdrawals and water consumption is added to the effects of climate change on runoffs in the Mediterranean region (Haddeland et al., 2014).

Changes in hydrology due to climate changes and anthropogenic activities, such as resource overexploitation, flow diversions, droughts changes in runoff,

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Figure 2.3: Schematic map highlighting in brown the regions where droughts are expected to become worse as a result of climate change. This pattern is similar regardless of the emissions scenario; however, the magnitude of change increases under higher emissions. Extracted from FAQ 8 of IPCC (2021)

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streamflow or water level fluctuation, can have an effect on the inland waters carbon cycle (Kosten et al., 2018; Doubek and Carey, 2017; Weise et al., 2016; Catalán et al., 2014; Keller et al., 2021, 2020; Paranaíba et al., 2021; Liu et al., 2020). This makes the Mediterranean region a vulnerable zone due to expected hydrological changes that could alter natural carbon fluxes in aquatic ecosystems. Alterations of carbon fluxes in turn could enhance climate change through greenhouse gases emissions such as CO_2 and CH_4, and therefore generate a positive feedback effect.

Higher evaporation rates will favour decreases in natural lake level and surface water extent (Woolway et al., 2020) but Pekel et al. (2016) depicted that all continental regions (except Oceania) have shown a net increase in permanent water volume, mainly due to reservoir filling. Therefore, the water overall surface of reservoirs is expected to increase, although it is uncertain how dry drawdown areas will change in the future . This increase of area will probably lead to enhanced relative relevance of carbon fluxes from the water surface of reservoirs in the carbon budget of inland waters. Besides that, although knowledge about CO_2 and CH_4 emission from water surfaces has improved, there is still a great lack of temporal and spatial variability in these processes, especially from reservoir ecosystems (Paranaíba et al., 2018). In addition, hydrological changes could modify this natural variability. In this sense, although there are some studies carried out in Mediterranean reservoirs (Samiotis et al., 2018; Morales-Pineda et al., 2015; León-Palmero et al., 2020) most research is focused on temperate and tropical regions. Additionally, more information is necessary to anticipate the effect of hydrological changes on CH_4 and CO_2 fluxes from the water surface in Mediterranean reservoirs.

In addition to the decrease of water availability due to climate factors, there is a loss of permanent water bodies as a consequence of human activity such as river diversion or unregulated withdrawal (Zafarnejad, 2009; Micklin, 2016). Thus, it should be expected that a bigger area of sediments which used to be submerged become exposed to the atmosphere resulting in an increase of carbon fluxes from these areas. This impact will be particularly intense in reservoirs because, apart from being exposed to water level fluctuation arising from climate change (precipitation and evaporation), they are subject to direct anthropogenic pressures (water demand, withdrawals) (Keller et al., 2021). Actually, the global balance of carbon in reservoirs seems to be overturned by these drawdown areas (Keller et al., 2021). However, as far as we know there are no studies about CO_2 emissions from drawdown areas carried out in Mediterranean reservoirs. Therefore, quantification of carbon fluxes from drawdown areas in Mediterranean reservoirs is required in order to improve our knowledge and outline management strategies which allow us to evaluate the carbon footprint of reservoirs and reduce future emissions.

Climate change has increased lake surface temperature and modified mixing

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regimes (Woolway et al., 2020; Foley et al., 2012). Many lakes will mix less frequently in response to climate change (Woolway and Merchant, 2019). This will result in longer and more stable stratification periods with a higher associated risk of anoxia (Butcher et al., 2015; Burns et al., 2005; Jenny et al., 2016). Moreover, anoxia can be enhanced by primary production increase (Ladwig et al., 2021) as well as by a reduction of water input from rivers (Marcé and Armengol, 2009; Marcé et al., 2010; Azadi et al., 2019) impairing water quality. Longer stratification periods, induced by hydrological changes, increase the risk of anoxia in the hypolimnion and modify both water quality and organic matter cycling. Two previous studies have estimated DIC production in hypolimnion through different metabolic pathways in reservoirs (Wendt-Potthoff et al., 2014; McClure et al., 2021) but none of these studies have focused on the effect of hydrology in DIC production. Therefore, more research about the effect of hydrology is necessary to understand carbon dynamics in the hypolimnion under stratified circumstances in order to anticipate the impact of future hydrological changes both on carbon cycling and water quality in Mediterranean reservoirs.

Hydrological changes are directly related to climate change and human activities. In the cases of reservoirs direct human impact can be even higher because of water abstraction and management. Therefore, under this scenario of hydrological changes, intensity and distribution (both spatial and temporal) of carbon fluxes from water surface and drawdown areas, as well as carbon cycling and water quality in the hypolimnion, could undergo significant modifications. In spite of the Mediterranean region being a highly vulnerable area to climate change and human pressures, hydrological change effects in the carbon biogeochemistry of Mediterranean reservoirs have received little attention. Most studies have been carried out in temperate zones and the proportion of studies about effects of hydrological changes in carbon fluxes of Mediterranean reservoirs are scarce. Therefore, this thesis aims to contribute to the knowledge about the effect of hydrological changes on carbon dynamics in a Mediterranean reservoir.

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CHAPTER 3

Aim and objectives

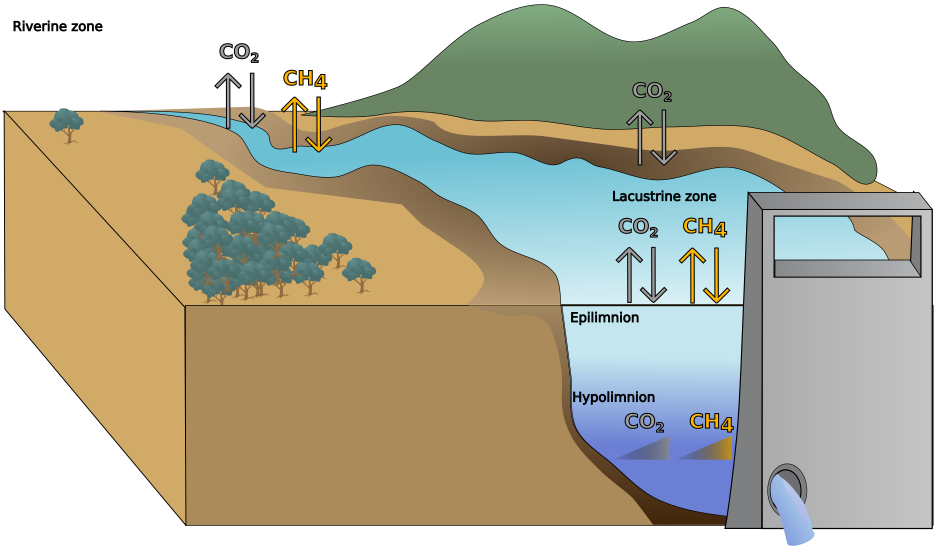

Figure 3.1: Schedule of CO_2 and CH_4 fluxes measure for this thesis dissertation

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The overall aim of this thesis is to understand how changes in hydrology and thermal structure affect carbon cycling in reservoirs. Here, carbon cycling is studied using three different approaches which measure carbon flux from/to three different compartments: water surface, drawdown areas and isolated hypolimnetic waters. Each of these compartments are addressed in a specific chapter. In addition, a secondary aim of this thesis is to contribute to the knowledge of carbon cycling in reservoirs quantifying temporally and spatially the magnitude CO_2 and CH_4 fluxes in a Mediterranean system.

The general hypothesis is that hydrological and thermal structure changes will modify carbon cycle in reservoirs. Greater drawdown areas will lead to higher CO_2 emissions from the area occupied by the reservoir because of alteration of the ratio between water surface and drawdown areas. Also, it is expected that longer stratification period will produce higher amounts of CO_2 and CH_4 in the hypolimnion.

Specific objectives:

1. The main goal in Chapter 4 is to analyse spatial and temporal variability in CO_2 and CH_4 fluxes from the water surface of a Mediterranean reservoir and to explore the relationship between the magnitude and sign of these fluxes and hydrological (i.e. water residence time and water level) and limnological (i.e chlorophyll-a and pH) variables.

2. In Chapter 5 the main objective is to quantify CO_2 fluxes from drawdown areas in a Mediterranean reservoir and to explore relations with physico-chemical sediment features in order to provide better local and global estimations of carbon fluxes from reservoir, specially Mediterranean reservoirs.

3. The objective of Chapter 6 is to quantify carbon fluxes through diverse heterotrophic metabolic pathways (aerobic respiration, denitrification, sulfate reduction, Fe and Mn reduction and methanogenesis) and their contribution to DIC production in the hypolimnion of a Mediterranean reservoir during two thermally stratified periods with contrasting hydrological features.

4. In Chapter 7, all results obtained for this thesis are combined in order to estimate an annual carbon balance and to obtain an overall view of carbon cycling in a Mediterranean reservoir.

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CHAPTER 4

Spatio-temporal variability of carbon dioxide and methane emissions from a Mediterranean reservoir

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This chapter have been published in Limnetica and the original publication can be found here.

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Abstract

Freshwater reservoirs constitute a significant source of carbon dioxide (CO_2) and methane (CH_4) to the atmosphere, and a precise quantification of the magnitude of these greenhouse gas emission on an annual scale is required. This quantification must consider both temporal and spatial variability of reservoir carbon gas fluxes. In addition, it is relevant to reinforce research focusing on the emission of CO_2 and CH_4 in Mediterranean reservoirs. Here, we simultaneously measured CO_2 fluxes and CH_4 ebullitive and diffusive emissions in the riverine and lacustrine zones of a Mediterranean reservoir (El Gergal, Spain) throughout a complete year to quantify their magnitude, explore their spatial and temporal variability, and investigate the potential limnological and hydrological factors influencing gases emissions. Our results show that during the study year El Gergal riverine zone was a CO_2 sink, while the lacustrine zone was a CO_2 source. In addition, both areas were CH_4 sources to the atmosphere. CO_2 and CH_4 fluxes in El Gergal showed a marked temporal variability, with significant differences between mixing and thermally stratified periods. CO_2 emissions were significantly influenced by surface chlorophyll-a concentration and pH, suggesting the prevalent role of primary production as CO_2 flux driver. CH_4 emissions were influenced by hypolimnetic methane concentration and hydrological factors potentially affected by climate change, such as water renewal rate and water column depth.

Reference

Montes-Pérez, Jorge J., Obrador, B., Conejo-Orosa, T., et al. (2022) Spatio-temporal variability of carbon dioxide and methane emissions from a Mediterranean reservoir. *Limnetica*, volume 41, page 43-60. DOI: 10.23818/limn.41.04

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CHAPTER 5

Carbon dioxide emission from drawdown areas of a Mediterranean reservoir

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Abstract

Sediment beds from drawdown areas of reservoirs constitute a relevant hotspot for carbon dioxide (CO_2) emission to the atmosphere. This CO_2 is especially relevant in the case of Mediterranean reservoirs, where hydrological variability favors the exposure of large sediment areas to air. In spite of this, the role of dry sediments as CO_2 emitters has been typically neglected in lakes and reservoirs greenhouse gas emission assessments, and there is also a lack of research on the spatial variability of CO_2 fluxes from drawdown sediments. In this study we contribute to this knowledge by combining drone-based aero-photogrammetry techniques with in situ infrared gas analyzer measurements to assess the magnitude and spatial variability of CO_2 fluxes from the drawdown area of a Mediterranean reservoir (El Gergal, Southwestern Spain) during one dry season. Our results show that during survey dry sediments in El Gergal were a relevant net CO_2 source to the atmosphere, with a mean emission of 0.36 ± 0.38 $gCO_2 \cdot m^{-2} \cdot h^{-1}$. In addition, CO_2 fluxes from El Gergal drawdown depict a marked spatial variability, with maximum values measured in areas influenced by river or intermittent streams discharges. Distance to the shore, sediment particle size, pH and temperature also have a significant effect on CO_2 emissions from the reservoir dry banks. The expected strengthening of droughts intensity and frequency in the Mediterranean region could enhance the role of exposed sediments from the drawdown of reservoirs as CO_2 source to the atmosphere.

Reference

Pozzo-Pirotta, L. J., Montes-Pérez, Jorge J., Sammartino, S., et al. Carbon dioxide emission from drawdown areas of a Mediterranean reservoir. *Limnetica*, volume 41, page 61-72. DOI: 10.23818/limn.41.05

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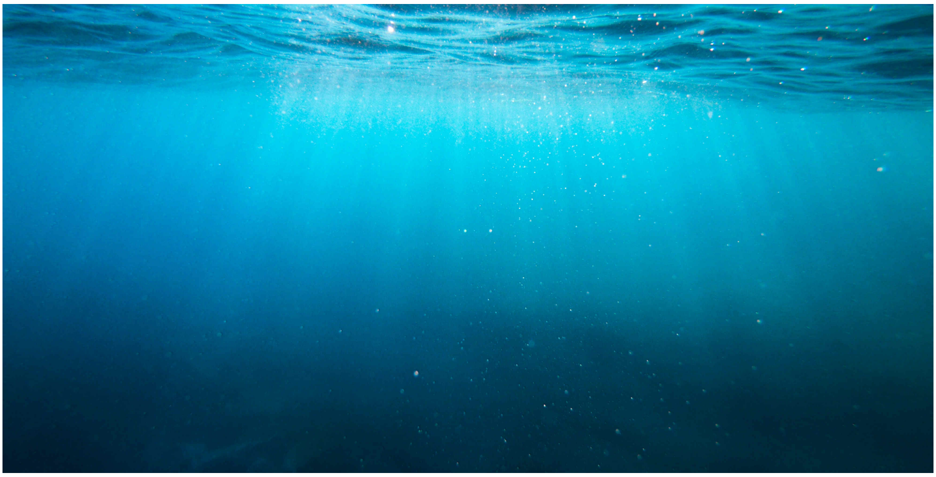
CHAPTER 6

Hydrology influences carbon flux through metabolic pathways in the hypolimnion of a Mediterranean reservoir

Published in Aquatic Sciences (2022), 84:1-16



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This chapter have been published in Aquatic Sciences and the original publication can be found here.

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Abstract

Global change is modifying meteorological and hydrological factors that influence the thermal regime of water bodies. These modifications can lead to longer stratification periods with enlarged hypolimnetic anoxic periods, which can promote heterotrophic anaerobic processes and alter reservoir carbon cycling. Here, we quantified aerobic and anaerobic heterotrophic processes (aerobic respiration, denitrification, iron and manganese reduction, sulfate reduction, and methanogenesis) on dissolved inorganic carbon (DIC) production in the hypolimnion of a Mediterranean reservoir (El Gergal, Spain) under two contrasting hydrological conditions: a wet year with heavy direct rainfall and frequent water inputs from upstream reservoirs, and a dry year with scarce rainfall and negligible water inputs. During the wet year, water inputs and rainfall induced low water column thermal stability and earlier turnover. By contrast, thermal stratification was longer and more stable during the dry year. During wet conditions, we observed lower DIC accumulation in the hypolimnion, mainly due to weaker sulfate reduction and methanogenesis. By contrast, longer stratification during the dry year promoted higher hypolimnetic DIC accumulation, resulting from enhanced methanogenesis and sulfate reduction, thus increasing methane emissions and impairing reservoir water quality. Aerobic respiration, denitrification and metal reduction produced a similar amount of DIC in the hypolimnion during the two studied years. All in all, biological and geochemical (calcite dissolution) processes explained most of hypolimnetic DIC accumulation during stratification regardless of the hydrological conditions, but there is still $\sim 30\%$ of hypolimnetic DIC production that cannot be explained by the processes contemplated in this study and the assumptions made.

Reference

Montes-Pérez, Jorge J., Marcé, R., Obrador, B., et al. Hydrology influences carbon flux through metabolic pathways in the hypolimnion of a Mediterranean reservoir. *Aquatic Sciences*, volume 84, pages 1–16. DOI: https://doi.org/10.1007/s00027-022-00867-2

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CHAPTER 7

General discussion

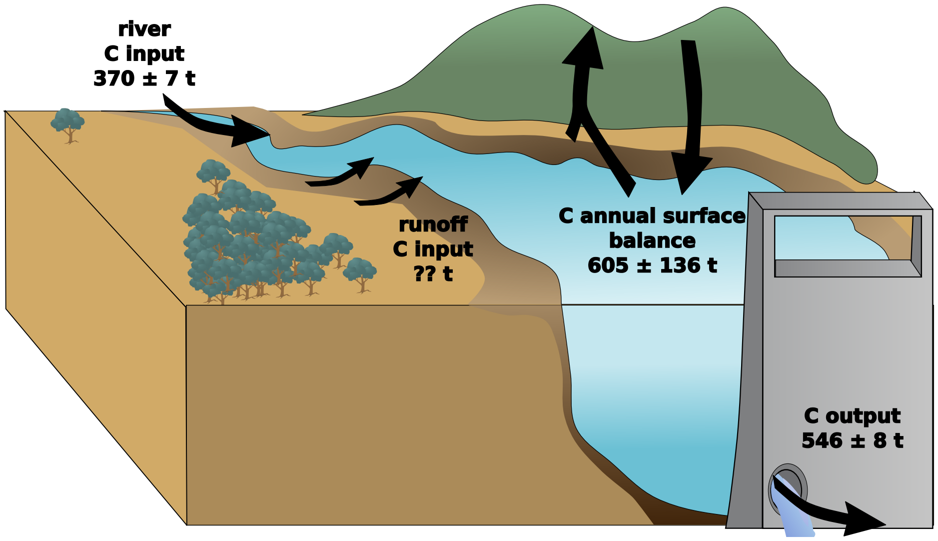

Figure 7.1: Conceptual schedule of carbon cycle for 2019 in El Gergal reservoir

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The construction of a dam alters the natural course of water and modifies biogeochemical cycles (Maavara et al., 2020). Among these impacts, the carbon cycle is one of the most important because of its great relevance for the climate (IPCC, 2021). Carbon cycling in a reservoir occurs in two main compartments: water column and sediments. In the water column, organic and inorganic carbon are biologically or abiotically processed and this carbon will have different fates: buried in the sediment, exported downstream, or emitted to the atmosphere (DelSontro et al., 2018; Deemer et al., 2016; Bastviken et al., 2008; Cole et al., 2007). However, during the stratification period, the water column is divided into two layers more or less isolated by the thermocline: epilimnion and hypolimnion. Epilimnion is in contact with the atmosphere and exchanges gases directly between water and air ,but hypolimnion is isolated from the atmosphere and emissions will occur mostly after fall turnover (Park and Chung, 2018; Halbedel and Koschorreck, 2013). On the other hand, sediments can process an important amount of carbon and they usually will exchange carbon with the water column but, when the water recedes due to water level variations, sediment will exchange carbon directly with the atmosphere (Marcé et al., 2019; Kosten et al., 2018; Almeida et al., 2019).

In addition to this alteration of natural water course, hydrological changes are modifying the role of each compartment in the reservoir carbon cycle. The purposes of this general discussion chapter are1) to recap main results obtained in previous chapters, 2) to depict an schedule of direction and magnitude of main fluxes measured in the reservoir, 3) to discuss about potential effects of future hydrological changes on studied fluxes, and 4) to highlight questions still open to be resolved by future research.

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7.1 Fluxes from water surface

In El Gergal, carbon dioxide and methane fluxes from the water surface showed a high spatial-temporal variability, with values similar to those reported in the literature both for CO_2 (Lazzarino et al., 2009; Trolle et al., 2012; Halbedel and Koschorreck, 2013; Morales-Pineda et al., 2014; Deshmukh et al., 2018; Soumis et al., 2004; Schrier-Uijl et al., 2011; Barros et al., 2011; Beaulieu et al., 2014; Samiotis et al., 2018) and CH_4 (Weyhenmeyer, 1999; Dove et al., 1999; Bastviken et al., 2004a, 2008; DelSontro et al., 2010; Wik et al., 2013; Xiao et al., 2013; Musenze et al., 2014; DelSontro et al., 2016; Natchimuthu et al., 2016; Samiotis et al., 2018).

As an annual average, the riverine zone is a net sink of CO_2 while the lacustrine zone is a source, a pattern also reported for tropical reservoirs Paranaíba et al. (2018). However, both zones showed a clear temporal pattern with positive fluxes (emissions) during the mixing period and negative fluxes (uptake) during stratification (Figure 5 Chapter 4), in line with findings from other studies (Halbedel and Koschorreck, 2013; Saidi and Koschorreck, 2017). Nonetheless, in reservoirs there is a daily scale variability of CO_2 fluxes which seems to be driven by biological activity and convective processes (Morales-Pineda et al., 2014). In this study, measures were carried out during the day, implying that, on a daily basis, fluxes have been most likely underestimated (Morales-Pineda et al., 2014; Liu et al., 2016; Ran et al., 2022). Actually, recent studies conducted in reservoirs, suggest that carbon fluxes measured at daytime could underestimate by 9-25% (Ran et al., 2022) or even by 42% (Liu et al., 2016) whole-day emissions. Thus, this can counteract to some extent the CO_2 uptake observed during the stratification and increase the emissions measured during the mixing period.

Regarding relationships between CO_2 fluxes and physico-chemical variables in El Gergal, uptake during stratification seems to be related to primary production, mainly pH and chlorophyll, as has also been reported for other reservoirs and lakes (Lazzarino et al., 2009; Trolle et al., 2012; Saidi and Koschorreck, 2017; Samiotis et al., 2018; Paranaíba et al., 2018). In the Mediterranean region, stratification is associated with an increase of temperature and a higher irradiance enhancing primary production and, therefore promoting the uptake of CO_2 by photosynthetic organisms (Likens, 1973). Moreover, during the stratification period a fraction of primary and secondary production that take place in the epilimnion will be exported through sedimentation to the hypolimnion and it will be partially or completely remineralized there. The very low mixing processes between both layers avoid that CO_2 produced in the hypolimnion crosses the thermocline into the epilimnion and is emitted to the atmosphere. Later on, CO_2 accumulated in the hypolimnion will be released during the fall turnover(Park and Chung, 2018; Deemer et al., 2016), representing a subsidiary emission of production and

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respiration that took place during the thermally stratified period. During the mixing period, respiration is favoured over primary production due to a decreasing irradiance and a higher input of allocthounus carbon through river discharges (Barros et al., 2011; St. Louis et al., 2000). Even more, a significant fraction of CO_2 accumulated in the hypolimnion during stratification will be emitted during this mixing period. This effect is more pronounced in the lacustrine zone as a result of its greater depth which favours a more stable and longer stratification period, a higher hypolimnetic volume and, therefore, a higher accumulation of CO_2.

Regarding CH_4 emissions, El Gergal reservoir was, during the study period, a net source of CH_4 to the atmosphere throughout the whole year. Spatial variability was more remarkable than temporal variability. Emissions were more intense in the riverine zone, where higher organic matter input and lower depth boots methane production in the sediment and bubble releasing (Beaulieu et al., 2020; West et al., 2016; Grinham et al., 2018; Sobek et al., 2012; Schubert and Wehrli, 2018). In El Gergal reservoir, ebullitive flux rates, which represent between 40-80% of total CH_4 emissions, were higher in shallow zones when residence time was higher. Higher residence time promotes anoxia enhancing methanogenesis and, therefore increasing dissolved CH_4 concentration in the sediment, which can be released as gas bubbles when hydrostatic pressure is low due to low water level.

7.2 Drawdown area

Drawdown areas in El Gergal reservoir were a net source of CO_2 to the atmosphere with an average emission rate of 196.36 ± 207.27 $mmol \cdot m^{-2} \cdot d^{-1}$ consistent with rates reported for other drawdown areas in reservoirs (Jin et al., 2016; Almeida et al., 2019; Marcé et al., 2019; Keller et al., 2021). However, there was a relevant spatial variability with higher emission fluxes close to river discharge zones in coherence with the higher carbon fluxes recorded for dry beds in streams (Gómez-Gener et al., 2016, 2015). In addition, a significant relationship were found in Gergal between carbon fluxes from drawdown areas and distance to the shore, temperature, pH and sediment particle size, suggesting that these variables could be important drivers for CO_2 emissions, in agreement with previous studies (Jin et al., 2016; Keller et al., 2020).

7.3 Hypolimnetic carbon cycling

During the stratification period, El Gergal reservoir hypolimnion became anoxic, accumulating reduced substances (such as HS^- and metals) and, therefore, impairing water quality. In addition, an important amount of CO_2 and CH_4 were

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accumulated in the hypolimnion, with rates ranging from 41 to 45 $\mathrm{mmol \cdot m^{-2} \cdot d^{-1}}$ for CO_2 and from 0.86 to 4.78 $\mathrm{mmol \cdot m^{-2} \cdot d^{-1}}$ for CH_4, values in the range of those reported in other studies Jones and Simon (1980); Schafran and Driscoll (1987); Kelly et al. (1988); Fahrner et al. (2008); Wendt-Potthoff et al. (2014); Matthews et al. (2008); McClure et al. (2020); Mattson and Likens (1993). When thermal stratification breaks down and hypolimnetic water is mixed with epilimnetic water, hypolimnetic CO_2 and CH_4 can be released to the atmosphere accounting for a relevant fraction of the CO_2 and CH_4 reservoir emissions (Fahrner et al., 2008; Encinas-Fernández et al., 2014; Vachon et al., 2019; Deemer et al., 2016; Park and Chung, 2018). The two studied years showed marked hydrological differences. On the one hand, during the dry year (2019), low precipitation, low water volume and high residence time lead to higher rates of CH_4 production, as has been found in previous studies (Hounshell et al., 2021; McClure et al., 2020). In addition, late summer rates seems to be enhanced by an increase of organic matter input into the hypolimnion from the epilimnion (Fahrner et al., 2008). On the other hand, during the wet year with higher water inputs and lower residence time, lower masses of reduced substances, CO_2, and CH_4 were accumulated in the reservoir hypolimnion.

7.4 Annual carbon balance in El Gergal reservoir

Carbon enters into the reservoir mainly from the river or from the atmosphere (uptake or deposition) and leaves it to downstream or to the atmosphere (emission). A fraction of this carbon can be sequestered inside the system, being buried into the sediment. Incoming carbon can be processed in the sediment as well as in the water column, and fluxes between both compartments can be established. Water column exchanges carbon directly with the atmosphere, while sediment exchanges carbon with the water column. However, during the low water level periods sediment becomes exposed to the air, and exchanges gases directly with the atmosphere. Also, during the stratification period, an important fraction of the water column (hypolimnion) and of the sediment remains isolated from atmospheric exchange for months. Carbon cycled under the thermocline will be accumulated in the hypolimnion. Unravelling these fluxes provides a global picture of the carbon cycle in the reservoir. In this PhD Thesis fluxes between the atmosphere and both water surfaces and drawdown areas, as well as carbon produced in the hypolimnion, were measured. In addition, for this section of general discussion, carbon fluxes from upstream (input) and to downstream (output) have been estimated (Section B.0.5). Therefore, here information from the three previous chapters is integrated to build a simplified model/picture of the carbon cycle in El Gergal reservoir.

El Gergal is a warm monomictic Mediterranean reservoir. This implies that

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the reservoir undergoes two hydrodynamic situations well defined along the year: turbulent mixing and thermally stratified period. During the stratification period, water level is usually lower, drawdown areas of exposed sediments is larger, and the water column is split into two layers: epilimnion and hypolimnion. On the other hand, during the mixing period, water level is higher, there is less surface of sediments exposed to the air, and the water column is completely mixed.

7.4.1 Thermally stratified period

During the stratification period, riverine and lacustrine zones depict the same CO_2 emissions pattern, overall, both uptaking CO_2 from the atmopsphere. However, total CO_2 emissions (tons of CO_2 per year) were much lower in the riverine than in the lacustrine zone. This is due to surface area in this zone represents just ~18% of total reservoir surface, both areas show similar rates ($mmol \cdot m^{-2} \cdot d^{-1}$) but riverine zone represents a smaller area of the total reservoir surface.

In this situation, the water surface of the whole reservoir can be considered as a CO_2 sink. However, during all this period, hypolimnetic respiration processes accumulate CO_2 in the reservoir deep layers. This accumulated carbon will be released eventually upon fall turnover (Park and Chung, 2018), becoming a carbon time bomb. In addition, drawdown areas are a net source of carbon to the atmosphere as has been observed in others systems (Deshmukh et al., 2018; Jin et al., 2016), the surface of drawdown areas is larger during stratification, and consequently the ratio dry sediment:water surface is higher, thus increasing the total emission from these drawdown areas and its relative importance with respect to the total reservoir balance (Figure 7.2). Therefore, during the stratification period, drawdown areas counteract the uptake from the water surface. Actually, in this period drawdown areas usually represented around 34% (out of 276 ha) of the total reservoir surface. In this situation, emissions from drawdown areas could represent $\sim 1323 \pm 424$ t CO_2 meanwhile uptake from water surface would account for $\sim -198 \pm 63$ t CO_2 (Figure 7.2). Therefore, CO_2 emissions in El Gergal from drawdown areas are relevant during stratification period and the uptake from water surface could be offset by these sedimentary emissions. Moreover, during the stratification period, DIC produced in the hypolimnion doubled the C fixed in the epilimnion (Figure 7.2). This highlights the relevance of hypolimnetic carbon cycling in the mass balance of carbon in the reservoir.

CH_4 emissions during stratification were always positive. Both in riverine and in lacustrine zone, bubbling is the dominant flux probably due to higher anoxia in the sediment, which enhance methanogenesis, and a lower water level during this period which promote formation and releasing of CH_4 bubbles (West et al., 2016; Bastviken et al., 2004b). During August it could be observed a noticeable rise of CH_4 diffusion emissions, while bubbling experienced a decrease

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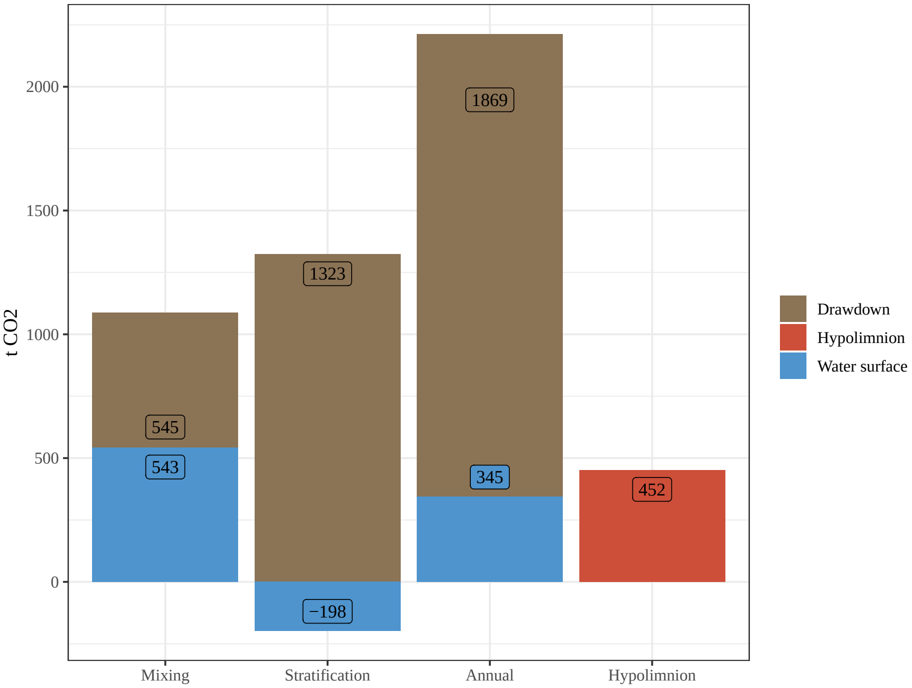

Figure 7.2: Total CO_2 emitted (positive values) or taken up (negative values) in El Gergal reservoir during 2019. “Mixing” and “Stratification” columns show total balance during theses periods, “Annual” column shows the balance for the whole year and “Hypolimnion” column shows the total CO_2 produced in the hypolimnion during the stratification period

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in both zones. This seems to be related to an important water level drop due to a great withdrawal carried out previously during that month. Water level drop could promote bubbling and a thermocline sink (Figure 1 Chapter 6; Beaulieu et al. (2018); Painuly and Katsman (2022); Casamitjana et al. (2003); Li et al. (2018); Moreno-Ostos et al. (2008)). We posit that a large proportion of bubbles accumulated in the sediment were released in a short period of time and bubbling was reduced after that episode. In addition, thermocline sinks would provoke a mixing of hypolimnetic water with epilimnetic water increasing CH_4 concentration and, therefore enhancing CH_4 diffusion. This particular event suggests that reservoir management has a short-term effect on CH_4 emissions. CH_4 emission from dry exposed sediments were not measured in this work, but it could be expected to be high during first moment of sediment exposition to the atmosphere Kosten et al. (2018); Jin et al. (2016), and to diminish as drying progress and oxygen reaches the sediment (Yang et al., 2014; Freeman et al., 1993). Moreover, Paranaíba et al. (2020) showed that after a drying process and a rewetting, CH_4 emission from the sediment does not experience a peak. This could suggest that shallow drawdown areas, frequently exposed to water level fluctuation, should not emit an important amount of CH_4. In relation to total CH_4 produced in the hypolimnion, it was an order of magnitude higher than CH_4 emitted to the atmosphere, reinforcing the idea of the importance of hypolimnetic carbon cycling in the whole reservoir carbon cycle.

7.4.2 Turbulent mixing period

During the mixing period, carbon produced in the sediment and in the water column is exchanged with the atmosphere throughout the water surface. Mean measured CO_2 flux for this period was 543 ± 55 t CO_2 (Figure 7.2) which shows that water surface is a source of CO_2. It should be noticed that a particularly high rate of CO_2 emission was measured during January. This high rate is probably a consequence of the release of the CO_2 accumulated in the hypolimnion during stratification, as suggested by other authors (Park and Chung, 2018). In fact, rates in the riverine and lacustrine zone were similar during the whole year meanwhile in January, after fall turnover, rates were much higher in the lacustrine zone. Keeping in mind that stratification in the reservoir riverine zones is anecdotal, because of its shallowness, this reinforces the hypothesis that hypolimnetic CO_2 is responsible for this emission.

Furthermore, CH_4 diffusive flux was also higher during this month, supporting that the mixing process is responsible for this pattern. In El Gergal reservoir there are relevant water level fluctuations even during the mixing period, exposing sediment to dessication. Actually, drawdown area represents around 22% of the total reservoir surface during this period. In this situation drawdown areas can

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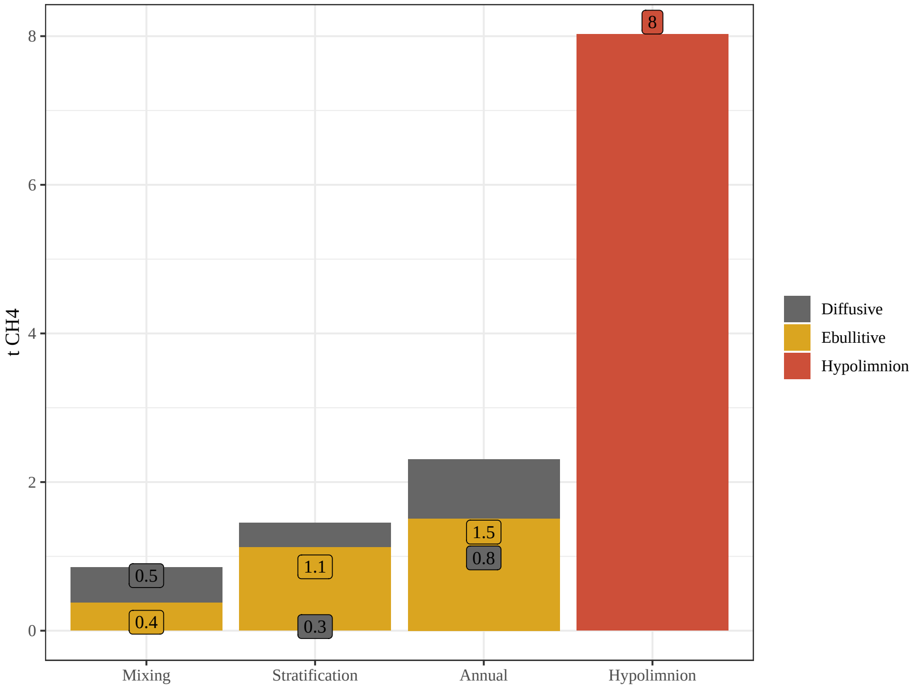

Figure 7.3: Total CH_4 emitted in El Gergal reservoir during 2019. “Mixing” and “Stratification” columns show total balance during theses periods, “Annual” column shows the balance for the whole year and “Hypolimnion” column shows the total CH_4 produced in the hypolimnion during the stratification period

emit as much CO_2 as water surface 545 ± 249 t de CO_2 (Figure 7.2). Therefore, emissions from drawdown areas during this period account for around 50% of total emissions.

In terms of CH_4 emission during mixing period diffusive and ebullitive fluxes were similar (Figure 7.3). However, diffusive flux is dominant over ebullitive in the lacustrine zone meanwhile ebullitive flux exceeds diffusive flux in the riverine zone probably due to lower depth, which favours bubbles release (Beaulieu et al., 2020; West et al., 2016) and a higher organic matter input from the river, which enhance methanogenesis and, therefore CH_4 bubbling (Hilgert et al., 2019; Kelly and Chynoweth, 1981).

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7.4.3 Annual carbon balance

The relevance of riverine and lacustrine zones in an annual balance for the whole reservoir was different for CO_2 and CH_4 emissions. For CO_2 emissions, riverine and lacustrine zones showed similar fluxes per unit of area ($mmol \cdot m^{-2} \cdot d^{-1}$) and as a consequence relative importance was based on the surface area that each zone occupied. On the contrary, CH_4 fluxes from the riverine zone were two fold higher than in the lacustrine zone. These higher fluxes make the riverine zone a hot spot of CH_4 emission despite the relatively small area that represents for the whole reservoir ($\sim$ 20%), this pattern was also found in other reservoirs (Yang, 2019; Paranaíba et al., 2018; Delsontro et al., 2011). The total mass of CH_4 emitted from the riverine zone is in the same order of magnitude as the lacustrine zone. In the whole reservoir, contribution of ebullition to total CH_4 emissions was around 60%, a value in the range reported for other ecosystems (Schubert and Wehrli, 2018; Weyhenmeyer, 1999; DelSontro et al., 2016; Natchimuthu et al., 2016). However, bubbling was the main way of CH_4 emission in the riverine meanwhile diffusion dominated emissions in the lacustrine zone. The two main factors under this pattern seem to be carbon input and water column depth. The carbon input is usually higher in the riverine zone because of river inflow and that promotes methanogenesis in the sediments (Kelly and Chynoweth, 1981). Water column depth is a key factor in CH_4 ebullition (Beaulieu et al., 2020; West et al., 2016) promoting bubble release when depth is shallow. On the other hand, when water level is high, CH_4 ebullition is hampered by hydrostatic pressure and, therefore diffusion increases (McGinnis et al., 2006). The implication of this is that when diffusive fluxes predominate, an important fraction of methane is oxidised in the water column; meanwhile when ebullition is more important, it represents a bypass of CH_4 from the sediment to the atmosphere.

CO_2 emissions from drawdown areas of the riverine and lacustrine zone were really important, representing one order of magnitude higher emissions than water surface in both cases. In a gross annual balance assuming these two situations, carbon emissions from drawdown areas could represent 85% of the total reservoir emissions, higher than estimations from Keller et al. (2021), who reported an increase by 53% due to drawdown areas, but similar to Deshmukh et al. (2018), who reported that these emissions could be 40-75% of total annual emissions. However, it must be underlined that 2019 was a specially dry year with precipitation below the annual mean of the last 20 years. During this year, drawdown areas represented up to 40% and 60% of total surface for the lacustrine and the riverine zone respectively. Therefore, due to this higher contribution of drawdown areas to total annual CO_2 emission from the reservoir, management strategies should try to keep water level of reservoirs as high as possible in order to mitigate total CO_2 emissions and reduce carbon footprint of hydropowers.

Hypolimnion played a key role in the reservoir carbon cycling. CH_4 production

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during stratification was an order of magnitude higher than total annual emissions from water surface. Regarding CO_2, production in the hypolimnion is so high that it can be compared with total emission during mixing and may account for up to 80% of these emissions. Additionally, in reservoirs, water withdrawals from depths under the thermocline can release a significant amount of CH_4 and CO_2 downstream which could be emitted to the atmosphere through degassing (Bastien et al., 2011). Assuming that total CH_4 emitted in the lacustrine is formed during stratification and deducing CH_4 released downstream, CH_4 oxidation in El Gergal must be around 80%, an estimation very similar to the percentage usually reported in the literature (Reeburgh, 1996; Frenzel et al., 1990; Hanson and Hanson, 1996).

Total annual emission from the reservoir was ∼2200 t CO_2 per year and ∼2 t CH_4 per year (Figures 7.2 and 7.3), with average areal rates similar to tropical reservoirs (Abril et al., 2005; Rodriguez and Casper, 2018; Kemenes et al., 2011). Considering these emissions and input and output estimation, the annual balance indicates that El Gergal reservoir in 2019 was a net source of carbon to the atmosphere. Note that during this year a significant net loss of water volume was recorded in the reservoir as a result of scarce precipitation and water inputs. Hence, the amount of carbon that was lost via water withdrawal was higher than the amount of carbon input by river inflow. If the effect of carbon loss due to volume deficit was removed, the reservoir will still be a net emitter but with a lower emission rate (600 t C per year) (Figure 7.4). This could be explained by different factors: water runoff inputs (Tranvik et al., 2018; DelSontro et al., 2018), pre-flooded buried carbon (Teodoru et al., 2011; Barros et al., 2011) or buried carbon previous years (Dean and Gorham, 1998; Mendonça et al., 2017). Water runoff could contribute to carbon input, however during the studied year precipitation was scarce (< 300 mm) therefore it could be expected that the effect of runoff was minimal. On the other hand, it is difficult to estimate the proportion of emissions due to this pre-flooded carbon because it depends on multiple factors (Teodoru et al., 2011; Barros et al., 2011). Nevertheless, it seems to be an important source of carbon just for young reservoirs (less than 15 years) (Barros et al., 2011). Moreover, emissions due to pre-flooded organic matter respiration seem to decrease exponentially with time (Barros et al., 2011; Teodoru et al., 2011) and El Gergal reservoir was flooded 40 years ago, therefore pre-flooded buried carbon should not be a relevant source now. Finally, El Gergal could act as an emitter or as a sink depending on hydrological conditions prevailing during the year. In this way, some years the reservoir could be a sink, burying carbon into the sediments meanwhile other years could act as a source remineralizing and emitting carbon buried previous years. Information gathered during this work does not allow us to confirm this changing role of the reservoir as sink or a source. Nevertheless, research about the hydrological factors influencing annual carbon

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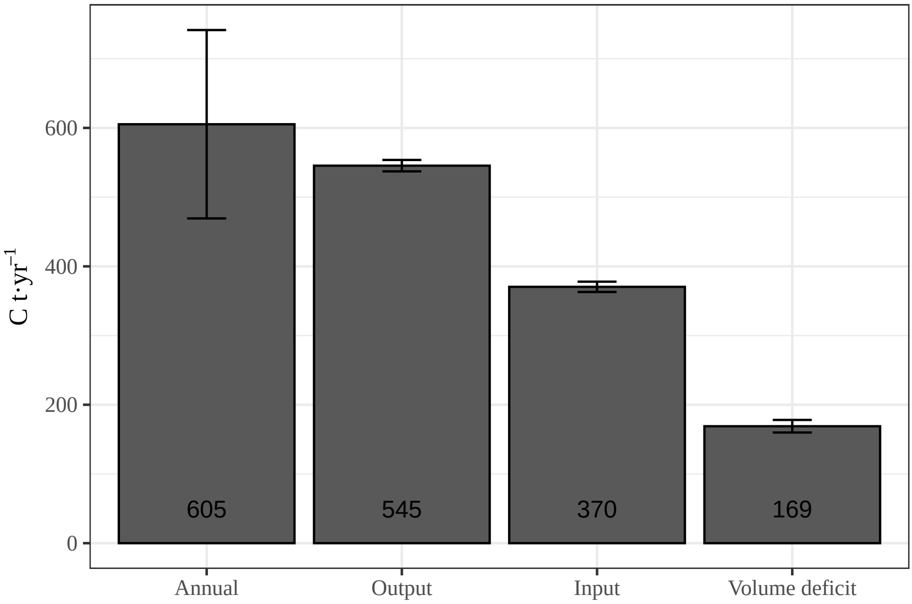

Figure 7.4: Total C emitted in El Gergal reservoir during 2019. “Annual” column shows the balance for the whole year from water surface and drawdown areas.“Output” and “Input” are the amount of carbon estimated output or input, respectively, from the river. “Volume deficit” is the estimated amount of carbon which should be entered in the system if the water volume would be the same at the beginning than at the end of the year

balance in reservoirs is necessary to anticipate future changes in the role that the reservoir plays in the global carbon balance.

7.5 Global warming potential

Global warming potential (GWP) is a measure of the amount of energy that a gas can absorb during a specific period of time (usually referred to 100 years) compared with the amount of energy absorbed by CO_2. This information makes it possible to compare different gasses and its effect on climate. The purpose of this section is just to add information about the GWP of fluxes studied in this thesis. Here, a conversion factor of 27 ± 11 of GWP was used to transform CH_4 to CO_2-eq, following the emission metrics proposed by IPCC (2021) for CH_4 non fossil.

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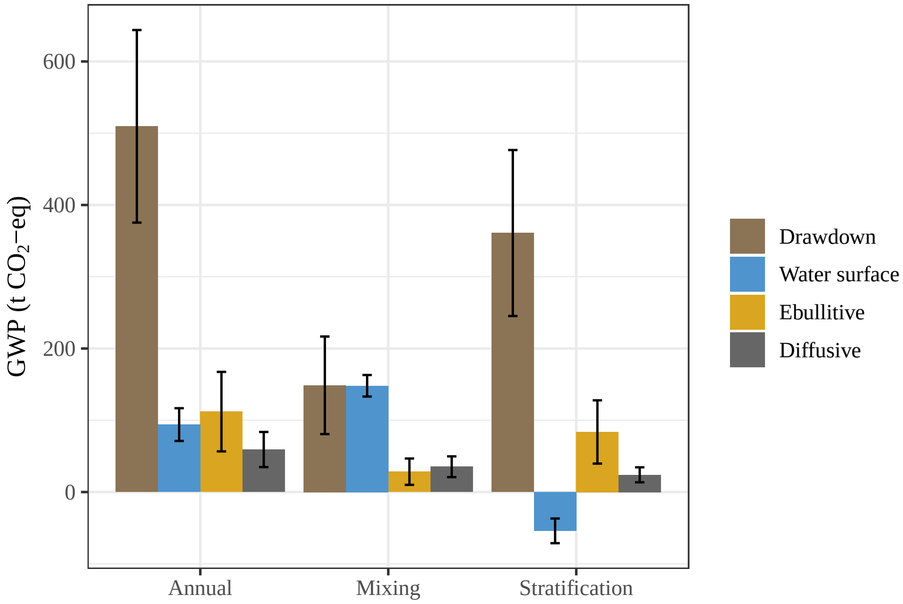

Figure 7.5: Global warming potential (GWP) of CO_2 from drawdown areas and reservoir water surface, and the contribution of water column diffusive and ebullitive CH_4 flux to total GWP. Data are shown for different periods: the whole year, mixing and stratification

During the mixing period, GWP of water surface (CO_2 and CH_4) was higher than the GWP of drawdown area (Figure 7.5). However, during the stratification period, GWP of drawdown area was higher than GWP of water surface. Although, during the stratification, water surface is absorbing CO_2 and therefore, reducing GWP potential of the reservoir, methane emission are higher and the surface of drawdown area is greater resulting in an increase of GWP of the reservoir. Thus, GWP during stratification is higher than during the mixing periods, as have been found for other Mediterranean reservoirs (Samiotis et al., 2018). In annual balance, CH_4 emission from the water surface contributes in a higher proportion to GWP than CO_2 emitted from water surface. However, CO_2 emitted from drawdown area seems to play a major role in GWP of the reservoir.

In El Gergal reservoir, CH_4 emissions from water surface and CO_2 emitted from the drawdown area are the most important contributors to GWP of the reservoir.

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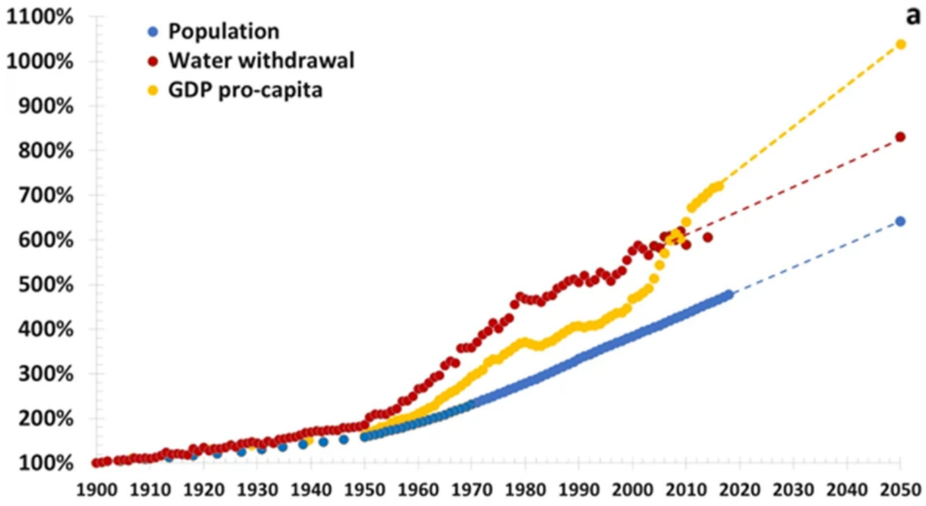

Figure 7.6: Evolution of water withdrawal, population and GDP pro-capita during the last century and projections until 2050. Extracted from Boretti and Rosa (2019)

7.6 Projections

Current projections of Coupled Model Intercomparison Project Phase 6 (CMIP6), overseen by Working Group on Coupled Modelling (WGCM) and included in the last report of IPCC (IPCC, 2021), present different future climate scenarios in which hydrology and thermal structure of inland waters could be altered. The projections are made in base on several Shared Socioeconomic Pathway (SSP) (Riahi et al., 2017), which depend on drivers such as population change, urbanization and economic growth combined with Representative Concentration Pathways (RCP) (Riahi et al., 2017), based on radiative forcing values. In this framework, five plausible scenarios have been selected in the last IPCC report (Sixth report 2021) combining SSP and RCP: SSP1-1.9, SSP1-2.6, SSP2-4.5, SSP3-7.0 and SSP5-8.5.

The most contrasting scenarios are SSP1-1.9 and SSP5-8.5. SSP1.9 represents a very ambitious scenario achieving the 1.5ºC goal proposed in the Paris Agreement meanwhile SSP5-8.5 corresponds with a scenario in which development is still based on fossil fuels.

In addition to these climate change scenarios, water demand, which directly modify hydrology specially reservoirs, have increased during the last century and is expected to increase in the future using up to 800% of the water consumption

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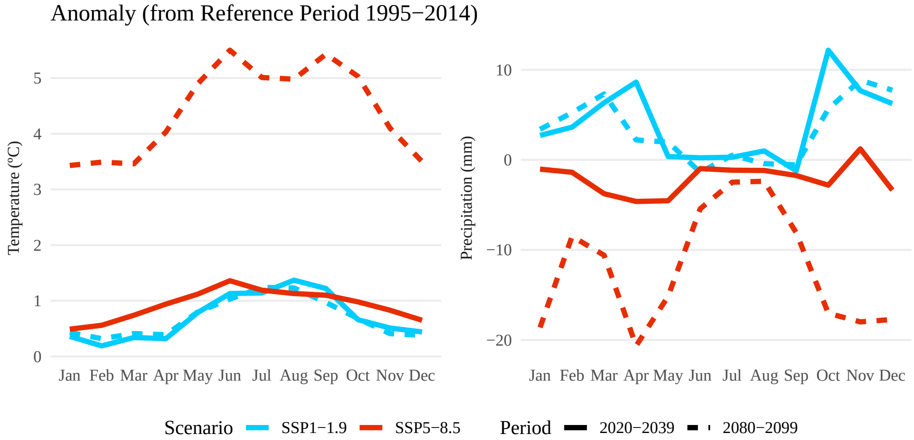

Figure 7.7: Medium and long-term projections (next two decades, solid line, and until the end of the 21th century, dashed line) in Andalusia (Spain) for two contrasting scenarios: SSP1-1.9 (blue) and SSP5-8.5 (red). Data source: https://climateknowledgeportal.worldbank.org

at the very beginning of 20th century by 2050 (Figure 7.6). Indeed, Boretti and Rosa (2019) highlighted an urgent need to implement measures in order to reduce water scarcity in the future.

In the best case scenario (SSP1-1.9), temperature will increase around 1 Celsius degree from April to November (Figure 7.7). This could have a direct effect on thermal structure of reservoirs inducing a higher water stability and a longer duration of the stratification as has been suggested by recent studies (Woolway et al., 2021, 2020; Woolway and Merchant, 2019). In the worst of plausible scenarios (SSP5-8.5), at the end of the century, temperature will increase more than 3 Celsius degrees over the average of the last 2 decades (1995-2014) during the whole year (Figure 7.7). This could lead to a more profound change on thermal structure, some currently monomitic water bodies will become permanently stratified systems (Woolway and Merchant, 2019).

Regarding precipitation, the best scenario will be similar both in medium and long-term projections (Figure 7.7). Otherwise, in the SSP5-8.5 scenario, an annual decrease of precipitation ($\sim$ 150 mm) will be experienced. A lower precipitation will lead to lower water inflow and, if water demand remain steady or even increase as is expected in the future (UN-Water, 2018; Boretti and Rosa, 2019), low water level situation will be more frequent, exposing large area of sediments which used to be permanently flooded. In base of this projection, it is expected a longer duration

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of the stratification and a lower water level. Under these circumstances, a longer stratification period could lead to a higher production of CH_4 and an impairing of water quality due to accumulation of reduced substances such as HS^-, $Fe_2{}^+$ or $Mn_2{}^+$ (Chapter 6). Furthermore, although during the stratification period, water surface is uptaking CO_2 from the atmosphere, DIC produced in the hypolimnion exceeds that uptake. Therefore, the balance for the whole stratification period indicates that the reservoir is a net CO_2 source (Chapters 4 and 6). In addition, lower precipitation and higher water demand, will lead to more frequent low water level events. This will expose a higher area of sediments. As it has been shown in this thesis, and supported by others studies (e.g. Deshmukh et al. (2018); Almeida et al. (2019); Kosten et al. (2018); Keller et al. (2020), drawdown areas are an important source of CO_2 to the atmosphere and contribute hugely to total C emissions in reservoirs (Chapter 5). Thus, these projections seem to show that the most common situation in the future, in a medium and long-term perspective, is going to enhance C emissions and impair water quality.

In conclusion, if measures to mitigate climate change and reduce water demand are not implemented, most likely we will face an impairment of water quality and will experience an increase of C emission from reservoirs which could lead to a positive feedback that reinforces hydrological changes.

7.7 Limitations and future research

CO_2 emissions from the water surface were measured during daytime. However, is already known that there is a daily cycle and that emission during the night are higher than during the day due to metabolic (Gómez-Gener et al., 2021; Morales-Pineda et al., 2014) and convection processes (Morales-Pineda et al., 2014). However, although in streams and rivers CO_2 fluxes during the night are 30-40% higher than those measures during the day, there is still no proper quantification of this underestimation in reservoirs. It would be necessary to increase the knowledge about this pattern in order to quantify this process on a global scale to obtain more precise annual balance emissions. Development of high frequency monitoring devices is booming and it is becoming easier to get access to cheap and even low cost devices for aquatic sciences(Oyola et al., 2022; Chan et al., 2021). The use of these devices could help researchers to fill this gap of daily CO_2 flux patterns in wider spatial resolution.

Emissions from drawdown areas measured in this thesis were just a snapshot of the reservoir in a situation of low water level at the end of the summer. Most studies about CO_2 emission from drawdown areas also have been carried out during a specific moment of the year (e.g. Deshmukh et al. 2018; Jin et al. 2016; Almeida et al. 2019). Actually this lack of information has been highlighted for some authors (e.g. Marcé et al. (2019); Deemer et al. (2016); Keller et al.

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(2020)). Emissions along the year are expected to vary because of changes on environmental factors such as temperature (Yang et al., 2017). Therefore, it is necessary to expand in time CO_2 emissions measurements from drawdown areas in order to catch annual variability and achieve better estimation of these fluxes. In addition, spatial variability of drawdown CO_2 emissions is conspicuous and seems to be controlled by some variables such as temperature, soil texture, moisture, distance to the shore, organic matter content or pH (Gómez-Gener et al., 2015; Gallo et al., 2014; Bolpagni et al., 2017; Deshmukh et al., 2018). However, more and better predictable relationships between variables and CO_2 emissions should be found in order to scale these emissions to a global balance with accuracy. Special attention should be paid to those variables which can be estimated from satellite images or digital terrain models, such as temperature, distance to the shore or soil texture, because it will allow better estimations of CO_2 emissions from these areas. Furthermore, combining high frequency monitoring of CO_2 emission drivers (temperature , moisture, etc.) with direct measure of CO_2 fluxes could improve models and estimations in a system scale.

In addition, the relevance of CO_2 emissions from drawdown areas in El Gergal reservoir have been also reported on a global scale Keller et al. (2021). Therefore, the drawdown area effect on carbon emissions of reservoirs should be included in the carbon footprint of the human activities that rely on its water. Moreover, this will give a more realistic picture of the impact of hydropower energy in the global carbon emissions. For instance, a striking case which took place during last year (2021), when the price of gas increased and, due to how electricity market is regulated (https://sede.cnmc.gob.es/), hydropower energy, considered as “green”, increase its profit margin. This was used by hydropower plants managers to increase their benefits at the expense of leaving the reservoir under critical water levels. This situation would lead to a large increase of the surface of drawdown areas and therefore, increasing carbon emissions and carbon footprint per Kwh of hydropower energy. Clearly, considering the overall C footprint of hydropower (i.e., with the effect of all potential sources of CO_2) may have resulted in a different management strategy and in a more careful consideration of the trade-offs between generation of electricity, carbon emissions, and other ecosystem services provided by a reservoir.

The duration of the stratification period in lakes is increasing all over the world (Woolway and Merchant, 2019; Woolway et al., 2021). Therefore, in the future it is expected that carbon cycling during this situation of vertical compartmentalization is going to become more relevant in the carbon cycle of the reservoir. Here it have been showed that the hypolimnion plays a key role in the annual C balance of the reservoir. Thus, understanding the mechanisms which regulate these fluxes is crucial to anticipate changes in carbon cycling. In this thesis, two contrasting hydrological years were covered. However, it would be necessary to study carbon

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cycling in the hypolimnion covering a longer period (using historical long-term monitoring programs) as well as including other Mediterranean systems in order to integrate a higher hydrological and watershed variability.

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CHAPTER 8

Conclusions

The recent concern about the role of reservoirs in the global carbon cycle is reflected by the increasing number of publication on this topic. However, there is still a lack in information about how the carbon cycle in reservoirs will be affected under future hydrological changes. This thesis contribute to improve this knowledge and help to fill the gap providing information about Mediterranean systems.

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From the results of this dissertation we can conclude that:

1. CO_2 and CH_4 fluxes present high spatio-temporal variability in Mediterranean reservoirs.
2. CO_2 flux from water surface are higher during mixing period and metabolism, specifically primary production (i.e. chlorophyll-*a* and pH) seems to influence over the magnitude and direction of this flux.
3. CH_4 flux is higher in the riverine zone and hydrological factors such as water residence time and water column depth affect CH_4 emissions.
4. CO_2 emission from drawdown areas present high spatial variability and pH and moisture seems to be the most important drivers affecting the magnitude of this emission.
5. Drawdown area of the reservoir is hotspot of CO_2 emissions and could have a huge impact in the annual carbon balance enhancing carbon footprint of this artificial systems.
6. CO_2 and CH_4 production in the hypolimnion ($\text{mmol}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$) are in the same order of magnitude than fluxes from the water surface (diffusion and diffusion + ebullition, respectively) highlighting the relevance of this compartment in carbon cycle of Mediterranean reservoirs.
7. Carbon cycling in the hypolimnion plays a significant role in annual carbon emissions from the reservoir.
8. Dry years with low precipitation and high water residence time could enhance CH_4, reduced metals, NH_4^+ and H_2S production in the hypolimnion impairing water quality and increasing the carbon footprint of the reservoir.
9. Longer stratification period promotes DIC, CH_4, and reduce substance accumulation in the hypolimnion which impair water quality and act as a “time bomb” emitting higher amount of CO_2 and CH_4 after fall turnover.
10. During 2019, El Gergal reservoir was a net carbon source emitting even more carbon than the estimated input. This suggests that its role could change from one year to another depending on hydrological conditions and more research in this direction is needed.
11. Global warning potential of El Gergal reservoir increase during the stratification period.
12. CH_4 emissions and CO_2 emissions from drawdown area are the major contributors to the global warning potential of El Gergal.

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CHAPTER 9

Bibliography

Abril, G., Guérin, F., Richard, S., Delmas, R., Galy-Lacaux, C., Gosse, P., Tremblay, A., Varfalvy, L., Dos Santos, M. A., and Matvienko, B. (2005). Carbon dioxide and methane emissions and the carbon budget of a 10-year old tropical reservoir (Petit Saut, French Guiana). *Global Biogeochemical Cycles*, 19(4):n/a–n/a.

Almeida, R. M., Paranaíba, J. R., Barbosa, Í., Sobek, S., Kosten, S., Linkhorst, A., Mendonça, R., Quadra, G., Roland, F., and Barros, N. (2019). Carbon dioxide emission from drawdown areas of a Brazilian reservoir is linked to surrounding land cover. *Aquatic Sciences*, 81(4):1–9.

Anderson, N. J., Heathcote, A. J., Engstrom, D. R., Ryves, D. B., Mills, K., Prairie, Y. T., del Giorgio, P. A., Bennion, H., Turner, S., Rose, N. L., Jones, V. J., Solovieva, N., Cook Shinneman, A., Umbanhowar, C. E., Fritz, S. C., Verschuren, D., Saros, J. E., Russell, J. M., Bindler, R., Valero-Garcés, B., Edlund, M. B., Dietz, R. D., and Myrbo, A. E. (2020). Anthropogenic alteration of nutrient supply increases the global freshwater carbon sink. *Science Advances*, 6(16):1–8.

Azadi, F., Ashofteh, P. S., and Loáiciga, H. A. (2019). Reservoir Water-Quality Projections under Climate-Change Conditions. *Water Resources Management*, 33(1):401–421.

UNIVERSIDAD DE MÁLAGA

Barros, N., Cole, J. J., Tranvik, L. J., Prairie, Y. T., Bastviken, D., Huszar, V. L., Del Giorgio, P., and Roland, F. (2011). Carbon emission from hydroelectric reservoirs linked to reservoir age and latitude. *Nature Geoscience*, 4(9):593–596.

Bastien, J., Demarty, M., and Tremblay, A. (2011). CO_2 and CH_4 diffusive and degassing emissions from 2003 to 2009 at Eastmain 1 hydroelectric reservoir. (2):113–123.

Bastviken, D., Cole, J., Pace, M., and Tranvik, L. (2004a). Methane emissions from lakes: Dependence of lake characteristics, two regional assessments, and a global estimate. *Global Biogeochemical Cycles*, 18(4):n/a–n/a.

Bastviken, D., Cole, J. J., Pace, M. L., and Van de Bogert, M. C. (2008). Fates of methane from different lake habitats: Connecting whole-lake budgets and CH_4 emissions. *Journal of Geophysical Research: Biogeosciences*, 113:G02024.

Bastviken, D., Persson, L., Odham, G., and Tranvik, L. (2004b). Degradation of dissolved organic matter in oxic and anoxic lake water. *Limnology and Oceanography*, 49(1):109–116.

Bastviken, D., Tranvik, L. J., Downing, J. A., Crill, P. M., and Enrich-Prast, A. (2011). Freshwater methane emissions offset the continental carbon sink.

Battin, T. J., Luyssaert, S., Kaplan, L. A., Aufdenkampe, A. K., Richter, A., and Tranvik, L. J. (2009). The boundless carbon cycle.

Beaulieu, J. J., Balz, D. A., Birchfield, M. K., Harrison, J. A., Nietch, C. T., Platz, M. C., Squier, W. C., Waldo, S., Walker, J. T., White, K. M., and Young, J. L. (2018). Effects of an Experimental Water-level Drawdown on Methane Emissions from a Eutrophic Reservoir. *Ecosystems*, 21(4):657–674.

Beaulieu, J. J., Smolenski, R. L., Nietch, C. T., Townsend-Small, A., and Elovitz, M. S. (2014). High methane emissions from a midlatitude reservoir draining an agricultural watershed. *Environmental Science and Technology*, 48(19):11100–11108.

Beaulieu, J. J., Waldo, S., Balz, D. A., Barnett, W., Hall, A., Platz, M. C., and White, K. M. (2020). Methane and Carbon Dioxide Emissions From Reservoirs: Controls and Upscaling. *Journal of Geophysical Research: Biogeosciences*, 125(12):e2019JG005474.

Bolpagni, R., Folegot, S., Laini, A., and Bartoli, M. (2017). Role of ephemeral vegetation of emerging river bottoms in modulating CO_2 exchanges across a temperate large lowland river stretch. *Aquatic Sciences*, 79(1):149–158.

UNIVERSIDAD
DE MÁLAGA

Boretti, A. and Rosa, L. (2019). Reassessing the projections of the World Water Development Report. *npj Clean Water*, 2(1):1–6.

Brook, H., Brook, H., Argaw, M., Sulaiman, H., and Abiye, T. A. (2011). The Impact of Land Use/Land Cover Change on Hydrological Components due to Resettlement Activity: SWAT Model Approach. *International Journal of Ecology and Environmental Sciences*, 37(1-2):49–60.

Burns, N. M., Rockwell, D. C., Bertram, P. E., Dolan, D. M., and Ciborowski, J. J. (2005). Trends in temperature, secchi depth, and dissolved oxygen depletion rates in the central basin of Lake Erie, 1983-2002. *Journal of Great Lakes Research*, 31(SUPPL. 2):35–49.

Butcher, J. B., Nover, D., Johnson, T. E., and Clark, C. M. (2015). Sensitivity of lake thermal and mixing dynamics to climate change. *Climatic Change*, 129(1-2):295–305.

Carey, C. C., Doubek, J. P., McClure, R. P., and Hanson, P. C. (2018). Oxygen dynamics control the burial of organic carbon in a eutrophic reservoir. *Limnology and Oceanography Letters*, 3(3):293–301.

Casamitjana, X., Serra, T., Colomer, J., Baserba, C., and Pérez-Losada, J. (2003). Effects of the water withdrawal in the stratification patterns of a reservoir. In *Hydrobiologia*, volume 504, pages 21–28. Springer.

Catalán, N., Von Schiller, D., Marcé, R., Koschorreck, M., Gomez-Gener, L., and Obrador, B. (2014). Carbon dioxide efflux during the flooding phase of temporary ponds. *Limnetica*, 33(2):349–360.

Chan, K., Schillereff, D. N., Baas, A. C., Chadwick, M. A., Main, B., Mulligan, M., O'Shea, F. T., Pearce, R., Smith, T. E., van Soesbergen, A., Tebbs, E., and Thompson, J. (2021). Low-cost electronic sensors for environmental research: Pitfalls and opportunities. *Progress in Physical Geography: Earth and Environment*, 45(3):305–338.

Chmiel, H. E., Kokic, J., Denfeld, B. A., Einarsdóttir, K., Wallin, M. B., Koehler, B., Isidorova, A., Bastviken, D., Ferland, M.-È., and Sobek, S. (2016). The role of sediments in the carbon budget of a small boreal lake. *Limnology and Oceanography*, 61(5):1814–1825.

Cole, J. J., Caraco, N. F., Kling, G. W., and Kratz, T. K. (1994). Carbon-dioxide supersaturation in the surface waters of lakes. *Science*, 265(5178):1568–1570.

Cole, J. J., Prairie, Y. T., Caraco, N. F., McDowell, W. H., Tranvik, L. J., Striegl, R. G., Duarte, C. M., Kortelainen, P., Downing, J. A., Middelburg, J. J., and

UNIVERSIDAD DE MÁLAGA

Melack, J. (2007). Plumbing the Global Carbon Cycle: Integrating Inland Waters into the Terrestrial Carbon Budget. *Ecosystems*, 10(1):172–185.

Cramer, W., Guiot, J., Fader, M., Garrabou, J., Gattuso, J. P., Iglesias, A., Lange, M. A., Lionello, P., Llasat, M. C., Paz, S., Peñuelas, J., Snoussi, M., Toreti, A., Tsimplis, M. N., and Xoplaki, E. (2018). Climate change and interconnected risks to sustainable development in the Mediterranean. *Nature Climate Change*, 8(11):972–980.

Dean, W. E. and Gorham, E. (1998). Magnitude and significance of carbon burial in lakes, reservoirs, and peatlands. *Geology*, 26(6):535–538.

Deemer, B. R., Harrison, J. A., Li, S., Beaulieu, J. J., DelSontro, T., Barros, N., Bezerra-Neto, J. F., Powers, S. M., dos Santos, M. A., and Vonk, J. A. (2016). Greenhouse Gas Emissions from Reservoir Water Surfaces: A New Global Synthesis. *BioScience*, 66(11):949–964.

DelSontro, T., Beaulieu, J. J., and Downing, J. A. (2018). Greenhouse gas emissions from lakes and impoundments: Upscaling in the face of global change. *Limnology And Oceanography Letters*, 3(3):64–75.

DelSontro, T., Boutet, L., St-Pierre, A., del Giorgio, P. A., and Prairie, Y. T. (2016). Methane ebullition and diffusion from northern ponds and lakes regulated by the interaction between temperature and system productivity. *Limnology and Oceanography*, 61(S1):S62–S77.

Delsontro, T., Kunz, M. J., Kempter, T., Wüest, A., Wehrli, B., and Senn, D. B. (2011). Spatial heterogeneity of methane ebullition in a large tropical reservoir. *Environmental Science and Technology*, 45(23):9866–9873.

DelSontro, T., Mcginnis, D. F., Sobek, S., Ostrovsky, I., and Wehrli, B. (2010). Extreme methane emissions from a swiss hydropower Reservoir: Contribution from bubbling sediments. *Environmental Science and Technology*, 44(7):2419–2425.

Deshmukh, C., Guérin, F., Vongkhamsao, A., Pighini, S., Oudone, P., Sopraseuth, S., Godon, A., Rode, W., Guédant, P., Oliva, P., Audry, S., Zouiten, C., Galy-Lacaux, C., Robain, H., Ribolzi, O., Kansal, A., Chanudet, V., Descloux, S., and Serça, D. (2018). Carbon dioxide emissions from the flat bottom and shallow Nam Theun 2 Reservoir: Drawdown area as a neglected pathway to the atmosphere. *Biogeosciences*, 15(6):1775–1794.

Dokulil, M. T., de Eyto, E., Maberly, S. C., May, L., Weyhenmeyer, G. A., and Woolway, R. I. (2021). Increasing maximum lake surface temperature under climate change. *Climatic Change*, 165(3-4):56.

UNIVERSIDAD DE MÁLAGA

Doubek, J. P. and Carey, C. C. (2017). Catchment, morphometric, and water quality characteristics differ between reservoirs and naturally formed lakes on a latitudinal gradient in the conterminous United States. *Inland Waters*, 7(2):171–180.

Dove, A., Roulet, N., Crill, P., Chanton, J., and Bourbonniere, R. (1999). Methane dynamics of a northern Boreal beaver pond. *Ecoscience*, 6(4):577–586.

Duchemin, E., Lucotte, M., Canuel, R., and Chamberland, A. (1995). Production of the greenhouse gases CH_4 and CO_2 by hydroelectric reservoirs of the boreal region. *Global Biogeochemical Cycles*, 9(4):529–540.

Einsele, G., Yan, J., and Hinderer, M. (2001). Atmospheric carbon burial in modern lake basins and its significance for the global carbon budget. *Global and Planetary Change*, 30(3-4):167–195.

Encinas-Fernández, J., Peeters, F., and Hofmann, H. (2014). Importance of the Autumn Overturn and Anoxic Conditions in the Hypolimnion for the Annual Methane Emissions from a Temperate Lake. *Environ. Sci. Technol*, 48:7297–7304.

Fahrner, S., Radke, M., Karger, D., and Blodau, C. (2008). Organic matter mineralisation in the hypolimnion of an eutrophic Maar lake. *Aquatic Sciences*, 70(3):225–237.

Fekete, B. M., Wisser, D., Kroeze, C., Mayorga, E., Bouwman, L., Wollheim, W. M., and Vörösmarty, C. (2010). Millennium Ecosystem Assessment scenario drivers (1970-2050): Climate and hydrological alterations. *Global Biogeochemical Cycles*, 24(4):n/a–n/a.

Fenchel, T., King, G. M., and Blackburn, T. H. (2012). *Bacterial biogeochemistry: The ecophysiology of mineral cycling*. Academic Press, Amsterdam, Boston, Heidelberg, London, New York, Oxford, Paris, San Diego, San Francisco, Singapore, Sydney, Tokyo, third edit edition.

Fenner, N. and Freeman, C. (2011). Drought-induced carbon loss in peatlands. *Nature Geoscience*, 4(12):895–900.

Flury, S., Glud, R. N., Premke, K., and McGinnis, D. F. (2015). Effect of Sediment Gas Voids and Ebullition on Benthic Solute Exchange. *Environmental Science and Technology*, 49(17):10413–10420.

Foley, B., Jones, I. D., Maberly, S. C., and Rippey, B. (2012). Long-term changes in oxygen depletion in a small temperate lake: Effects of climate change and eutrophication. *Freshwater Biology*, 57(2):278–289.

UNIVERSIDAD
DE MÁLAGA

Forzieri, G., Feyen, L., Rojas, R., Flörke, M., Wimmer, F., and Bianchi, A. (2014). Ensemble projections of future streamflow droughts in Europe. *Hydrology and Earth System Sciences*, 18(1):85–108.

Freeman, C., Lock, M. A., and Reynolds, B. (1993). Fluxes of CO_2, CH_4 and N_2O from a Welsh peatland following simulation of water table draw-down: Potential feedback to climatic change. *Biogeochemistry*, 19(1):51–60.

Frenzel, P., Thebrath, B., and Conrad, R. (1990). Oxidation of methane in the oxic surface layer of a deep lake sediment (Lake Constance). *FEMS Microbiology Letters*, 73(2):149–158.

Gallo, E. L., Lohse, K. A., Ferlin, C. M., Meixner, T., and Brooks, P. D. (2014). Physical and biological controls on trace gas fluxes in semi-arid urban ephemeral waterways. *Biogeochemistry*, 121(1):189–207.

Getu Engida, T., Nigussie, T. A., Aneseyee, A. B., and Barnabas, J. (2021). Land Use/Land Cover Change Impact on Hydrological Process in the Upper Baro Basin, Ethiopia. *Applied and Environmental Soil Science*, 2021.

Gómez-Gener, L., Obrador, B., Marcé, R., Acuña, V., Catalán, N., Casas-Ruiz, J. P., Sabater, S., Muñoz, I., and von Schiller, D. (2016). When Water Vanishes: Magnitude and Regulation of Carbon Dioxide Emissions from Dry Temporary Streams. *Ecosystems*, 19(4):710–723.

Gómez-Gener, L., Obrador, B., von Schiller, D., Marcé, R., Casas-Ruiz, J. P., Proia, L., Acuña, V., Catalán, N., Muñoz, I., and Koschorreck, M. (2015). Hot spots for carbon emissions from Mediterranean fluvial networks during summer drought. *Biogeochemistry*, 125(3):409–426.

Gómez-Gener, L., Rocher-Ros, G., Battin, T., Cohen, M. J., Dalmagro, H. J., Dinsmore, K. J., Drake, T. W., Duvert, C., Enrich-Prast, A., Horgby, Å., Johnson, M. S., Kirk, L., Machado-Silva, F., Marzolf, N. S., McDowell, M. J., McDowell, W. H., Miettinen, H., Ojala, A. K., Peter, H., Pumpanen, J., Ran, L., Riveros-Iregui, D. A., Santos, I. R., Six, J., Stanley, E. H., Wallin, M. B., White, S. A., and Sponseller, R. A. (2021). Global carbon dioxide efflux from rivers enhanced by high nocturnal emissions. *Nature Geoscience*, 14(5):289–294.

Grasset, C., Mendonça, R., Villamor Saucedo, G., Bastviken, D., Roland, F., and Sobek, S. (2018). Large but variable methane production in anoxic freshwater sediment upon addition of allochthonous and autochthonous organic matter. *Limnology and Oceanography*, 63(4):1488–1501.

UNIVERSIDAD DE MÁLAGA

Grinham, A., Dunbabin, M., and Albert, S. (2018). Importance of sediment organic matter to methane ebullition in a sub-tropical freshwater reservoir. *Science of The Total Environment*, 621:1199–1207.

Gruca-Rokosz, R. (2020). Quantitative Fluxes of the Greenhouse Gases CH4 and CO2 from the Surfaces of Selected Polish Reservoirs. *Atmosphere*, 11(3):286.

Guérin, F. and Abril, G. (2007). Significance of pelagic aerobic methane oxidation in the methane and carbon budget of a tropical reservoir. *Journal of Geophysical Research: Biogeosciences*, 112(G3):G03006.

Haddeland, I., Heinke, J., Biemans, H., Eisner, S., Flörke, M., Hanasaki, N., Konzmann, M., Ludwig, F., Masaki, Y., Schewe, J., Stacke, T., Tessler, Z. D., Wada, Y., and Wisser, D. (2014). Global water resources affected by human interventions and climate change. *Proceedings of the National Academy of Sciences of the United States of America*, 111(9):3251–3256.

Halbedel, S. and Koschorreck, M. (2013). Regulation of CO_2 emissions from temperate streams and reservoirs. *Biogeosciences*, 10(11):7539–7551.

Hanson, R. S. and Hanson, T. E. (1996). Methanotrophic bacteria.

Harrison, J. A., Deemer, B. R., Birchfield, M. K., and O'Malley, M. T. (2017). Reservoir Water-Level Drawdowns Accelerate and Amplify Methane Emission. *Environmental Science and Technology*, 51(3):1267–1277.

Hilgert, S., Scapulatempo Fernandes, C. V., and Fuchs, S. (2019). Redistribution of methane emission hot spots under drawdown conditions. *Science of The Total Environment*, 646:958–971.

Hounshell, A. G., McClure, R. P., Lofton, M. E., and Carey, C. C. (2021). Whole-ecosystem oxygenation experiments reveal substantially greater hypolimnetic methane concentrations in reservoirs during anoxia. *Limnology and Oceanography Letters*, 6:33–42.

Ingvorsen, K. and Brock, T. D. (1982). Electron flow via sulfate reduction and methanogenesis in the anaerobic hypolimnion of Lake Mendota. *Limnology and Oceanography*, 27(3):559–564.

IPCC (2013). *Climate Change 2013: The Physical Science Basis. Contribution of Working Groups I, II and III to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change.* Cambrigde University Press, Cambrigde, United Kingdom and New York, NY, USA.

UNIVERSIDAD
DE MÁLAGA

IPCC (2021). *Climate Change 2021: The Physical Science Basis. Contribution of Working Group I to the Sixth Assessment Report of the Intergovernmental Panel on Climate Change.* Cambridge University Press.

Jenny, J. P., Francus, P., Normandeau, A., Lapointe, F., Perga, M. E., Ojala, A., Schimmelmann, A., and Zolitschka, B. (2016). Global spread of hypoxia in freshwater ecosystems during the last three centuries is caused by rising local human pressure. *Global Change Biology*, 22(4):1481–1489.

Jeppesen, E., Moss, B., Bennion, H., Carvalho, L., Demeester, L., Feuchtmayr, H., Friberg, N., Gessner, M. O., Hefting, M., Lauridsen, T. L., Liboriussen, L., Malmquist, H. J., May, L., Meerhoff, M., Olafsson, J. S., Soons, M. B., and Verhoeven, J. T. (2010). Interaction of Climate Change and Eutrophication. In Kernan, M., Battarbee, R. W., and Moss, B., editors, *Climate Change Impacts on Freshwater Ecosystems*, pages 119–151. John Wiley & Sons, Ltd.

Jiménez Cisneros, B., Oki, T., Arnell, N. W., Benito, G., Cogley, G., Döll, P., Jiang, T., and Mwakalila, S. S. (2014). Freshwater Resources. In Field, C. B., Barros, V. R., Dokken, D. J., Mastrandrea, M. D., Mach, K. J., Bilir, T. E., Chatterjee, M., Ebi, K. L., Estrada, Y. O., Genova, R. C., Girma, B., Kissel, E. S., Levy, A. N., MacCracken, S., Mastrandrea, P. R., and White, L. L., editors, *Climate Change 2014 – Impacts, Adaptation and Vulnerability: PContribution of Working Group II to the Sixth Assessment Report of the Intergovernmental Panel on Climate Change*, pages 229–269. Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA.

Jin, H., Yoon, T. K., Lee, S.-H., Kang, H., Im, J., and Park, J.-H. (2016). Enhanced greenhouse gas emission from exposed sediments along a hydroelectric reservoir during an extreme drought event. *Environmental Research Letters*, 11(12):124003.

Jones, J. G. and Simon, B. M. (1980). Decomposition Processes in the Profundal Region of Blelham Tarn and the Lund Tubes. *Journal of Ecology*, 68(2):493–512.

Keller, P. S., Catalán, N., von Schiller, D., Grossart, H. P., Koschorreck, M., Obrador, B., Frassl, M. A., Karakaya, N., Barros, N., Howitt, J. A., Mendoza-Lera, C., Pastor, A., Flaim, G., Aben, R., Riis, T., Arce, M. I., Onandia, G., Paranaíba, J. R., Linkhorst, A., del Campo, R., Amado, A. M., Cauvy-Fraunié, S., Brothers, S., Condon, J., Mendonça, R. F., Reverey, F., Rõõm, E. I., Datry, T., Roland, F., Laas, A., Obertegger, U., Park, J. H., Wang, H., Kosten, S., Gómez, R., Feijoó, C., Elosegi, A., Sánchez-Montoya, M. M., Finlayson, C. M., Melita, M., Oliveira Junior, E. S., Muniz, C. C., Gómez-Gener, L., Leigh, C., Zhang, Q., and Marcé, R. (2020). Global CO_2 emissions from dry inland waters share common drivers across ecosystems. *Nature Communications*, 11(1):1–8.

UNIVERSIDAD DE MÁLAGA

Keller, P. S., Marcé, R., Obrador, B., and Koschorreck, M. (2021). Global carbon budget of reservoirs is overturned by the quantification of drawdown areas. *Nature Geoscience*, pages 1–7.

Kelly, C. A. and Chynoweth, D. P. (1981). The contributions of temperature and of the input of organic matter in controlling rates of sediment methanogenesis1. *Limnology and Oceanography*, 26(5):891–897.

Kelly, C. A., Rudd, J. W. M., and Schindler, D. W. (1988). Carbon and electron flow via methanogenesis, $SO_4{}^{2-}$, $NO_3{}^{-}$, Fe^{3+}, and Mn^{4+} reduction in the anoxic hypolimnia of three lakes. *Archive für Hydrobiologie*, 31(January 1988):333–344.

Kelly, C. A., Rudd, J. W. M., St. Louis, V. L., and Moore, T. (1994). Turning attention to reservoir surfaces, a neglected area in greenhouse studies. *Eos, Transactions American Geophysical Union*, 75(29):332.

Kemenes, A., Forsberg, B. R., and Melack, J. M. (2011). CO_2 emissions from a tropical hydroelectric reservoir (Balbina, Brazil). *Journal of Geophysical Research*, 116(G3):G03004.

Kosten, S., van den Berg, S., Mendonça, R., Paranaíba, J. R., Roland, F., Sobek, S., Van Den Hoek, J., and Barros, N. (2018). Extreme drought boosts CO_2 and CH_4 emissions from reservoir drawdown areas. *Inland Waters*, 8(3):329–340.

Kovats, R. S., Valentini, R., Bouwer, L. M., Georgopoulou, E., Jacob, D., Martin, E., Rounsevell, M., and Soussana, J. F. (2014). Europe. In Field, C. B., Barros, V. R., Dokken, D. J., Mastrandrea, M. D., Mach, K. J., Bilir, T. E., Chatterjee, M., Ebi, K. L., Estrada, Y. O., Genova, R. C., Girma, B., Kissel, E. S., Levy, A. N., MacCracken, S., Mastrandrea, P. R., and White, L. L., editors, *Climate Change 2014: Impacts, Adaptation and Vulnerability. Part B: Regional Aspects. Contribution of Working Group II to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change*, pages 1267–1326. Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA.

Ladwig, R., Hanson, P. C., Dugan, H. A., Carey, C. C., Zhang, Y., Shu, L., Duffy, C. J., and Cobourn, K. M. (2021). Lake thermal structure drives interannual variability in summer anoxia dynamics in a eutrophic lake over 37 years. *Hydrology and Earth System Sciences*, 25(2):1009–1032.

Lazzarino, J. K., Bachmann, R. W., Hoyer, M. V., and Canfield, D. E. (2009). Carbon dioxide supersaturation in Florida lakes. *Hydrobiologia*, 627(1):169–180.

UNIVERSIDAD
DE MÁLAGA

León-Palmero, E., Morales-Baquero, R., and Reche, I. (2020). Greenhouse gas fluxes from reservoirs determined by watershed lithology, morphometry, and anthropogenic pressure. *Environmental Research Letters*, 15(4):044012.

Li, Y., Huang, T. L., Zhou, Z. Z., Long, S. H., and Zhang, H. H. (2018). Effects of reservoir operation and climate change on thermal stratification of a canyon-shaped reservoir, in northwest China. *Water Science and Technology: Water Supply*, 18(2):418–429.

Likens, G. E. (1973). Primary production: Freshwater ecosystems. *Human Ecology*, 1(4):347–356.

Liu, H., Zhang, Q., Katul, G. G., Cole, J. J., Chapin, F. S., and MacIntyre, S. (2016). Large CO_2 effluxes at night and during synoptic weather events significantly contribute to CO_2 emissions from a reservoir. *Environmental Research Letters*, 11(6):064001.

Liu, L., De Kock, T., Wilkinson, J., Cnudde, V., Xiao, S., Buchmann, C., Uteau, D., Peth, S., and Lorke, A. (2018). Methane Bubble Growth and Migration in Aquatic Sediments Observed by X-ray μcT. *Environmental Science and Technology*, 52(4):2007–2015.

Liu, M., Zhang, Y., Shi, K., Zhang, Y., Zhou, Y., Zhu, M., Zhu, G., Wu, Z., and Liu, M. (2020). Effects of rainfall on thermal stratification and dissolved oxygen in a deep drinking water reservoir. *Hydrological Processes*, 34(15):3387–3399.

Maavara, T., Chen, Q., Van Meter, K., Brown, L. E., Zhang, J., Ni, J., and Zarfl, C. (2020). River dam impacts on biogeochemical cycling. *Nature Reviews Earth & Environment*, 1(2):103–116.

Marcé, R. and Armengol, J. (2009). Water Quality in Reservoirs Under a Changing Climate. In *Hdb Env Chem*, volume 8, pages 73–94. Springer, Berlin, Heidelberg.

Marcé, R., Obrador, B., Gómez-Gener, L., Catalán, N., Koschorreck, M., Arce, M. I., Singer, G., and von Schiller, D. (2019). Emissions from dry inland waters are a blind spot in the global carbon cycle. *Earth-Science Reviews*, 188:240–248.

Marcé, R., Obrador, B., Morguí, J.-A., Lluís Riera, J., López, P., and Armengol, J. (2015). Carbonate weathering as a driver of CO_2 supersaturation in lakes. *Nature Geoscience*, 8(2):107–111.

Marcé, R., Rodríguez-Arias, M. A., García, J. C., and Armengol, J. (2010). El Niño Southern Oscillation and climate trends impact reservoir water quality. *Global Change Biology*, 16(10):2857–2865.

UNIVERSIDAD DE MÁLAGA

Matthews, D. A., Effler, S. W., Driscoll, C. T., O'Donnell, S. M., and Matthews, C. M. (2008). Electron budgets for the hypolimnion of a recovering urban lake, 1989-2004: Response to changes in organic carbon deposition and availability of electron acceptors. *Limnology and Oceanography*, 53(2):743–759.

Mattson, M. D. and Likens, G. E. (1993). Redox Reactions of Organic Matter Decomposition in a Soft Water Lake. *Biogeochemistry*, 19(3):149–172.

McClure, R. P., Lofton, M. E., Chen, S., Krueger, K. M., Little, J. C., and Carey, C. C. (2020). The Magnitude and Drivers of Methane Ebullition and Diffusion Vary on a Longitudinal Gradient in a Small Freshwater Reservoir. *Journal of Geophysical Research: Biogeosciences*, 125(3):e2019JG005205.

McClure, R. P., Schreiber, M. E., Lofton, M. E., Chen, S., Krueger, K. M., and Carey, C. C. (2021). Ecosystem-Scale Oxygen Manipulations Alter Terminal Electron Acceptor Pathways in a Eutrophic Reservoir. *Ecosystems*, 24:1281–1298.

McGinnis, D. F., Greinert, J., Artemov, Y., Beaubien, S. E., and Wüest, A. (2006). Fate of rising methane bubbles in stratified waters: How much methane reaches the atmosphere? *Journal of Geophysical Research: Oceans*, 111(9).

Meerhoff, M., Audet, J., Davidson, T. A., Meester, L. D., Hilt, S., Kosten, S., Liu, Z., Mazzeo, N., Paerl, H., Scheffer, M., and Jeppesen, E. (2022). Feedback between climate change and eutrophication: revisiting the allied attack concept and how to strike back. *Inland Waters*, pages 1–18.

Mendoça, R., Barros, N., O., L., Pacheco, F., Kosten, S., and Rol, F. (2012). Greenhouse Gas Emissions from Hydroelectric Reservoirs: What Knowledge Do We Have and What is Lacking? *Greenhouse Gases - Emission, Measurement and Management.*

Mendonça, R., Kosten, S., Sobek, S., Jaqueline Cardoso, S., Paulo Figueiredo-Barros, M., Henrique Duque Estrada, C., and Roland, F. (2016). Organic carbon burial efficiency in a subtropical hydroelectric reservoir. *Biogeosciences*, 13(11):3331–3342.

Mendonça, R., Müller, R. A., Clow, D., Verpoorter, C., Raymond, P., Tranvik, L. J., and Sobek, S. (2017). Organic carbon burial in global lakes and reservoirs. *Nature Communications*, 8(1694):1–7.

Micklin, P. (2016). The future Aral Sea: hope and despair. *Environmental Earth Sciences*, 75(9):1–15.

UNIVERSIDAD DE MÁLAGA

Morales-Pineda, M., Cózar, A., Laiz, I., Úbeda, B., and Gálvez, J. Á. (2014). Daily, biweekly, and seasonal temporal scales of p CO 2 variability in two stratified Mediterranean reservoirs. *Journal of Geophysical Research: Biogeosciences*, 119(4):509–520.

Morales-Pineda, M., Úbeda, B., Cózar, A., Obrador, B., and Gálvez, J. (2015). Organic carbon sedimentation dominates over CO_2 emission in two net heterotrophic Mediterranean reservoirs during stratification. *Aquatic Sciences*, 78(2):279–290.

Moreno-Ostos, E., Marcé, R., Ordóñez, J., Dolz, J., and Armengol, J. (2008). Hydraulic Management Drives Heat Budgets and Temperature Trends in a Mediterranean Reservoir. *International Review of Hydrobiology*, 93(2):131–147.

Moss, B., Kosten, S., Meerhoff, M., Battarbee, R. W., Jeppesen, E., Mazzeo, N., Havens, K., Lacerot, G., Liu, Z., De Meester, L., Paerl, H., and Scheffer, M. (2011). Allied attack: climate change and eutrophication. *Inland Waters*, 1(2):101–105.

Mulligan, M., van Soesbergen, A., and Sáenz, L. (2020). GOODD, a global dataset of more than 38,000 georeferenced dams. *Scientific Data*, 7(1).

Musenze, R. S., Grinham, A., Werner, U., Gale, D., Sturm, K., Udy, J., and Yuan, Z. (2014). Assessing the spatial and temporal variability of diffusive methane and nitrous oxide emissions from subtropical freshwater reservoirs. *Environmental Science and Technology*, 48(24):14499–14507.

Natchimuthu, S., Sundgren, I., Gålfalk, M., Klemedtsson, L., Crill, P., Danielsson, Å., and Bastviken, D. (2016). Spatio-temporal variability of lake CH_4 fluxes and its influence on annual whole lake emission estimates. *Limnology and Oceanography*, 61(S1):S13–S26.

Nilsson, C., Reidy, C. A., Dynesius, M., and Revenga, C. (2005). Fragmentation and flow regulation of the world's large river systems.

Oyola, P., Carbone, S., Timonen, H., Torkmahalleh, M., and Lindén, J. (2022). Editorial: Rise of Low-Cost Sensors and Citizen Science in Air Quality Studies. *Frontiers in Environmental Science*, 10(March):1–2.

Painuly, A. and Katsman, R. (2022). Mechanism of Faster CH4 Bubble Growth Under Surface Waves in Muddy Aquatic Sediments: Effects of Wave Amplitude, Period, and Water Depth. *Frontiers in Earth Science*, 10:136.

Paranaíba, J. R., Barros, N., Almeida, R. M., Linkhorst, A., Mendonça, R., do Vale, R., Roland, F., and Sobek, S. (2021). Hotspots of Diffusive CO 2

UNIVERSIDAD DE MÁLAGA

and CH 4 Emission From Tropical Reservoirs Shift Through Time. *Journal of Geophysical Research: Biogeosciences*, 126(4):e2020JG006014.

Paranaíba, J. R., Barros, N., Mendonça, R., Linkhorst, A., Isidorova, A., Roland, F., Almeida, R. M., and Sobek, S. (2018). Spatially Resolved Measurements of CO_2 and CH_4 Concentration and Gas-Exchange Velocity Highly Influence Carbon-Emission Estimates of Reservoirs. *Environmental Science and Technology*, 52(2):607–615.

Paranaíba, J. R., Quadra, G., Josué, I. I. P., Almeida, R. M., Mendonça, R., Cardoso, S. J., Silva, J., Kosten, S., Campos, J. M., Almeida, J., Araújo, R. L., Roland, F., and Barros, N. (2020). Sediment drying-rewetting cycles enhance greenhouse gas emissions, nutrient and trace element release, and promote water cytogenotoxicity. *PLOS ONE*, 15(4):e0231082.

Park, H. and Chung, S. (2018). ρCO_2 Dynamics of Stratified Reservoir in Temperate Zone and CO_2 Pulse Emissions During Turnover Events. *Water*, 10(10):1347.

Pekel, J. F., Cottam, A., Gorelick, N., and Belward, A. S. (2016). High-resolution mapping of global surface water and its long-term changes. *Nature*, 540(7633):418–422.

Prairie, Y. T., Alm, J., Beaulieu, J., Barros, N., Battin, T., Cole, J., del Giorgio, P., DelSontro, T., Guérin, F., Harby, A., Harrison, J., Mercier-Blais, S., Serça, D., Sobek, S., and Vachon, D. (2018). Greenhouse Gas Emissions from Freshwater Reservoirs: What Does the Atmosphere See? *Ecosystems*, 21(5):1058–1071.

Ran, L., Yue, R., Shi, H., Meng, X., Ngai Chan, C., Fang, N., and Shi, Z. (2022). Seasonal and diel variability of CO_2 emissions from a semiarid hard-water reservoir. *Journal of Hydrology*, 608.

Raymond, P. A., Hartmann, J., Lauerwald, R., Sobek, S., McDonald, C., Hoover, M., Butman, D., Striegl, R., Mayorga, E., Humborg, C., Kortelainen, P., Dürr, H., Meybeck, M., Ciais, P., and Guth, P. (2013). Global carbon dioxide emissions from inland waters. *Nature*, 503(7476):355–359.

Reeburgh, W. S. (1996). “Soft Spots” in the Global Methane Budget. In *Microbial Growth on C1 Compounds*, pages 334–342. Springer Netherlands.

Riahi, K., van Vuuren, D. P., Kriegler, E., Edmonds, J., O'Neill, B. C., Fujimori, S., Bauer, N., Calvin, K., Dellink, R., Fricko, O., Lutz, W., Popp, A., Cuaresma, J. C., KC, S., Leimbach, M., Jiang, L., Kram, T., Rao, S., Emmerling, J., Ebi, K., Hasegawa, T., Havlik, P., Humpenöder, F., Da Silva, L. A., Smith, S., Stehfest, E., Bosetti, V., Eom, J., Gernaat, D., Masui, T., Rogelj, J., Strefler, J.,

UNIVERSIDAD DE MÁLAGA

Drouet, L., Krey, V., Luderer, G., Harmsen, M., Takahashi, K., Baumstark, L., Doelman, J. C., Kainuma, M., Klimont, Z., Marangoni, G., Lotze-Campen, H., Obersteiner, M., Tabeau, A., and Tavoni, M. (2017). The Shared Socioeconomic Pathways and their energy, land use, and greenhouse gas emissions implications: An overview. *Global Environmental Change*, 42:153–168.

Rinke, K., Keller, P. S., Kong, X., Borchardt, D., and Weitere, M. (2019). Ecosystem Services from Inland Waters and Their Aquatic Ecosystems. In Schröter, M., Bonn, A., Klotz, S., Seppelt, R., and Baessler, C., editors, *Atlas of Ecosystem Services: Drivers, Risks, and Societal Responses*, pages 191–195. Springer International Publishing.

Rodriguez, M. and Casper, P. (2018). Greenhouse gas emissions from a semi-arid tropical reservoir in northeastern Brazil. *Regional Environmental Change*, 18(7):1901–1912.

Rudd, J., Hecky, R., Harris, R., and Kelly, C. (1993). Are hydroelectric reservoirs significant sources of greenhouse gases. *Ambio*, 22(4):246–248.

Saidi, H. and Koschorreck, M. (2017). CO_2 emissions from German drinking water reservoirs. *Science of the Total Environment*, 581-582:10–18.

Samiotis, G., Pekridis, G., Kaklidis, N., Trikoilidou, E., Taousanidis, N., and Amanatidou, E. (2018). Greenhouse gas emissions from two hydroelectric reservoirs in Mediterranean region. *Environmental monitoring and assessment*, 190(6):1–13.

Schafran, G. C. and Driscoll, C. T. (1987). Comparison of Terrestrial and Hypolimnetic Sediment Generation of Acid Neutralizing Capacity for an Acidic Adirondack Lake. *Environmental Science and Technology*, 21(10):988–993.

Schindler, D. W., Turner, M. A., Stainton, M. P., and Linsey, G. A. (1986). Natural Sources of Acid Neutralizing Capacity in Low Alklinity Lakes of the Precambrian Shield. *Science*, 232:844–847.

Schleussner, C. F., Lissner, T. K., Fischer, E. M., Wohland, J., Perrette, M., Golly, A., Rogelj, J., Childers, K., Schewe, J., Frieler, K., Mengel, M., Hare, W., and Schaeffer, M. (2016). Differential climate impacts for policy-relevant limits to global warming: The case of 1.5 °c and 2 °c. *Earth System Dynamics*, 7(2):327–351.

Schrier-Uijl, A. P., Veraart, A. J., Leffelaar, P. A., Berendse, F., and Veenendaal, E. M. (2011). Release of CO_2 and CH_4 from lakes and drainage ditches in temperate wetlands. *Biogeochemistry*, 102(1):265–279.

UNIVERSIDAD DE MÁLAGA

Schubert, C. J. and Wehrli, B. (2018). Contribution of Methane Formation and Methane Oxidation to Methane Emission from Freshwater Systems. In *Biogenesis of Hydrocarbons*, pages 1–31. Springer International Publishing.

Shiklomanov, I. A. (2009). Anthropogenic effects on the hydrological cycle. In Shiklomanov, I. A., editor, *The Hydrological Cycle*, volume I, page 27. Eolss Publishers, Paris, France.

Sobek, S., DelSontro, T., Wongfun, N., and Wehrli, B. (2012). Extreme organic carbon burial fuels intense methane bubbling in a temperate reservoir. *Geophysical Research Letters*, 39(1):n/a–n/a.

Sobek, S., Durisch-Kaiser, E., Zurbrug, R., Wongfun, N., Wessels, M., Pasche, N., and Wehrli, B. (2009). Organic carbon burial efficiency in lake sediments controlled by oxygen exposure time and sediment source. *Limnology and Oceanography*, 54(6):2243–2254.

Sobek, S., Zurbrügg, R., and Ostrovsky, I. (2011). The burial efficiency of organic carbon in the sediments of Lake Kinneret. *Aquatic Sciences*, 73(3):355–364.

Soumis, N., Duchemin, É., Canuel, R., and Lucotte, M. (2004). Greenhouse gas emissions from reservoirs of the western United States. *Global Biogeochemical Cycles*, 18(3):GB3022.

St. Louis, V. L., Kelly, C. A., Duchemin, É., Rudd, J. W., and Rosenberg, D. M. (2000). Reservoir surfaces as sources of greenhouse gases to the atmosphere: A global estimate. *BioScience*, 50(9):766–775.

Stohlgren, T. J., Chase, T. N., Pielke, R. A., Sr, ., Kittel, T. G. F., and Baron, J. S. (1998). Evidence that local land use practices influence regional climate, vegetation, and stream flow patterns in adjacent natural areas. *Global Change Biology*, 4(5):495–504.

Stumm, W. and Morgan, J. J. (1996). Oxidation and Reduction; Equilibria and Microbial Mediation. In *Aquatic Chemistry: Chemical Equilibria and Rates in Natural Waters.*, number 1995, pages 425–515.

Teodoru, C. R., Prairie, Y. T., and del Giorgio, P. A. (2011). Spatial Heterogeneity of Surface CO_2 Fluxes in a Newly Created Eastmain-1 Reservoir in Northern Quebec, Canada. *Ecosystems*, 14(1):28–46.

Tranvik, L. J., Cole, J. J., and Prairie, Y. T. (2018). The study of carbon in inland waters—from isolated ecosystems to players in the global carbon cycle. *Limnology and Oceanography Letters*, 3(3):41–48.

UNIVERSIDAD
DE MÁLAGA

Tranvik, L. J., Downing, J. A., Cotner, J. B., Loiselle, S. A., Striegl, R. G., Ballatore, T. J., Dillon, P., Finlay, K., Fortino, K., Knoll, L. B., Kortelainen, P. L., Kutser, T., Larsen, S., Laurion, I., Leech, D. M., McCallister, S. L., McKnight, D. M., Melack, J. M., Overholt, E., Porter, J. A., Prairie, Y. T., Renwick, W. H., Roland, F., Sherman, B. S., Schindler, D. W., Sobek, S., Tremblay, A., Vanni, M. J., Verschoor, A. M., von Wachenfeldt, E., and Weyhenmeyer, G. A. (2009). Lakes and reservoirs as regulators of carbon cycling and climate. *Limnology and Oceanography*, 54(6part2):2298–2314.

Tremblay, A., Therrien, J., Hamlin, B., Wichmann, E., and LeDrew, L. J. (2005). GHG Emissions from Boreal Reservoirs and Natural Aquatic Ecosystems. pages 209–232. Springer, Berlin, Heidelberg.

Trolle, D., Staehr, P. A., Davidson, T. A., Bjerring, R., Lauridsen, T. L., Søndergaard, M., and Jeppesen, E. (2012). Seasonal Dynamics of CO_2 Flux Across the Surface of Shallow Temperate Lakes. *Ecosystems*, 15(2):336–347.

UN-Water (2018). *The United Nations world water development report 2018: Nature-Based Solutions for Water.*

Vachon, D., Langenegger, T., Donis, D., and McGinnis, D. F. (2019). Influence of water column stratification and mixing patterns on the fate of methane produced in deep sediments of a small eutrophic lake. *Limnology and Oceanography*, 64(5):2114–2128.

Vachon, D., Prairie, Y. T., Guillemette, F., and del Giorgio, P. A. (2016). Modeling Allochthonous Dissolved Organic Carbon Mineralization Under Variable Hydrologic Regimes in Boreal Lakes. *Ecosystems*, 20(4):781–795.

Vicente-Serrano, S. M., Lopez-Moreno, J. I., Beguería, S., Lorenzo-Lacruz, J., Sanchez-Lorenzo, A., García-Ruiz, J. M., Azorin-Molina, C., Morán-Tejeda, E., Revuelto, J., Trigo, R., Coelho, F., and Espejo, F. (2014). Evidence of increasing drought severity caused by temperature rise in southern Europe. *Environmental Research Letters*, 9(4):044001.

Weise, L., Ulrich, A., Moreano, M., Gessler, A., Kayler, Z. E., Steger, K., Zeller, B., Rudolph, K., Knezevic-Jaric, J., and Premke, K. (2016). Water level changes affect carbon turnover and microbial community composition in lake sediments. *FEMS Microbiology Ecology*, 92(5).

Wendt-Potthoff, K., Kloß, C., Schultze, M., and Koschorreck, M. (2014). Anaerobic metabolism of two hydro-morphological similar pre-dams under contrasting nutrient loading (Rappbode Reservoir System, Germany). *International Review of Hydrobiology*, 99(5):350–362.

UNIVERSIDAD DE MÁLAGA

West, W. E., Creamer, K. P., and Jones, S. E. (2016). Productivity and depth regulate lake contributions to atmospheric methane. *Limnology and Oceanography*, 61(S1):S51–S61.

Weyhenmeyer, C. E. (1999). Methane emissions from beaver ponds: Rates, patterns, and transport mechanisms. *Global Biogeochemical Cycles*, 13(4):1079–1090.

Weyhenmeyer, G. A., Kosten, S., Wallin, M. B., Tranvik, L. J., Jeppesen, E., and Roland, F. (2015). Significant fraction of CO_2 emissions from boreal lakes derived from hydrologic inorganic carbon inputs. *Nature Geoscience*, 8(12):933–936.

Wik, M., Crill, P. M., Varner, R. K., and Bastviken, D. (2013). Multiyear measurements of ebullitive methane flux from three subarctic lakes. *Journal of Geophysical Research: Biogeosciences*, 118(3):1307–1321.

Winslow, L., Read, J., Woolway, R., Brentrup, J., Leach, T., Zwart, J., Albers, S., and Collinge, D. (2019). rLakeAnalyzer: Lake Physics Tools.

Woolway, R. I., Kraemer, B. M., Lenters, J. D., Merchant, C. J., O'Reilly, C. M., and Sharma, S. (2020). Global lake responses to climate change. *Nature Reviews Earth & Environment*, 1(8):388–403.

Woolway, R. I. and Merchant, C. J. (2019). Worldwide alteration of lake mixing regimes in response to climate change. *Nature Geoscience*, 12(4):271–276.

Woolway, R. I., Sharma, S., Weyhenmeyer, G. A., Debolskiy, A., Golub, M., Mercado-Bettín, D., Perroud, M., Stepanenko, V., Tan, Z., Grant, L., Ladwig, R., Mesman, J., Moore, T. N., Shatwell, T., Vanderkelen, I., Austin, J. A., DeGasperi, C. L., Dokulil, M., La Fuente, S., Mackay, E. B., Schladow, S. G., Watanabe, S., Marcé, R., Pierson, D. C., Thiery, W., and Jennings, E. (2021). Phenological shifts in lake stratification under climate change. *Nature Communications*, 12(1):2318.

Xiao, S., Liu, D., Wang, Y., Yang, Z., and Chen, W. (2013). Temporal variation of methane flux from Xiangxi Bay of the Three Gorges Reservoir. *Scientific Reports*, 3(1):1–8.

Yang, G., Wang, M., Chen, H., Liu, L., Wu, N., Zhu, D., Tian, J., Peng, C., Zhu, Q., and He, Y. (2017). Responses of CO_2 emission and pore water DOC concentration to soil warming and water table drawdown in Zoige Peatlands. *Atmospheric Environment*, 152:323–329.

UNIVERSIDAD DE MÁLAGA

Yang, L. (2019). Contrasting methane emissions from upstream and downstream rivers and their associated subtropical reservoir in eastern China. *Scientific Reports*, 9(1):1–10.

Yang, M., Geng, X., Grace, J., Lu, C., Zhu, Y., Zhou, Y., and Lei, G. (2014). Spatial and Seasonal CH_4 Flux in the Littoral Zone of Miyun Reservoir near Beijing: The Effects of Water Level and Its Fluctuation. *PLOS ONE*, 9(4):e94275.

Yang, Y., Chen, J., Li, B., Liu, Y., and Xie, S. (2018). Anaerobic methane oxidation potential and bacteria in freshwater lakes: Seasonal changes and the influence of trophic status. *Systematic and Applied Microbiology*, 41(6):650–657.

Zafarnejad, F. (2009). The contribution of dams to Iran's desertification. *International Journal of Environmental Studies*, 66(3):327–341.

Zarfl, C., Lumsdon, A. E., Berlekamp, J., Tydecks, L., and Tockner, K. (2015). A global boom in hydropower dam construction. *Aquatic Sciences*, 77(1):161–170.

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APPENDIX A

Supplementary material I

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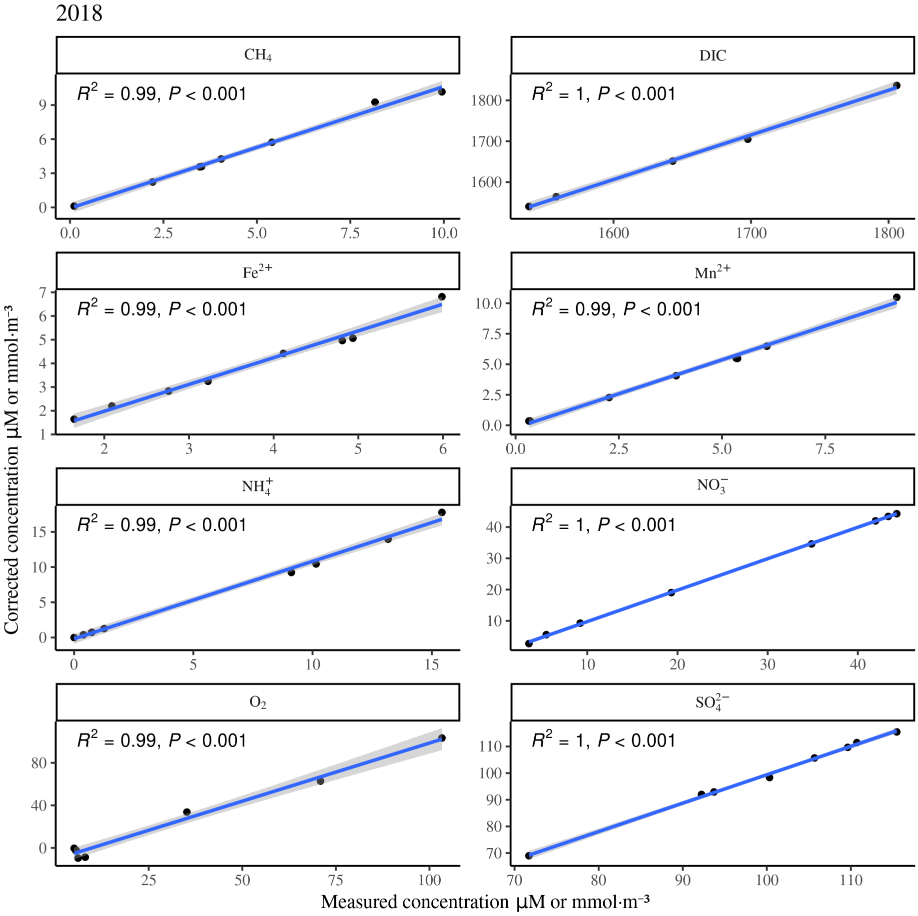

Figure A.1: Relationship between measured concentration and corrected concentration which included vertical diffusion effect, for the year 2018. Blue line are linear regression, R^2 is coefficient of determination and P is the p-value

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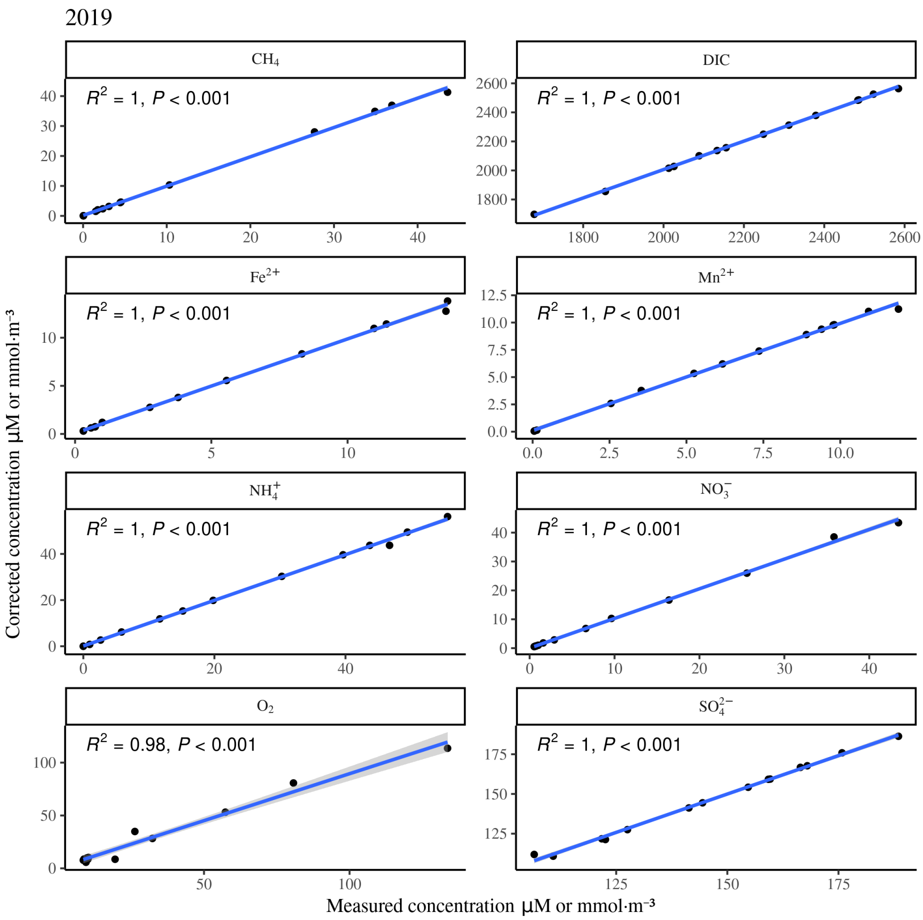

Figure A.2: Relationship between measured concentration and corrected concentration which included vertical diffusion effect, for the year 2019. Blue line are linear regression, R^2 is coefficient of determination and P is the p-value

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APPENDIX B

Supplementary material II

B.0.1 Riverine Vs lacustrine zone

For Chapter 7, the reservoir was split into two zones, riverine and lacustrine, based on a entrance of the river-dam axis. Riverine zone was define as the area closest to river entrance with a depth shallower than 10 meters (Figure B.1).

B.0.2 Drawdown Vs Water surface area

Daily water level measurements and hypsographic curve with 1 mm vertical resolution (Figure B.2), provide by El Gergal water management enterprise (EMASESA), were use to estimate the proportion of the total reservoir surface which was covered by water or by sediment exposed to the atmosphere.

B.0.3 Stratification Vs mixing period

Based of temperature profiles, schmidt stability was calculated using a modified function, `schmidt.stability()` from the R package rlakeAnalyzer (Winslow et al., 2019) to include water level fluctuation. Then, stratification period was define using the criteria of Schmidt schmidt stability < 600 J·m^{-2}. Each month was classified into stratified or mixing as shown in Figure B.3.

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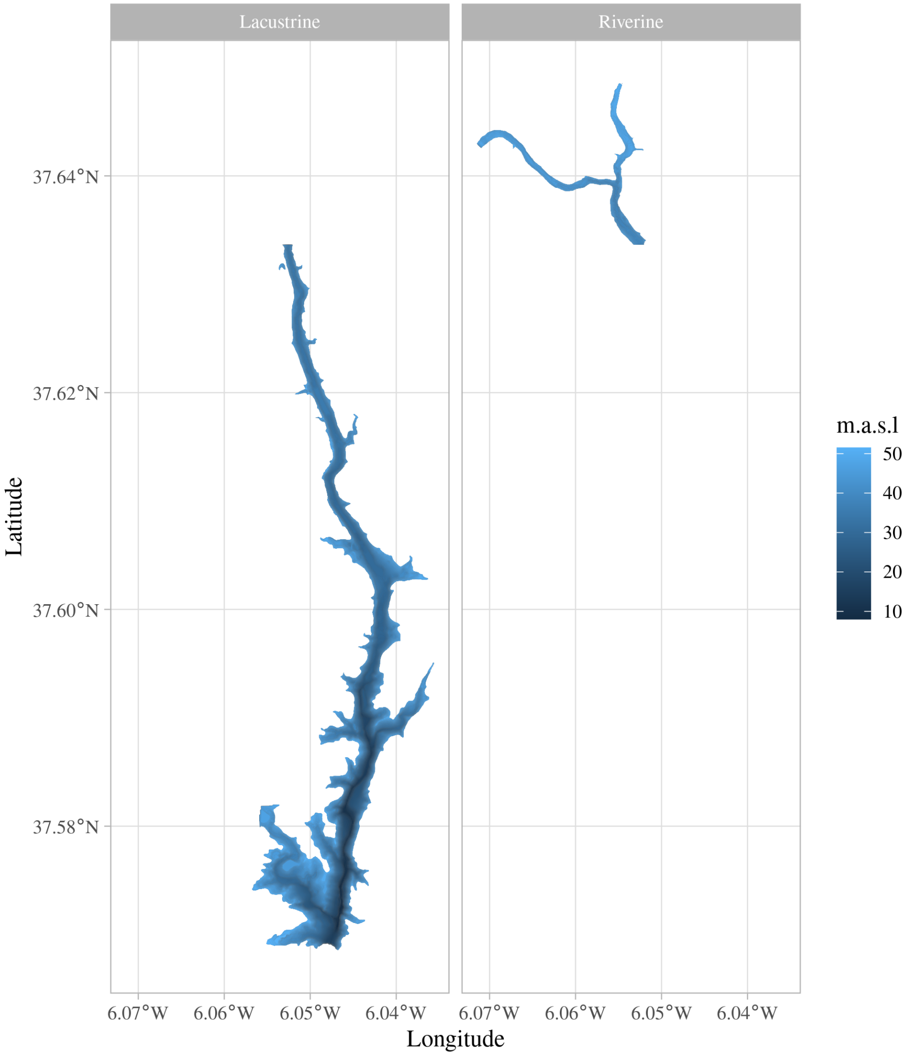

Figure B.1: Map of the riverine and lacustrine zone define for Chapter 7

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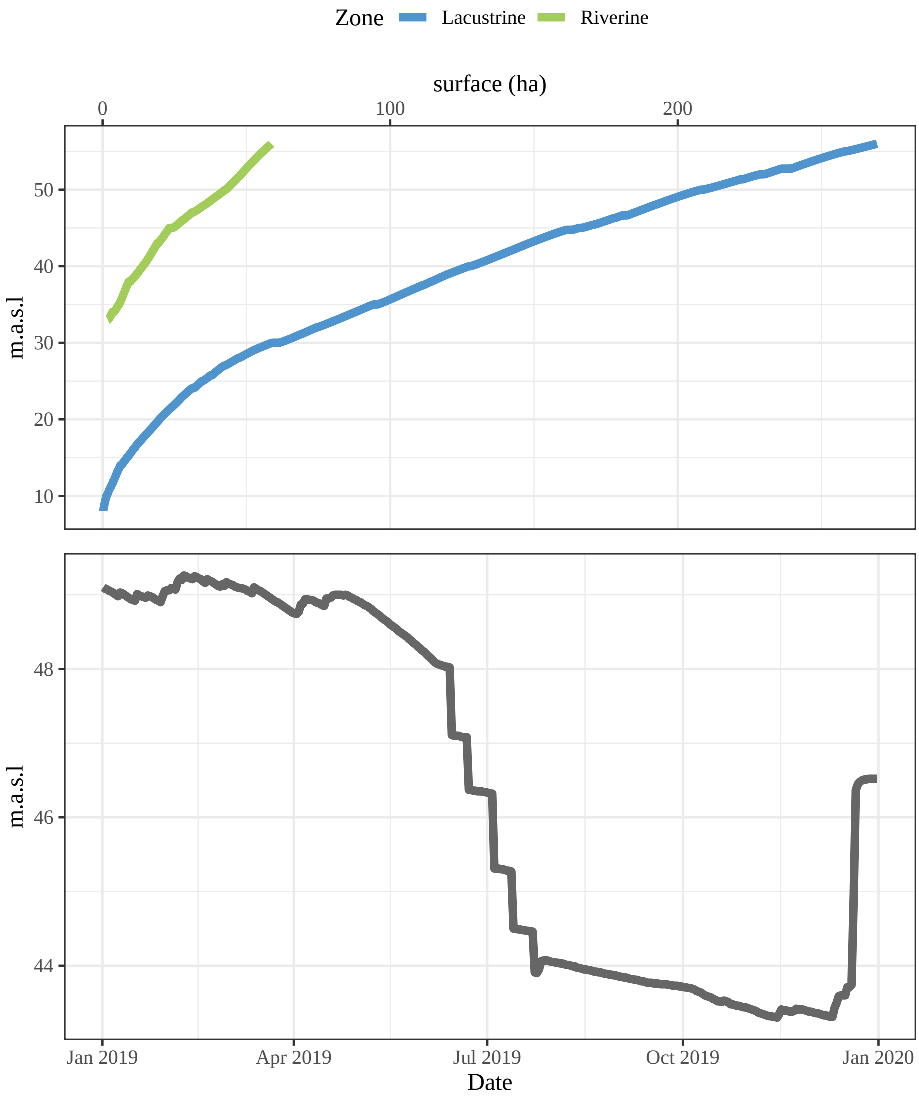

Figure B.2: Hypsographic curve of El Gergal for the riverine and lacustrine zones (above). Water level during 2019 (bellow)

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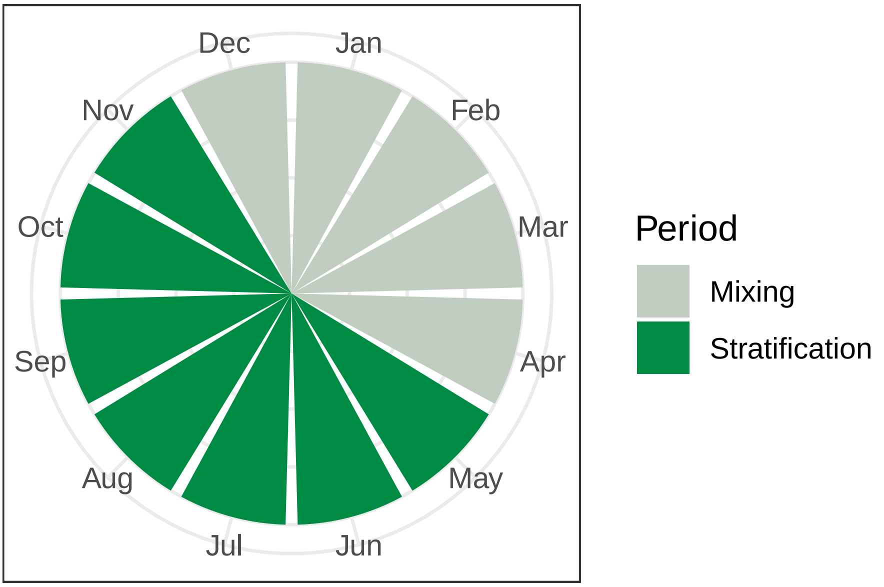

Figure B.3: Conceptual schedule of months in which water column was considered stratified and mixed for 2019 in El Gergal reservoir

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B.0.4 CO_2 and CH_4 fluxes

CO2 fluxes, in tons of CO2 per year, were calculated for water surface, drawdown area and the amount produced in the hypolimnion for each period: stratification and mixing. Fluxes from Chapter 4, Chapter 5 and Chapter 6 were used to estimated flux from water surface, drawdown areas and the hypolimnetic production, respectively.

For water surface and drawdown areas, mean monthly fluxes ($g{\cdot}m^{-2}{\cdot}d^{-1}$) measured in riverine or lacustrine zone were multiplied by the area of water surface or drawdown areas of each day of the month to obtain the flux of carbon per month and zone, using the following equation:

$$\mathrm{CO_2}\ flux\ (g \cdot month^{-1}) = \sum_{d=1}^{l} \mathrm{CO_2}\ rate\ (g \cdot m^{-2} \cdot d^{-1}) \cdot Area_d\ (m^{-2}) \tag{B.1}$$

CO_2 flux ($g{\cdot}month^{-1}$) is the total flux of CO_2 in one month, d is the day of the month from first day (1) until the last day l, CO_2 rate is the mean rate for a specific month and zone (riverine of lacustrine) and $Area_d$ is the surface of water or drawdown areas of a specific day of the month.

This equation was used to estimate the amount of carbon emitted/uptaken per month from the riverine and lacustrine zone. Then, annual emission and total emissions during stratification and mixing period was calculated summing the amount of carbon emitted/uptaken during each specific period. Finally, units were converted to tons in order to make interpretation easier.

For the amount of CO_2 produced in the hypolimnion ($\mathrm{CO_{2hypo}}$), the areal rate ($\mathrm{CO_2}$*areal rate*) calculated for Chapter 6 was multiply by the area of the mean thermocline depth ($Area_{thermo}$) and the length (in days) of stratification (d_{stra}).

$$\begin{aligned}\mathrm{CO_{2hypo}}\ flux\ (\mathrm{g}) = \mathrm{CO_2}\ areal\ rate\ (\mathrm{g}{\cdot}\ \mathrm{m}^{-2}{\cdot}\ \mathrm{d}^{-1}) \\ \cdot\ Area_{thermo}\ (\mathrm{m}^{-2}) \cdot d_{stra}(\mathrm{d})\end{aligned} \tag{B.2}$$

The same method was applied to CH_4, as followed for CO_2 fluxes.

B.0.5 Total C balance

Total carbon balance was calculated as:

$$Carbonbalance = C_{input} - C_{surface} - C_{output} + Volume_{deficit} \tag{B.3}$$

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Annual emission of CO_2 and CH_4 from the reservoir surface (i.e. water surface and drawdown area) were converted to tons of C and summed up to obtain total annual C emission from the reservoir surface ($C_{surface}$).

C_{output} from El Gergal was estimated multiplying mean total carbon (TC) concentration in the reservoir by volume of water withdrawn during that period.

C_{input} from Minilla reservoir into El Gergal was estimated multiplying mean total carbon (TC) concentration in Minilla reservoir by volume of water inflow during that period.

TC was calculated as the sum of DIC and total organic carbon (TOC). Mean DIC and total dissolved organic carbon (TOC) concentration was obtained from sampling of this thesis (El Gergal) and from the monitoring program of the water enterprise EMASESA (El Gergal and Minilla) carried out with frequency between 2 weeks and one and a half months.

$Volume_{deficit}$ is the amount of carbon which would be input into the reservoir if the volume at the beginning and at the end of the studied period were the same. This estimation was calculated using annual mean concentration of TC in the reservoir and the difference of volume between the beginning and the end of the studied period.

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