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The ecology of the Iberian inland waters: Homage to Ramon Margalef

Nutrient fluxes through boundaries in the hypolimnion of Sau reservoir: expected patterns and unanticipated processes

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ABSTRACT

By contrast to many natural lakes, the summer hypolimnion in advection-dominated systems like canyon-shaped reservoirs is not isolated from direct inputs from the river. This has important implications in the evolution of limnological features of the hypolimnion through the stratified period, especially if the river water directly plunges as a density current into the hypolimnion as a consequence of temperature differences. Taking the Sau Reservoir (Spain) as a prototype for this kind of systems, we present data from 11 years of monitoring to show how the river water entering the reservoir during summer is the main factor determining hypolimnetic nutrient concentrations. The empirical regression approach used all through the paper also stressed the effect of the improvement in water quality experienced by the river during the studied period on the improvement of the water quality stored in the summer hypolimnion of the reservoir. Since the change in river water quality was the consequence of the implementation of remediation measures at the basin scale, we advocate these solutions to manage reservoir eutrophication problems in this type of systems, which, in addition, had other unexpected benefits for the hypolimnetic water quality in Sau Reservoir.

Keywords: denitrification, empirical modelling, density currents, eutrophication, biological treatment.

RESUMEN

A diferencia de muchos lagos naturales, el hipolimnion que se forma en verano en sistemas dominados por la advección, como los embalses que inundan valles profundos y estrechos, no está aislado de las entradas directas desde el río. Esto tiene importantes implicaciones en la evolución de las características limnológicas del hipolimnion durante el periodo de estratificación, especialmente si el agua del río entra al embalse como una corriente de densidad directamente en el hipolimnion debido a diferencias de temperatura. Tomando el Embalse de Sau (España) como prototipo de este tipo de sistemas, mostramos 11 años de datos de un programa de monitoreo para ejemplificar cómo el agua del río que entra en verano al embalse es el factor determinante de la concentración de nutrientes en el hipolimnion. La aproximación de regresión empírica utilizada en el artículo también puso de manifiesto el efecto de la mejora en la calidad del agua que sufrió el río durante el periodo de estudio en la mejora del agua del agua embalsada en el hipolimnion. Ya que esta mejora en el río fue consecuencia de la implementación de medidas de restauración a nivel de la cuenca, promovemos estas soluciones para la gestión de problemas de eutrofización en este tipo de sistemas, que por otra parte mostraron ventajas inesperadas en el caso del hipolimnion del Embalse de Sau.

Palabras clave*: desnitrificación, modelado empírico, corrientes de densidad, eutrofización, tratamiento biológico.*

INTRODUCTION

Most deep natural lakes from the temperate and subtropical regions develop a well-defined layered structure during summer (Wetzel, 2001). The strengthening of a stable seasonal thermocline usually leads to a summer hypolimnion virtually isolated from the atmosphere. Since the runoff penetration into stratified waters tends to be small and dispersive for several reasons (runoff via low-order tributaries or diffusive sources, and interception by wetlands or littoral interface regions; Wetzel, 1990), the surface water input is not a recurrent driver on these systems during the summer months (Margalef, 1983). Thus, for most natural, non-manipulated lakes the biogeochemistry of hypolimnetic water during summer stratification can be approached considering this layer isolated from direct atmospheric or tributaries interactions. Lakes with significant groundwater recharge (e.g. Casamitjana *et al*., 1993), lakes of damming-like origin (e.g. Gibbs, 1992), and large lakes with high order tributaries draining vast watersheds (e.g. Vandelannoote *et al*., 1999) are the main exceptions.

By contrast, mainstream deep reservoirs show a relatively high drainage basin area: water body area ratio (Straškraba, 1998), implying a strong advective flux from the drained basin even during the low-flow summer conditions. In these systems the horizontal component of water fluxes have a major impact on its physical, chemical, and biological dynamics (Ford, 1990), to an extent that they are often considered as hybrid systems between lakes and rivers (Margalef, 1983). Additionally, if the continuous river input is overloaded with nutrients and organic matter, not only hydrology, but also the chemical load helps to define a marked longitudinal heterogeneity in the reservoir limnological characteristics (Kimmel *et al*., 1990). Canyon-shaped reservoirs are prototypical at this respect, because their morphology forces a very clear advective flux (Armengol *et al*., 1999).

Apart from these considerations, partially based in a plug-flow view of advective movements in reservoirs, one of the most striking limnological features of reservoirs (and specially in canyon-type ones) is the recurrent presence of the river water as density currents reaching the end-wall of the system (Ford, 1990). This exerts a paramount effect on the vertical physical structure of the reservoir: directly affects the density gradients and magnifies the differences in residence time between different layers if the river input goes to a well delimited water parcel (Rueda *et al*., 2006). Nevertheless, suspended and dissolved materials coming from the watershed will also be transported in these flows, enhancing chemical and biological vertical heterogeneity. These have an important implication for hypolimnetic water biogeochemistry during stratification: if the river water enters with little entrainment directly to the hypolimnion via a density current, the dynamics on this layer will be directly forced by a driver which is essentially independent of in-lake processes. This is quite a different situation compared to classical load-response models assumptions, which implicitly suppose a lagged, indirect effect in the hypolimnion through epilimnetic processes (Chapra and Canale, 1991; Chapra, 1997). All in all, not only the sediment boundary and the fluxes through thermocline need to be considered in these advective-dominated systems. Also the tributary inflow will play a role shaping the hypolimnetic biogeochemistry.

In this study we illustrate how interaction with sediments, flux through thermocline, and river inflow combine to explain the water chemical composition in the summer hypolimnion of a canyon-shaped reservoir showing summer density currents induced by the river inflow. In addition, we demonstrate how a change in the nutrient stoichiometry of the water entering the reservoir had a major impact on the water quality of the hypolimnion, using the oxygen content as an appropriate surrogate. Since data for this study comes from a long-term monitoring program collecting classical descriptive variables (in-situ probe-ready measures and nutrient analysis), we used an inductive empirical regression approach to understand the mechanisms driving the hypolimnetic dynamics.

THE RESERVOIR AND THE DATABASE

Sau Reservoir was first filled in 1963 in a middle stretch of the Ter River (NE Spain, 10 m^3 s^{-1} of median flow), which accounts for ca 90 % of the land drained by the Sau Reservoir (Fig. 1). The Ter river basin at Sau is 1380 km^2, and consists in a populated area (109 people km^{-2}), mainly covered by woodland (78 %) and agricultural land (16 %). Since the Sau dam was built, the water body experienced a process of

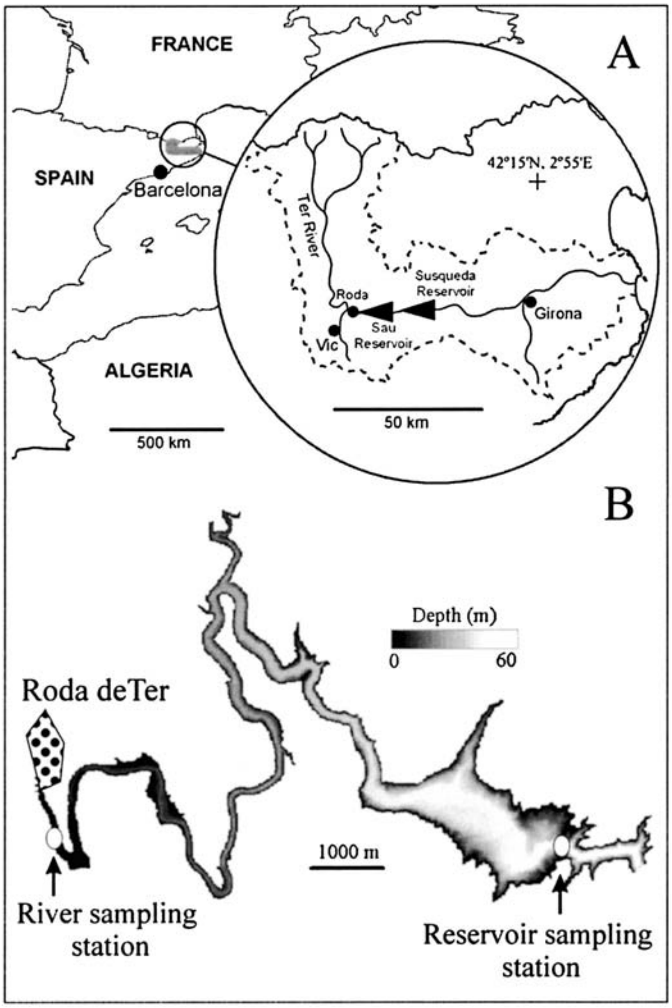

Figure 1. Location of (A) Sau Reservoir and (B) of sampling points. *Localización (A) del Embalse de Sau y (B) de los puntos de muestreo.*

increasing eutrophication (Vidal and Om, 1993), from moderately eutrophic during the first years, to severe eutrophication in the early 1990s. Several human activities in the basin contributed to the process: pig farming development, intensive use of agricultural fertilizers, proliferation of industrial clusters, and changes in land use (Sabater *et al*., 1990; Sabater *et al*., 1991; Vidal and Om, 1993; Sabater *et al*., 1995; Espadaler *et al*., 1997). Physical-chemical wastewater treatment plants (WWTP) were built in the main urban and industrial areas during the early 1990s, leading to a moderate improvement of the water quality of the reservoir. During the fall of 1999 the most sizeable from these WWTP (located at Vic, just a few kilometres upstream from the reservoir) was improved with additional biological treatment.

Limnological characterization of the Sau Reservoir started in 1963, conducted by the local water supply company (Aigües Ter-Llobregat, ATLL), and in agreement with the Department of Ecology (University of Barcelona) since 1994. Thus, an extended database is available on both changes in the water body and on incoming materials through the Ter River. Extended limnological descriptions and detailed processes in the reservoir can be found elsewhere (Armengol *et* *al*., 1986; Armengol and Vidal, 1988; Vidal and Om, 1993; Sommaruga *et al*., 1995; Armengol *et al*., 1999; 2000; Han *et al*., 2000; Comerma *et al*., 2001; Šimek *et al*., 2001; Gasol *et al*., 2002; Armengol *et al*., 2003; Comerma *et al*., 2003; Armengol *et al*., 2005; Rueda *et al*., 2006). As stated above, this study has two objectives: 1) to explain how different drivers affect the hypolimnion dynamics, and 2) to stress the effect of the change in the water quality of the Ter River inflow on the water quality of the hypolimnion. Because of the last point, we use data for the period 1995-2005, in order to avoid including many historical processes in the analysis. The aim is to directly point to the biological treatment implementation at the Vic WWTP.

The database consists of monthly samplings, covering the main inlet (Ter River at Roda de Ter, Fig. 1), and a sampling station located at the lacustrine section of the reservoir. For this station, vertical profiles of temperature, pH, conductivity, and oxygen concentration are available. Based on these profiles, analysis of a variety of dissolved and suspended elements from several water samples collected at selected depths are also accessible. Although not all of them are mentioned explicitly in the paper (to avoid specifying a plethora of non-significant results), we used the following variables: suspended solids, total nitrogen (TN), total phosphorus (TP), particulate N, P, and C, nitrate, nitrite, ammonia, soluble reactive phosphorus (SRP), silicate, alkalinity, dissolved organic carbon (DOC), chloride, and sulphate. The sampling at the river location was identical, but consisting only of one integrated water sample.

The government water agency (Agència Catalana de l'Aigua, ACA) supplied the daily hydrological and hydromorphological data of Sau Reservoir.

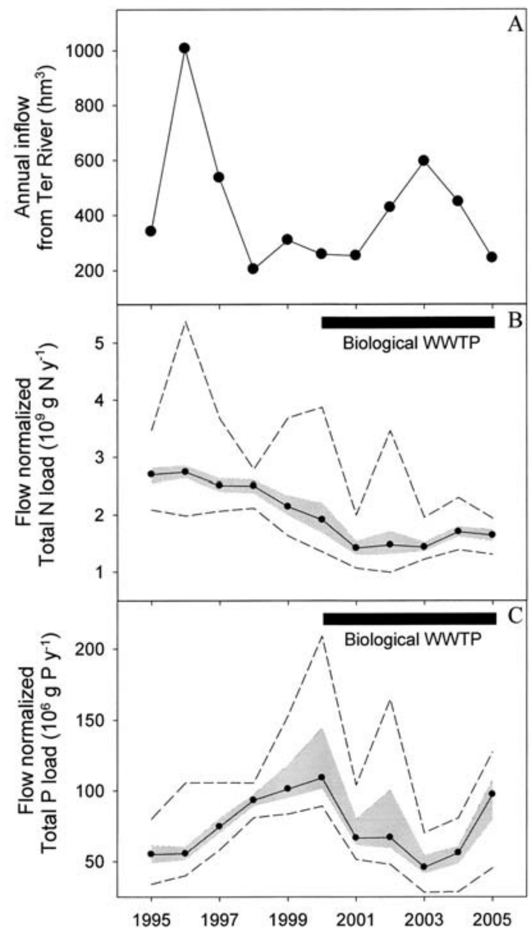

Figure 2. (A) Annual water inflow to Sau Reservoir from the Ter River, and (B, C) flow normalized TN and TP load to the reservoir during the studied period. Black bars mark the period with biological treatments in the WWTP of the basin. The dots in B and C denote the median value, whereas gray area is the interquartile range. Dashed lines delimit the 95 % confidence interval. For a detailed description of the load calculation and the uncertainty analysis see Marcé *et al*. (2004). *(A) Aporte anual de agua al embalse de Sau por el río Ter, y (B,C) carga de TN y TP normalizada por el volumen entrado durante el periodo estudiado. Las barras negras señalan el periodo con tratamientos biológicos en las WWTP de la cuenca. Los puntos en B y C representan el valor mediano, mientras que el área gris es el rango intercuartil. Las líneas discontinuas delimitan el intervalo de confianza al 95 %. Para una descripción detallada de los cálculos de cargas y su incertidumbre consultar Marcé* et al. *(2004)*

NUTRIENT LOAD HISTORY FROM THE TER RIVER

Like many other rivers located in developed countries (Alexander *et al*., 2000), the Ter River has experienced a profound time-varying human impact during the last forty years. Marcé *et al*. (2004) showed that the nutrient load coming into the Sau reservoir rose dramatically until the early 1990s, and then partially recovered during the last decade, as remediation measures were implemented in the basin. This has been a common pattern for many polluted rivers located in populated areas (e.g. CERN, 2000).

Figure 2 shows the detail of this load history for the period of this study, expressed as flow normalized loads (i.e. the load times the inflow volume for the corresponding year divided by the mean inflow for the whole period). Remarkably, the eleven-year period includes almost all the annual inflow range found in the whole history of Sau reservoir (Armengol *et al*., 1991). The series contains the driest year (1998), and the third most humid year on record (1996), only marginally inferior (12 %) than the observed maximum (1972). Thus, both very wet years and dry periods are lumped in the subsequent analysis. This is a very important point, because hydrology is usually taken as a main driver in shaping reservoir processes in the Mediterranean region (Geraldes and Boavida, 2004), where interannual variability of inflows is large.

The time evolution of TN and TP loads shows disparate patters (Fig. 2). TP did not follow any clear trend, with values ranging from 50 to 100 Mg P y^{-1}. By contrast, the flow normalized TN load showed a crisp decrease during the late 1990s, to maintain a value around 1.5 Gg N y^{-1} from 2001 to the present. The different behaviour showed by TN and TP load is due to the different timing of implementation of conventional WWTP and additional biological treatments. Whereas conventional treatments are efficient sequestering phosphorus from the effluents, the nitrogen compounds are only efficiently removed by biological treatments. The effect of the WWTP on the TP load was apparent just after the WWTP were built during the early 1990s (see Marcé *et al*., 2004), but not afterwards as figure 2 shows. This is a clear indication that most of the TP load comes nowadays from diffusive sources, conclusion also reached by Marcé *et al.* (2004) using a neuro-fuzzy regression modelling approach. By contrast, the TN load rapidly reacted to the implementation of biological treatments in the WWTP on the watershed.

The effect of the implementation of biological WWTP on the nitrogen load was not exclusively quantitative, but also qualitative. Whereas the nitrate load rose during the last years, the ammonia load showed a two-fold decrease (Fig. 3). In terms of the NH_4^+:NO_3^- molar ratio, these opposite trends are equivalent to a reduction from ca 2.5 to ca 0.1 (Fig. 3).

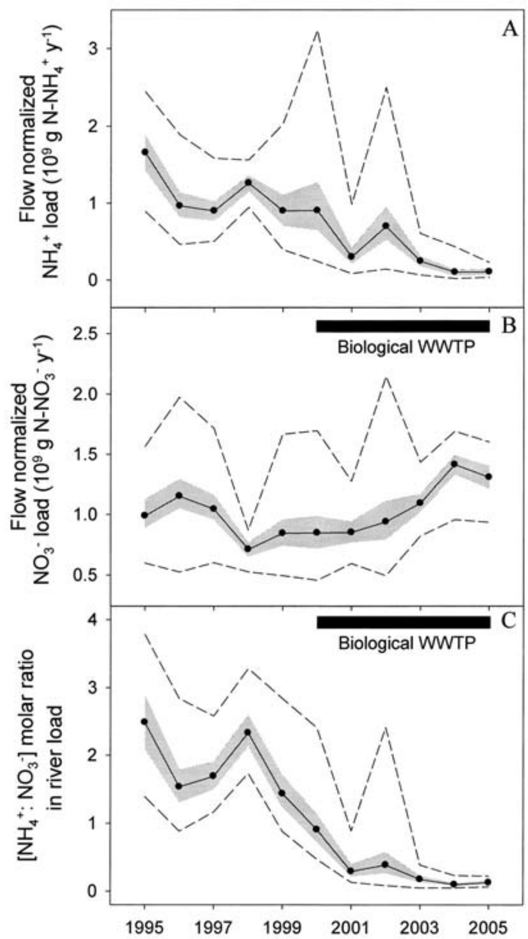

Figure 3. (A, B) Flow normalized ammonia and nitrate load to the reservoir during the studied period, and (C) ammonia:nitrate molar ratio during the same period. Black bars mark the period with biological treatments in the WWTP of the basin. Dots denote the median value, whereas the grey area is the interquartile range. Dashed lines delimit the 95 % confidence interval. For a detailed description of the load calculations and their uncertainty see Marcé *et al*. (2004). *(A, B) Carga de amonio y nitrato normalizada por el volumen entrado durante el periodo estudiado y (C) relación molar entre la carga de amonio y nitrato durante el mismo periodo. Las barras negras señalan el periodo con tratamientos biológicos en las WWTP de la cuenca. Los puntos representan el valor mediano, mientras que el área gris es el rango intercuartil. Las líneas discontinuas delimitan el intervalo de confianza al 95 %. Para una descripción detallada de los cálculos de cargas y su incertidumbre consultar Marcé* et al. *(2004).*

THE FATE OF THE TER RIVER WATER IN THE RESERVOIR

Although some aspects of the river circulation are difficult to simplify (e.g. location and mixing at the plunge point and entrainment with reservoir water across the reservoir; Ford, 1990), the depth of intrusion of river water in the reservoir can be reasonably well predicted from measured temperatures in the river and the reservoir, specially in systems like the Sau reservoir where water density is almost exclusively characterized by temperature (see Rueda *et al*., 2006).

Twelve years of Ter river temperature observations and the corresponding temperature profiles in the limonitic part of Sau reservoir has lead to a clear definition of the circulation pattern of the river water in the reservoir. Figure 4 summarizes this pattern for an average year (i.e. both the depth of the seasonal thermocline and the depth of intrusion of river water traces are smoothed functions of the monthly averages for the whole period). There are underflows during the first part of the winter, when the river water cools down much faster than the reservoir water. Soon in the spring, this situation is entirely reversed, and the river flows into the reservoir as an overflow during a short period. When the snow melts in the mountains later on during the spring the river water temperature rises significantly slower than the reservoir surface water, and the river arrives at the end-wall of the reservoir as an interflow. This situation will persist until the winter, when an underflow develops and the pattern is resumed. For detailed longitudinal transects and modelling results that supports the previous description, see Armengol *et al*. (1999) and Rueda *et al*. (2006).

Comparing this pattern with the depth of the seasonal thermocline that develops in the reservoir (Fig. 4) is apparent that during the summer months (from June to September) the river inflow always plunges deeper than the seasonal thermocline. Thus, during summer the river inputs go directly into the hypolimnion. This assertion assumes that the entrainment of river water into the surface waters during plunge and transport to the end-wall side of the reservoir is negligible in terms of the river load. Although in some situations this would not hold, for most density currents this is not an unreasonable assumption (Ford, 1990).

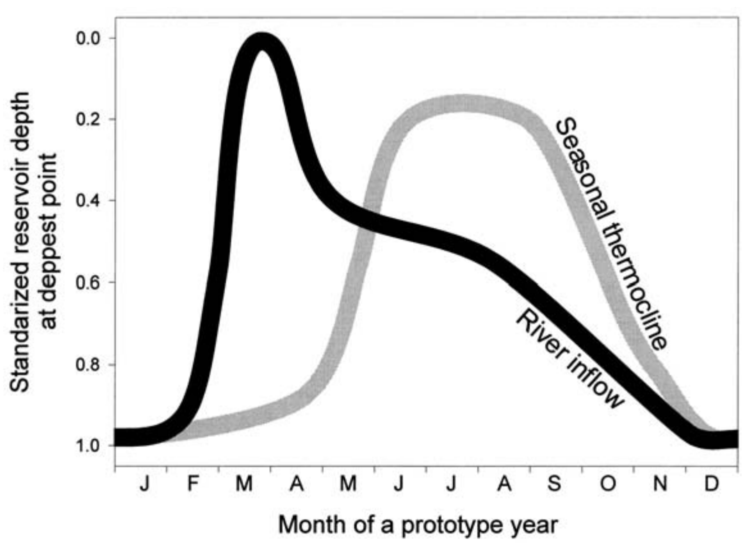

Figure 4. Schematic representation of the circulation of the Ter River water in the Sau Reservoir. The depth of the seasonal thermocline was estimated with the location of a density gradient of at least 0.15 Kg m^{-4}. The level of insertion of river water was calculated following Armengol *et al.* (1999). *Representación esquemática de la circulación del río Ter en el embalse de Sau. La profundidad de la termoclina estacional se ha estimado a partir de la localización de un gradiente de densidad mínimo de 0.15 Kg m^{-4}. La profundidad de inserción del río se calculó según Armengol* et al. *(1999).*

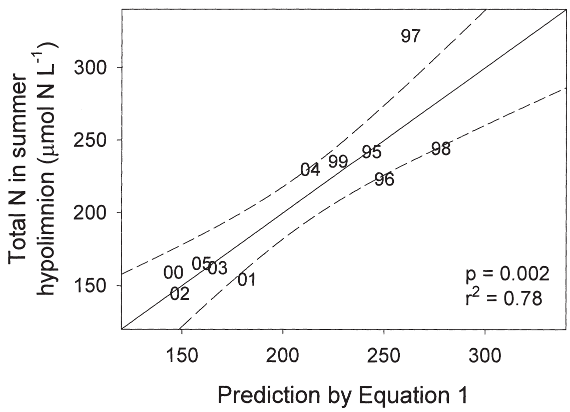

Figure 5. Observed TN concentration in the hypolimnion of Sau reservoir against the prediction by equation 1 in the text. Numbers in the figure denote the year of the corresponding summer. Continuous trace is the best prediction, and dashed lines the 95 % confidence intervals. *Concentración de TN observada en el hipolimnion del embalse de Sau respecto la predicción con la ecuación 1 del texto. Los números en la figura expresan el año del correspondiente verano. La línea continua es la mejor predicción, y las discontinuas el intervalo de confianza al 95 %.*

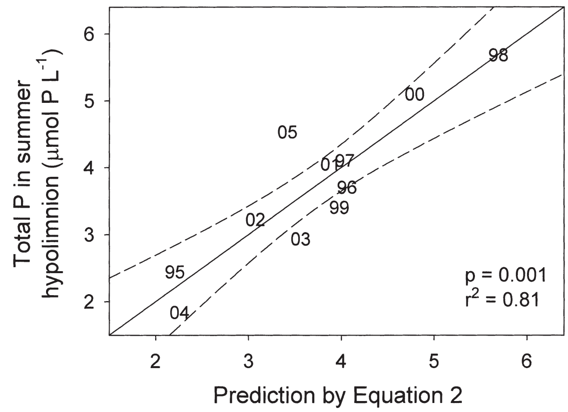

Figure 6. Observed TP concentration in the hypolimnion of Sau reservoir against the prediction by equation 2 in the text. Numbers in the figure denote the year of the corresponding summer. Continuous trace is the best prediction, and dashed lines the 95 % confidence intervals. *Concentración de TP observada en el hipolimnion del embalse de Sau respecto la predicción con la ecuación 2 del texto. Los números en la figura expresan el año del correspondiente verano. La línea continua es la mejor predicción, y las discontinuas el intervalo de confianza al 95 %.*

HYPOLIMNION BIOGEOCHEMISTRY: FLUXES THROUGH BOUNDARIES

Due to the characteristics of our database, and in consonance with the Rigler's "recognition of the possible" (Rigler, 1982), we did not try to develop a deductive, process-based model for the hypolimnetic biogeochemistry. Instead, we calculated volume-weighted summer averages for the available variables in the database (see *The Reservoir and the Database*), plus some other variables derived from these potentially candidates for playing a significant role in the hypolimnion dynamics (stability of the water column, water residence time, surface of anoxic sediment, and volume of anoxic water). Then, we explored linear relationships between all the variables, with the hope that this empirical regression approach would help to explain the main processes driving hypolimnetic nutrient chemistry. Although the significant correlations found by this analysis can be only regarded as empirical relationships or predictions in the sense of Rigler and Peters (1995), we inferred causal explanations supported by two facts. First, we worked in a single system with a seasonal time step. Thus, we avoided limitations that usually affect regressions including annual data for several systems, which necessarily lump a considerable number of processes. Second, we carefully examined alternative explanations to avoid extracting conclusions from spurious or indirect relationships. However, we acknowledge that more detailed, processes inspired experiments are necessary to definitively prove the conclusions outlined hereafter.

Concerning the main nutrients, the TN and TP summer hypolimnetic mean concentrations showed significant correlations with variables related with different boundaries (Figs. 5 and 6). The TN (µmol·L^{-1}) content could be explained by:

$$TN = 39.08 + 0.00086 \cdot \mathit{TN\ River\ Load} - 7.91 \cdot \mathit{Chl} \quad (1)$$

where *TN River Load* stands for the flow normalized TN load during summer (mol N·$season^{-1}$), and *Chl* for the chlorophyll-*a* concentration (µg·L^{-1}) in the hypolimnion (independent variables not correlated, r^2=0.11, p=0.31, n=11). Whereas the close relationship between TN and

TN load (partial r^2=0.77, p<0.001, n=11) is easily explained, the combined effect with *Chl* (partial r^2=0.49, p=0.02, n=11) is more cryptic. Since the chlorophyll-*a* concentration in the hypolimnion is a consequence of the settling of the epilimnetic phytoplankton community (a linear regression with epilimnetic *Chl* and thermal stability explains the 82 % of the variability in hypolimnetic *Chl*, p=0.001, n=11), the negative effect of *Chl* on TN concentration should be attributed to N that is passed to the particulate fraction and eventually lost via sedimentation of dead phytoplankton. I.e. we are assuming that the chlorophyll concentration in the hypolimnion is proportional to the sedimentation of algal cells. Remarkably, the same relationship was found between epilimnetic TN and chorophyll-*a*. Thus, the TN concentration in the hypolimnion is largely defined by both an external process (i.e. river load) which supplies N and an internal process (i.e. sedimentation) that consumes N.

TP (μmol $P \cdot L^{-1}$) showed dependency on the surface of anoxic sediment during summer and nitrate concentration in the hypolimnion (Fig. 6):

$$TP = 3.27 + 8.7 \cdot 10^{-7} \cdot \textit{Surface Anoxic Sediment} - 0.015 \cdot NO_3^- \qquad (2)$$

where *Surface Anoxic Sediment* (m^2) is the surface of reservoir bottom that is in contact with water containing less than 1 mg $O_2 \cdot L^{-1}$ (*sensu* Nürnberg, 1995), and NO_3^- (μmol $N\text{-}NO_3^- \cdot L^{-1}$) denotes nitrate concentration in the hypolimnion. Again, independent variables were not correlated (r^2=0.11, p=0.32, n=11). The combination of *Surface Anoxic Sediment* (partial r^2=0.46, p=0.03, n=11) and NO_3^- (partial r^2=0.66, p=0.004, n=11) in the equation suggests that internal load processes linked to anoxic conditions control phosphorus dynamics. Whereas the surface of anoxic sediment defines the extent in which internal load processes work, the presence of high nitrate concentrations inhibits strictly anaerobic reactions implying reduction of iron hydroxides (Schlesinger, 1997). Consequently, the P bounded to these oxidised iron compounds remains at the sediment, and internal load is curtailed. We did not find any inverse relationship relating TP and particulate matter similar to that found with TN. This is probably because the high efficiency of P recycling in Sau Reservoir, due to the huge alkaline phosphatase activities found in the reservoir (J. C. García, unpublished results).

We did not find any variable significantly correlated with the DOC concentration in the hypolimnion. Only some combinations of by-products of DOC decay gave significant regressions (e.g. ammonia and volume of anoxic water). Thus, no causal mechanisms could be inferred for the DOC hypolimnetic concentration.

Although particulate fractions constitute a minor portion of the nutrient pool in Sau Reservoir (dissolved fraction accounted for the 96 %, 83 %, and 77 % of TN, TP, and TC respectively), a very clear linear relationship was established between the summer mean concentration of hypolimnetic particulate fractions and the combination of epilimnetic concentration and thermal stability during the corresponding summer period (Fig. 7):

$$PN = 6.05 + 0.57 \cdot \textit{Epi PN} - 1.5 \cdot 10^{-3} \cdot \textit{Stability} \qquad (3a)$$

$$PP = 0.48 + 0.91 \cdot \textit{Epi PP} - 1.4 \cdot 10^{-4} \cdot \textit{Stability} \qquad (3b)$$

$$PC = 59.7 + 0.65 \cdot \textit{Epi PC} - 1.6 \cdot 10^{-2} \cdot \textit{Stability} \qquad (3c)$$

where *PX* (μmol $X \cdot L^{-1}$) stands for the particulate fraction in the hypolimnion, *Epi PX* (μmol $X \cdot L^{-1}$) for the particulate fraction in the epilimnion, and *Stability* ($J \cdot m^{-2}$) is the Schmidt's thermal stability of the water column (Schmidt, 1928). No significant correlation was found between independent variables. The number of cases for the regression against PP was only n= 6, because the analysis for this variable started in 1999. We interpreted the relationships in equation 3 as an indication of the sestonic flux from the epilimnion through the thermocline, which must be enhanced during periods of weak stratification. This relationship was less clear with the PP (Fig. 7b), which did not include 1999 (1.12 μmol$\cdot L^{-1}$), considered an outlier. This high PP value during this year, which coincides with the minimum value for the hypolimnetic volume stored in the

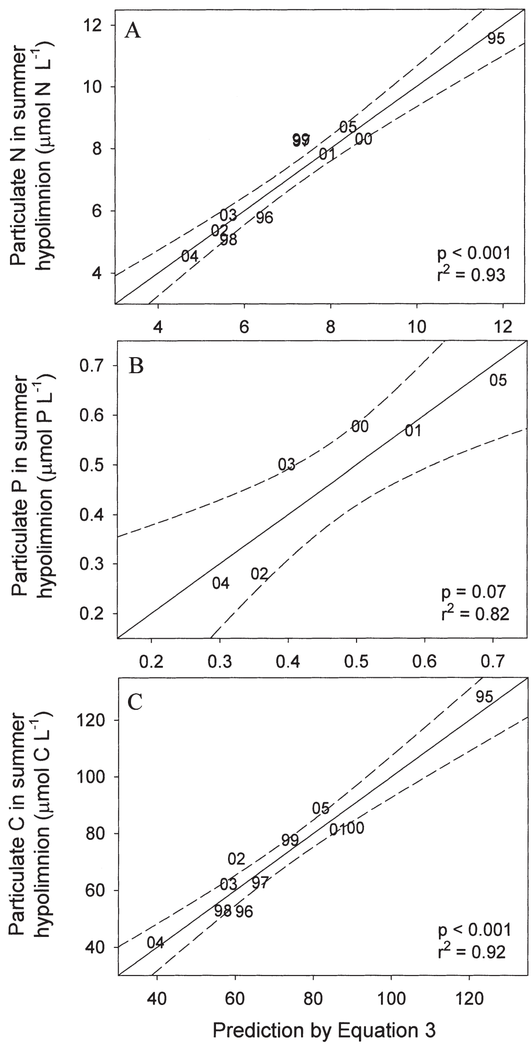

Figure 7. (A) Observed particulate nitrogen (PN) concentration in the hypolimnion of Sau reservoir against the prediction by equation 3a in the text. (B) Observed particulate phosphorus (PP) concentration in the hypolimnion of Sau reservoir against the prediction by equation 3b in the text. (C) Observed particulate carbon (PC) concentration in the hypolimnion of Sau reservoir against the prediction by equation 3c in the text. Numbers in the figures denote the year of the corresponding summer. Continuous traces are best predictions, and dashed lines the 95 % confidence intervals. *(A) Concentración observada de nitrógeno particulado (PN) en el hipolimnion del embalse de Sau respecto la predicción con la ecuación 3a del texto. (B) Concentración observada de fósforo particulado (PP) en el hipolimnion del embalse de Sau respecto la predicción con la ecuación 3b del texto. (C) Concentración observada de carbono particulado (PN) en el hipolimnion del embalse de Sau respecto la predicción con la ecuación 3c del texto. Los números en la figura expresan el año del correspondiente verano. Las líneas continuas son la mejor predicción, y las discontinuas el intervalo de confianza al 95 %.*

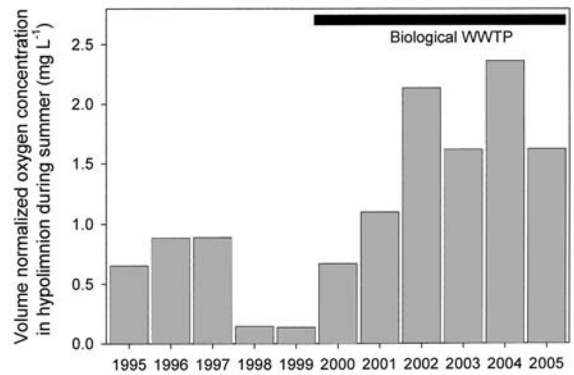

Figure 8. Volume-normalized oxygen concentration in the hypolimnion of Sau reservoir during summer. Black bar mark the period with biological treatments in the WWTP of the basin. *Concentración de oxígeno normalizada por el volumen en el hipolimnion del embalse de Sau en verano. La barra negra señala el periodo con tratamientos biológicos en las WWTP de la cuenca.*

reservoir, seems to point to a resuspension mechanism. However, there is not enough data to contrast the existence of such a process.

All in all, two main fluxes shape the nutrient concentration in the hypolimnion of Sau. First, the sestonic flux that controls the particulate fractions and to some extent the TN concentration. The sestonic flux partially depends on the degree of water thermal stability, and consequently on hydrologic conditions. Second, the input from the Ter River, which accounts for most of the variability showed by TN concentration. The TP concentration also depends on the river input, but in an indirect way. As we will see in the next section, anoxic episodes in the hypolimnion have been largely controlled by the river input. Thus, the river will also control the TP concentration, which depends on an internal load process that needs anaerobic conditions.

THE HYPOLIMNETIC OXYGEN CONTENT CONTROLLED BY THE RIVER: AN UNANTICIPATED SYSTEM-BROAD REMEDIATION MEASURE

One of the most conspicuous changes in the limnological characteristics of Sau Reservoir during the last years was the decrease in magnitude and extension of the hypolimnetic anoxic episodes. Figure 8 shows this trend for the last years, expressed as the volume weighted mean oxygen concentration in hypolimnion during summer. Also, the reservoir did not react to some extreme forcing as expected for a highly eutrophic limnetic system. For example, in autumn 2005, one of the driest years during the studied period, the reservoir was almost dried up for management purposes. Under these circumstances (low volume during summer followed by an intense dropping in the water level during the overturn), the managers were worried about the possibility of a fast degradation of the reservoir water quality in the deep layers during the management operation, specially taking into consideration similar episodes during the late 1980's that implied the presence of high concentrations of reduced compounds in the hypolimnion. A bit surprisingly, reduced compounds in the hypolimnion remained at very low levels all through the operation. Two questions arise from these observations: 1) Why are the anoxic episodes in the hypolimnion of the reservoir of less magnitude during the last years if the biomass of producers has not changed for decades? And 2) why the reservoir seems to have some extra oxidizing power to control reduced substances in the hypolimnion during the last years?

The answer lays in the dramatic changes in the quality of the water supplied by the river during the last decade. As stated earlier, the implementation of biological treatments in the WWTP of the basin leads to a change in the quality of the water transported by the river. The nitrogen present now is mainly in the form of nitrate (Fig. 3), and the quantity of DOC loaded to the reservoir has been reduced four times (from 6.2 Mg $C \cdot y^{-1}$ to 1.5 Mg $C \cdot y^{-1}$). These two facts acted together to improve the quality of the water stored in the hypolimnion, specially taking into account that during summer the river water virtually *plunges* into the hypolimnion. On one hand, the diminution in the DOC load curtailed the reducing power of hypolimnetic waters, thus reducing the oxygen consumption in this layer. On the other hand, the enhanced nitrate load proceeded like a nitrate bioremediation measure, supplying recourses for the denitrifying bacteria that inhibits other energetically less-efficient reactions that supply reduced compounds to the water (e.g. manganese and iron reduction, and sulphatoreduction). These two facts also inhibited the internal load of P, as we discussed in the previous section.

The above conclusions are derived from the close relationships found between the volume

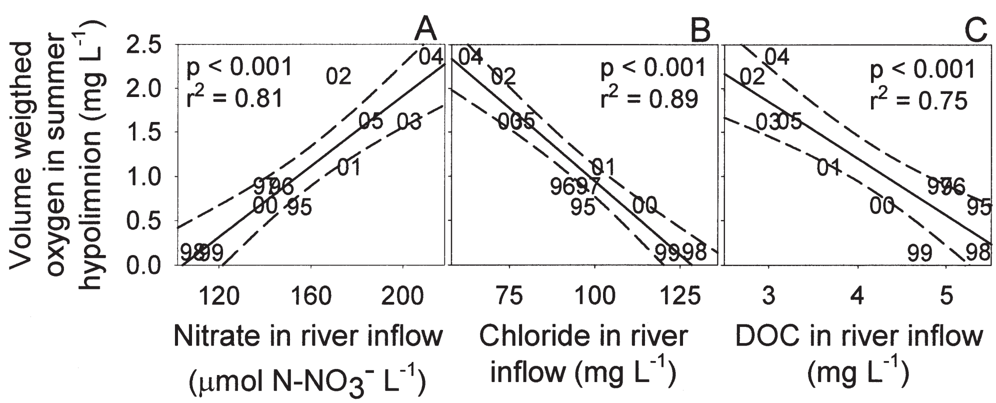

Figure 9. Volume-normalized oxygen concentration observed in the hypolimnion of Sau reservoir in summer against (A) nitrate concentration in the river inflow during summer, (B) chloride concentration in the river inflow during summer, and (C) DOC concentration in the river during the same period. Numbers in the figures denote the year of the corresponding summer. Continuous traces are linear regressions, and dashed lines the 95 % confidence intervals. *Concentración de oxígeno normalizada por el volumen en el hipolimnion del embalse de Sau en verano respecto (A) la concentración de nitrato en el río durante el verano, (B) la concentración de cloruro en el río durante el verano, y (C) la concentración de DOC en el río para el mismo periodo. Los números en las figuras expresan el año del correspondiente verano. Las líneas continuas son regresiones lineales, y las discontinuas el intervalo de confianza al 95 %.*

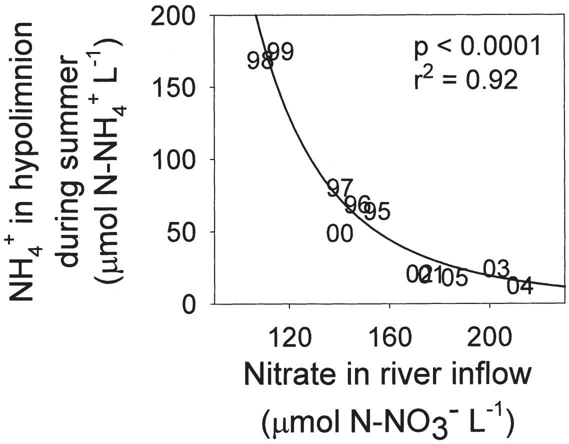

Figure 10. Ammonia concentration in the hypolimnion of Sau reservoir against nitrate concentration in the river inflow during summer. Numbers in the figures denote the year of the corresponding summer. Continuous trace is a power regression (see equation 4 in the text). *Concentración de amonio en el hipolimnion del embalse de Sau en verano respecto la concentración de nitrato en el río durante el verano. Los números en las figuras expresan el año del correspondiente verano. La línea continua es una regresión potencial (ver ecuación 4 en el texto).*

weighted mean oxygen concentration in the hypolimnion during summer and some variables related to the summer concentration of substances in the river inflow (Fig. 9). The inverse relationship between DOC concentration in the river and the oxygen content is highly significant (Fig. 9c), and their dynamics coincides with that showed by the relationship between hypolimnetic oxygen concentration and chloride concentration in the river (Fig. 9b). Due to the fact that there is no significant natural source of chloride in the basin (except rain related inputs), chloride concentrations in the river are a good surrogate of the impact of human related spills in the river. Thus, these two regressions express the same idea, best represented by the chlorine river concentration because it better integrates the effects over the hypolimnetic oxygen concentration that can exert a complex mixture of dissolved and particulate organic compounds.

There also exists a clear relationship between the nitrate concentration in the river inflow during summer and the hypolimnetic river concentration (Fig. 9a). Since chloride and DOC concentrations in the river showed a highly significant correlation with the nitrate river concentration (r^2=0.81, p>0.001, n=11), the regression pictured in figure 9a should not be interpreted as a causal relationship. However, the nitrate concentration in the river inflow correlates in a non-linear way with the ammonia concentration in the hypolimnion (Fig. 10):

$$\log_{10} NH_4^+ = 10.51 - 4.04 \cdot \log_{10} River\ NO_3^- \quad (4)$$

NH_4^+ being the ammonia mean concentration in the summer hypolimnion (µmol $N\text{-}NH_4^+ \cdot L^{-1}$), and $River\ NO_3^-$ the river mean nitrate concentration during summer (µmol $N\text{-}NO_3^- \cdot L^{-1}$). It is worth to mention that this power relationship is highly significant (r^2=0.92, p<0.0001, n=11), whereas the regression of the same dependent variable against chloride and DOC river concentrations is much less powerful (respectively, r^2=0.66, p=0.002, and r^2=0.53, p=0.01, both n=11). Interestingly, the hypolimnetic ammonia concentration and the ammonia river concentration are not significantly correlated (r^2=0.34, p=0.06, n=11). Thus, the nitrate entering from the Ter River controls the presence of this reduced substance in the hypolimnion, probably via maintaining a redox potential unfavourable to the persistence of decomposition-related NH_4^+. High nitrate inputs are probably keeping other reduced substances at low levels (e.g. Fe^{+2}, Mn^{+2}, or H_2S), and consequently the internal load of P, because denitrifying bacteria outcompete other less-efficient heterotrophs (Schlesinger, 1997).

The plunge of a nitrate-enriched inflow into the hypolimnion during the last summers can be compared to a nitrate bioremediation measure (Ripl, 1976), in which nitrate is injected in the hypolimnion to oxidize the bottom water and the surface sediment. However, as Margalef (1983) pointed out, the chemical oxidation (with nitrate or oxygen) of the hypolimnetic waters only "*maintains in the cycle more nutrients, and delay the solution of the problem derived by the excess of these nutrients*" (Margalef, 1983, p. 866). Talking about air injection, but totally applicable to nitrate injection, the same author mentioned that this measure "*do not mitigate eutrophication, but substitutes the excretion* (of nutrients) *by the acceleration*, *maintaining in* *the gyre more materials*" (Margalef, 1983, p. 657. See also figure on p. 832). In fact, Jansson (1986) alerts that if nitrate is totally consumed after its application in the hypolimnion, the release of P trapped in the sediment is dangerously enhanced. Thus, the positive effect of the nitrate injection by the river into the hypolimnion in Sau Reservoir was possible because the concurrent reduction of nutrients and organic matter entering the reservoir. It is worth to note that if the water outlet of the reservoir is located below the level of the thermocline (as in Sau Reservoir), this additional export of nutrients through the exit will assist in maintaining a hypolimnion with a reasonably good water quality. This is another key difference between lake and reservoir hypolimnetic dynamics.

In conclusion, the hypolimnetic water quality in reservoirs depends to a large extent on the water supplied by the river. Consequently, successfully system-broad remediation measures should take into account nutrient and organic matter diversion programmes before other measures related to internal processes (e.g. sediment sealing) are implemented. As we showed, if diversion is combined with concomitant inflow quality changes other unanticipated, zero cost benefits can arise.

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