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## **STATISTICAL BEHAVIOUR OF LOAD ESTIMATORS BASED ON ROUTINE MONTHLY DATA SERIES**

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**Abstract.** *Irrigation contributes to the pollution of water bodies through the pollutant loads in the irrigation return flows. Establishing the relationship between changing irrigation and agricultural practices and pollutant loads over long periods may help to identify the irrigation-related factors that most affect water quality.*

*This paper aims to ascertain the statistical performance of 5 salt and nitrate load estimators based on the long-term monthly records of the surface water quality monitoring network (SWQ) of the Ebro Basin Authority (CHE). These estimates were compared with daily estimates in the Arba River*

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monitoring station at Tauste (taken as reference loads), included in the newer irrigation return flows network (ReCor-Ebro; R-E) during April 2004 to September 2010.

Three estimation methods used grab-samples monthly  $TDS_i$  and  $NO_{3i}$  from the SWQ network (multiplied by instant,  $Q_i$ , mean daily,  $Q_d$ , or monthly,  $Q_m$ , flows), whilst the other two were the product of the regression estimates of TDS and  $NO_3$  from  $Q_d$  by  $Q_d$  or  $Q_m$ . The instant concentration-based models were also tested with daily data from the R-E network, with more complete records.

The regression estimators performed better than the models based on instant samples for salt loads. But for nitrogen loads, the estimators based on  $NO_{3i}$  and  $Q_d$  or  $Q_m$  also performed well when drawing data from the more complete R-E data series. Although the biases for the 5 methods were not significant; only these estimators presented errors low enough to allow their use in generating reliable load time series.

**Keywords.** Water quality, salt loads, nitrate loads, sampling frequency, agreement indexes.

## Introduction

The European Water Framework Directive (WFD) aims to protect and enhance the status of aquatic ecosystems, prevent further deterioration and promote sustainable water use based on long-term protection of available water resources. Member States shall implement the necessary measures to prevent deterioration of the status of water bodies to reach a good ecological status of European water bodies in year 2015. The new basin hydrologic plans are required to collect and maintain information on the type and magnitude of the significant anthropogenic pressures to which the surface water bodies in each river basin district are subject to. These include irrigation diffuse pollution, with identification of long term anthropogenic induced trends in pollutant concentrations and the response of the identified trends to the correction measures applied.

In the last 30 years, the salt and nitrate concentrations have apparently increased in the basin as a result of both a concentration increase per-se and generalized flow decrease (CHE, 2007), whereas the salt and nitrate loads have remained constant or decreased slightly (CHE, 2011). These effects, among other factors, may result from the increase in irrigated surface in the last 40 years and on-going changes in irrigation systems (especially the shift from traditional surface irrigation to pressurized systems) that may be affecting the salt and nitrogen loads in the basin through the irrigation return flows. The study of the historic evolution of salt and nitrate loads in the basin rivers along with the evolution of irrigated surface, characteristics of the irrigated soils, crops, types of irrigation, and water withdrawals may shed light on the effect of irrigation on water quality. The Ebro River Basin Authority (CHE) started a systematic sampling of water quality with monthly frequency in October 1961 with six control points; in 2012 the different CHE control networks include more than 497 monitoring points. The instantaneous character of the samples and the monthly frequencies introduce some uncertainty in the calculation of monthly loads from these data. In 2004, CHE initiated the Irrigation return flow control network (RecoR-Ebro) that analyze electrical conductivity (EC) and nitrate ( $\text{NO}_3$ ) concentrations of daily grab samples. The Arba River at Tauste was the first control point in this network. The Arba River collects the drainage outflow of the Bardenas irrigation District with more than 62,000 irrigated ha upstream of the control point at Tauste. The daily information collected in this station provides an excellent data source to evaluate uncertainty of load estimation from long-term data series recorded by CHE with monthly frequency.

The objective of this work is to compare different estimation methods of monthly salt and nitrate loads using the monthly frequency long-term data series collected by CHE, with reference loads obtained from the daily information collected in the station of Arba in Tauste in the RecoR-Ebro network for the period April 2004 to September 2010.

## Material and Methods

The Arba River is a left-margin tributary of the Ebro River with a surface area of 220,000 ha and an irrigated surface above 62,000 ha (Bardenas Irrigation Scheme). Irrigation water is diverted from the Yesa reservoir in the Aragón River through the Bardenas Canal, this irrigation water has low salt ( $\text{EC}=0.35$  dS/m) and nitrate concentration ( $1.49$  mg/L) (CHE, 2005a).

The soils, developed over glacial and quaternary alluvial deposits, are relatively shallow and very permeable; lying over tertiary deposits of low permeability composed of clays, marls and sandstone with some saline and gypsum-rich strata. These materials are considered the main natural source of salt loads in the basin (Causapé et al., 2004). The basin has a Mediterranean climate, characterized by mean annual precipitation of 400-500 mm higher in spring and fall,

and mean average temperature between 13°C and 14°C. In the natural flow regime, the average flow has been estimated in 172.8 Mm<sup>3</sup>/year with a peak between January and April and minimum values from July to October (CHE, 2005b). Irrigation return flows have affected the natural regime, with a contribution of 56 Mm<sup>3</sup>/year and a shift of the maximum values to the summer months and the minimum values to fall-winter (CHE, 2005b).

The Bardenas Irrigation Scheme started operations in 1960. The irrigated surface has increased since then, with changes in distribution canals, average plot sizes, crop distribution and in the last years with changes from surface irrigation methods to pressure systems (sprinkler and pivots). All these changes are supposed to affect the contribution of salt and nitrate loads draining to the Arba River.

Data for this study have been taken from four different networks controlled by CHE active at the Arba River in Tauste; the monitoring networks and the variables taken from each are:

1. ReCoR-Ebro network (R-E). Control station Arba in Tauste. Data series of instantaneous electrical conductivity (EC, dS/m) and nitrate concentration (NO<sub>3</sub>, mg/l) of grab samples taken daily at 12:00 suntime for the period April 2004 to September 2012.
2. Surface Water Quality control network (SWQ), control point no. 60, Arba de Luesia in Tauste with data since October 1974. Data of instantaneous electrical conductivity (EC<sub>i</sub>, dS/m), and nitrate concentration (NO<sub>3i</sub>, mg/l) in grab samples taken once a month and instantaneous flow at the moment of sampling (Q<sub>i</sub>, m<sup>3</sup>/s) for the period April 2004 to September 2010.
3. Stream-flow gauging network (SFG). Control point EA- 260, Arba de Luesia in Tauste with data since January 1973: average daily streamflow (Q<sub>d</sub>, m<sup>3</sup>/s) for the period April 2004 to September 2010.
4. Hydrological information automatic system network (SAIH). Control point A-260 Arba-Tauste, with instantaneous streamflow recorded every 15 minutes since September 2003. The information collected in the SAIH has been used to restore incomplete streamflow records in SWQ networks and to take the streamflow at the time of sampling in instantaneous series generated from RecoR-Ebro concentrations for the period April 2004 to September 2010.

Table 1. Statistics of the variables used in this study: number of data in the series (N), mean, maximum (Max.), minimum (Min.), median and standard deviation (SD). Q<sub>d</sub>, EC and NO<sub>3</sub> are the mean daily flow, the electrical conductivity and the nitrate concentration respectively taken from RecoR-Ebro network(R-E); Q<sub>i</sub>, EC<sub>i</sub> and NO<sub>3i</sub> are the instantaneous flow, electrical conductivity and nitrate concentration respectively derived from the surface water quality network (SWQ) and Q<sub>q</sub>, the instantaneous flow, taken from the gauging network (SAIH) at the sampling time of RecoR-Ebro.

	<b>Q<sub>d</sub></b>	<b>EC</b>	<b>NO<sub>3</sub></b>	<b>Q<sub>i</sub></b>	<b>EC<sub>i</sub></b>	<b>NO<sub>3i</sub></b>	<b>Q<sub>q</sub></b>
Network	SFG	R-E	R-E	SWQ	SWQ	SWQ	SAIH
<i>N</i>	2237	2299	2299	31	66	52	56
<i>Mean</i>	6.31	2.8	39.0	9.22	2.6	35.9	6.3
<i>Max.</i>	111.1	7.5	94	28.6	5.2	65.1	17.6
<i>Min.</i>	0.8	0.9	1	2.6	0.9	10.3	1.2
<i>Median</i>	5.0	2.6	39.3	7.0	2.5	36.3	5.2
<i>SD</i>	6.6	1.3	14.2	6.2	1.0	12.5	3.5

### **Methods for estimation of salt and nitrate loads**

Five estimation methods were compared to reference loads. The first three methods use directly the instantaneous EC<sub>i</sub> and NO<sub>3i</sub> measured monthly in the water quality control network of CHE (SWQ), whilst the two last methods are based on flow records and the relationships between EC or NO<sub>3</sub> and daily flow (Q<sub>d</sub>). Reference monthly salt (SL<sub>o</sub>) and nitrate (NL<sub>o</sub>) loads were

calculated using the daily information of the RecoR-Ebro network, considered to be the best possible estimate of salt and nitrate loads.

For all methods, electrical conductivity (EC, dS/m) was converted to salt concentration or total dissolved solids, (TDS, mg/L) using a conversion factor of 733.56 [TDS (mg/L) = 733.56 • EC (dS/m, 25°C), n=52, R<sup>2</sup> =0.96, p<0.05] obtained with all data available of major ions concentrations (Cl, SO<sub>4</sub>, HCO<sub>3</sub>, Ca, Mg and Na) in the SWQ network for the Arba in Tauste station.

The model used to relate EC to mean daily flow was selected from Hall (1970) (Eq. [1]) and fitted to the data of RecoR-Ebro network. This model was used to estimate EC from mean daily or monthly flow in estimation methods 4 and 5.

$$EC = \frac{(6.37 - 0.92)}{1 + 0.22 \cdot Q_d^{1/0.69}} + 0.92 \quad n=2236, R^2=0.73, p<0.05 \quad [1]$$

There was no clear relationship between nitrate concentration and streamflow. However a significant linear relation was established between nitrate concentration and EC (Eq [2]).

$$NO_3 = 13.23 + 27.70 \quad Ln \quad EC \quad n=2114, R^2=0.77, p<0.05 \quad [2]$$

To estimate nitrate concentration from flow in estimation methods 4 and 5, EC was first estimated from Q<sub>d</sub> using Eq.[1] and then NO<sub>3</sub> was estimated from that EC estimate using Eq.[2].

Reference monthly salt loads (SLo) and nitrate loads (NLo) were calculated as the sum for each month of the product of salt concentration (TDS) or nitrate concentration of daily samples and mean daily flow (Q<sub>d</sub>) of the RecoR-Ebro network.

$$SLo = \sum_{month} Q_d \cdot TDS(EC) \quad NLo = \sum_{month} Q_d \cdot NO_3 \quad [3]$$

1. Monthly instantaneous salt or nitrate loads and instantaneous flow (MSi, MNi) were calculated as the product of instantaneous TDS<sub>i</sub> or nitrate concentrations (NO<sub>3i</sub>) and instantaneous flow (Q<sub>i</sub>) recorded in the SWQ network:

$$MSi = Q_i \cdot TDS_i(EC_i) \quad MNi = Q_i \cdot NO_{3i} \quad [3.1]$$

2. Monthly instantaneous salt or nitrate loads and mean daily flow (MSid, MNid) were calculated as the product of instantaneous TDS<sub>i</sub> or nitrate concentrations (NO<sub>3i</sub>) from the SWQ network and average daily flow of the sampling date (SFG network):

$$MSid = Q_d \cdot TDS_i(EC_i) \quad MNid = Q_d \cdot NO_{3i} \quad [3.2]$$

3. Monthly instantaneous salt loads (MSim) and nitrate loads (MNim) were calculated as the product of instantaneous TDS<sub>i</sub> or nitrate concentrations (NO<sub>3i</sub>) from the SWQ network and average monthly flow (SFG network) of the corresponding month:

$$MSim = Q_m \cdot TDS_i(EC_i) \quad MNim = Q_m \cdot NO_{3i} \quad [3.3]$$

4. Daily salt (MSd) and nitrate loads (MNd) were calculated as the sum for each month of the product of salt concentration obtained from daily flow using Eq [1], or nitrate concentration estimated from daily flow using Eq. [1] and [2], and mean daily flow (Q<sub>d</sub>):

$$MSd = \sum_{month} Q_d \cdot TDS(EC(Q_d)) \quad MNd = \sum_{month} Q_d \cdot NO_3(EC(Q_d)) \quad [3.4]$$

5. Monthly salt loads (MSm) and nitrate loads (MNm) were calculated as the product of salt concentration obtained from monthly flow using Eq [1] or nitrate concentration estimated from monthly flow using Eq. [1] and [2], and mean monthly flow ( $Q_m$ ):

$$MSm = Q_m \cdot TDS(EC(Q_m)) \quad MNm = Q_m \cdot NO_3(EC(Q_m)) \quad [3.5]$$

The data series of instantaneous values obtained from SWQ network, methods 1, 2 and 3 (Eq. 3.1, 3.2 y 3.3) had numerous missing data. For that reason a more complete data series of EC and  $NO_3$  was drafted from the R-E series, drawing instantaneous flow ( $Q_q$ ) from the information recorded in the SAIH network.

### Statistical analysis

The coefficient of determination ( $R^2$ ) of the linear regression between salt and nitrate loads estimates and reference loads was used to analyze the strength of the relationship between reference and estimated loads. Although regression analysis shows the strength of the relationship between reference and estimated loads, it does not indicate the agreement between estimated and reference values. The agreement between salt and nitrate load estimates and reference loads was evaluated using the following indexes: Mean Bias (MB), Root Mean Square Error (RMSE), Mean Absolute Error (MAE), and Nash-Sutcliffe Efficiency (NSE) defined in Table 2.

The mean bias is the average of the differences between reference and estimated loads, and measures the average tendency of the estimated values to be larger or smaller than reference data (Moriassi, 2007). Root mean square error (RMSE) is the standard deviation of the differences between reference and estimated loads and indicates if bias is significant. Mean Absolute error (MAE) is the absolute deviation of the differences between reference and estimated loads. RMSE and MAE are among the best overall measures of method performance, although MAE is less sensitive to extreme values than RSME (Willmott, 1982). The Nash-Sutcliffe Efficiency (NSE) is a normalized statistic that determines the relative magnitude of the residual variance (noise) compared to the measured data variance (information) (Nash and Sutcliffe, 1970). NSE ranges between  $-\infty$  and 1, with  $NSE = 1$  for a perfect fit. Values between 0 and 1 are generally viewed as acceptable levels of performance, whereas values  $\leq 0$  indicate that the mean reference value is a better predictor than the calculated value, pointing to an unacceptable performance of the indicator (Moriassi, 2007).

Table 2. Indexes to compare Reference loads and Estimated loads,  $Y_i^{ref}$  = reference value,  $Y_i^{est}$  = estimated value,  $\overline{Y^{ref}}$  = mean of reference loads

Mean Bias	Root mean square error	Mean absolute error	Nash-Sutcliffe Efficiency
$MB = \frac{\sum_{i=1}^N (Y_i^{ref} - Y_i^{est})}{N}$	$RMSE = \left[ \frac{\sum_{i=1}^N (Y_i^{ref} - Y_i^{est})^2}{N} \right]^{0,5}$	$MAE = \left[ \frac{\sum_{i=1}^N \ Y_i^{ref} - Y_i^{est}\ }{N} \right]$	$NSE = 1 - \left[ \frac{\sum_{i=1}^N (Y_i^{ref} - Y_i^{est})^2}{\sum_{i=1}^N (Y_i^{ref} - \overline{Y^{ref}})^2} \right]$

## RESULTS AND DISCUSSION

The methods that better matched the reference loads were those based on mean daily (MSd, MNd) or monthly (MSm, MNm) concentrations estimated from daily or monthly flows by regression, their values of MAE and RMSE were smaller than those obtained with the other methods. This can be expected in locations with strong flow-concentration relationship, because flow has a higher influence on load estimates than concentration (as its range of variation is normally much higher). For that reason too, estimates based on restitution of salt and nitrate concentration from mean daily flow (MSd, MNd) performed slightly better than those based on monthly flows (MSm, MNm) and the regression estimates were better for salts (more strongly linked to flow) than for nitrate (Tables 3 and 4).

Table 3. Statistical parameters for estimation methods of salt loads: number of data (N), Mean Bias, Percent Bias (% Bias) over the mean reference load, Root Mean Square Error (RMSE); Mean Absolute Error (MAE); maximum (Max) and minimum (Min) differences; Nash-Sutcliff Efficiency (NSE); coefficient of determination of the linear regression between estimates and reference loads ( $R^2$ ). For methods based on instant concentrations, results obtained with data from surface water quality (SWQ) and the ReCor-Ebro (R-E) networks are presented.

	MSi		MSid		MSim		Msd	Msm
	SWQ	R-E	SWQ	R-E	SWQ	R-E		
<b>Mg/month</b>								
<b>N</b>	45	54	56	70	62	70	70	70
<b>Mean Bias</b>	7.7	-286	-2699.9	-1617	1425	2050	-394	-18
<b>RMSE</b>	13491	13752	7857	6742	8463	8343	5183	5347
<b>MAE</b>	8670	7528	4827	3967	5229	5344	3598	3739
<b>MAX</b>	39889	60850	18702	14533	35970	38237	7603	7592
<b>MIN</b>	-43130	-41420	-38148	-36588	-9919	-9534	-17080	-18265
<b>Non- dimensional</b>								
<b>% Bias</b>	-1.5%	5.5%	8.0%	-0.1%	-10.2%	-6.3%	0.0%	-1.0%
<b>NSE</b>	-1.186	-1.272	0.258	0.454	0.140	0.164	0.677	0.657
<b>R<sup>2</sup></b>	0.014 <sup>NS</sup>	0.029 <sup>NS</sup>	0.424 <sup>***</sup>	0.480 <sup>***</sup>	0.689 <sup>***</sup>	0.678 <sup>***</sup>	0.685 <sup>***</sup>	0.668 <sup>***</sup>

<sup>NS</sup> Not significant (P>0.05). \*\*\* Significant at the 0.001 probability level.

Table 4. Statistical parameters for the five estimation methods of nitrate loads: number of data (N), Mean Bias, Percent Bias (% Bias) over the mean reference load, Root Mean Square Error (RMSE); Mean Absolute Error (MAE); Maximum (Max) and Minimum (Min) differences; Nash-Sutcliff Efficiency (NSE); coefficient of determination of the linear regression between estimates and reference loads ( $R^2$ ). For the methods based on instant concentrations, the results obtained with both the data from the surface water quality (SWQ) and the ReCor-Ebro (R-E) networks are presented.

	MNi		MNid		MNim		MNd	MNm
	SWQ	R-E	SWQ	R-E	SWQ	R-E		
<b>Mg N-NO<sub>3</sub>/month</b>								
<b>N</b>	32	50	42	70	48	70	70	70
<b>Mean Bias</b>	-5.4	-2.2	-15.0	-7.1	1.3	6.7	0.6	4.5
<b>RMSE</b>	78.4	64.2	54.4	35.5	44.0	31.6	33.6	34.8
<b>MAE</b>	41.5	38.7	27.3	22.5	26.6	20.8	21.0	23.0
<b>MAX</b>	196.2	234.3	53.9	63.9	86.4	127.2	67.4	75.5
<b>MIN</b>	-315.3	-204.3	-306.7	-176.7	-224.0	-59.1	-124.7	-125.4
<b>Non- dimensional</b>								
<b>% Bias</b>	0,6%	1,3%	6,7%	4,5%	-15,0%	-7,1%	-5,4%	-2,2%
<b>NSE</b>	-1.041	-0.370	0.018	0.581	0.356	0.668	0.625	0.598
<b>R<sup>2</sup></b>	0.009 <sup>NS</sup>	0.152 <sup>**</sup>	0.136 <sup>*</sup>	0.607 <sup>***</sup>	0.377 <sup>***</sup>	0.806 <sup>***</sup>	0.634 <sup>***</sup>	0.605 <sup>***</sup>

<sup>NS</sup> Not significant (P>0.05). \*, \*\*, \*\*\* Significant at the 0.05, 0.01 and 0.001 probability level respectively.

The mean bias was not significantly different from zero for any of the five estimation methods, so that the mean monthly load could be estimated by any method, the percent biases being always lower than 10% for salt load estimates (Table 3) and 15% for nitrate load estimates (Table 4) in absolute value. The errors of the estimates, however, were very different for the different methods. For the salt loads, the RMSE for MSi (~13000 Mg/month) was almost three-fold that of MSd and MSm (~5000 Mg/month), while methods MSid (RMSE~7000 Mg/month) and MSim (RMSE~8000 Mg/month) performing somewhat better than MSi (Table 3, Fig. 1). The same behavior was observed with the MAE and with the range (maximum and minimum values) of the differences between estimates and reference loads (Table 3). The quite higher NSE in the regression-based estimates (MSd and MSm) points to these two methods as the best salt loads estimators (Table 3). The MSi estimate was not acceptable according to the NSE criterion ( $NSE < 0$ ). The regression-based estimates presented the highest  $R^2$  ( $R^2 \sim 0.68$ ), along with MSim, although only the regression-based estimates showed a close agreement to reference values as shown by their high NSE (Table 3).

For the nitrate load estimators, the RMSE (~34 Mg/month) and MAE (~22 Mg/month) for the regression methods (MNd and MNm) were half than those of MNi (RMSE~70 Mg/month and MAE~40 Mg/month). In this case the methods based on instant concentrations and daily (MNid) or monthly (MNim) flows resulted in RMSE (~33 Mg/month) and MAE (~21 Mg/month) almost as low as the regression methods when used with the faulty SWQ series and even better with the more complete R-E series (RMSE~70 Mg/month and MAE~40 Mg/month) (Table 4). The methods using instantaneous Q, EC and  $NO_3$  (MSi, MNi) resulted in load estimates unacceptable by the NSE criterion ( $NSE < 0$ ). Generally, these series had more missing data and presented higher extreme (absolute) values (Fig. 1). The highest errors for these methods took place when the sampling date did not represent the average behaviour of the month in Q or concentrations. The coefficients of determination for these methods were also very low and not significant (Table 3 and 4).

For the methods based on instantaneous data, higher data availability improved the estimation, as shown by the improvement in the performance indicators for methods MSi, MSid, MSim and MNi, MNid and MNim with the more complete R-E series in relation to the SWQ series (Tables 3 and 4). However the improvement for salt loads is small as compared with nitrate loads, as shown by the increase in the NSE or  $R^2$  in Table 2 compared to Table 3. The reason is that nitrate is essentially unrelated to flow (unlike salinity), so that a more complete sampling (like the one based on R-E) will capture better the variability induced by climate and agronomical practices.

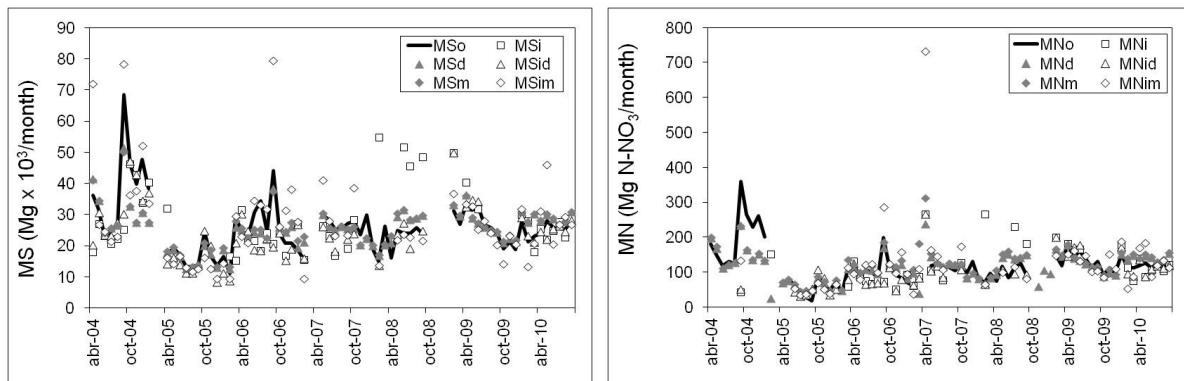


Figure 1. Mean monthly loads for each salt (MS) and nitrate load estimation method (MN) using the data from the SWQ network. The solid line presents the reference salt and nitrate loads.



In general, load estimators based in regression showed lower dispersion around the reference loads than the methods based on instant concentrations (Fig. 1). The use of the load estimates to assess the long term changes or trends and to relate them to changes in the basin management practices require that each individual estimate is as close to the real (reference) value as possible. For this purpose, the estimates should have low RMSE and MAE and especially high NSE, rather than only showing negligible bias. In this regard, only the regression-based estimators for salt (MSd and MSm) and nitrogen (MNd and MNm) loads, along with the nitrate estimates MNid and especially MNim (only when a complete data record is available) has been proved to fulfill this conditions although only for a short period of time (6 years).

## Conclusions

Estimates of salt loads based in the restitution of salt concentrations from flow values (either mean daily or monthly flows) were the best to represent the variability of salt loads with time. These methods only need flow data and the relationship between flow and salt concentration. Two important factors to consider in the future are the strength of the flow-concentration relationship and its stability with time. Changes in variables as irrigation surface, irrigation methods, or crop pattern can affect and change that relationship.

Statistical analysis of nitrate loads showed that method that uses instantaneous nitrate concentration and mean monthly flow has a good agreement with reference loads in particular when data derived from RecoR-Ebro are used. This fact indicates that monthly random nitrate concentrations from grab samples are representative measures of monthly values.

Estimation of nitrate loads from instantaneous nitrate concentrations and mean daily flow is also acceptable and does not require much instrumentation. Only a device to measure flow during one day and a single analysis of nitrate concentration in that day. This methodology would permit the evaluation of nitrate loads in points without have gauging and sampling stations. This methodology should be analyzed more in detail.

It is important to evaluate the proposed estimation methods for locations in the river network with different behaviour (flow-concentration relationships, e.g.) and also to test for longer periods of time, although this task entails difficulties due to the lack of good quality long-term reference series.

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