Daily variability of river concentrations and fluxes: indicators based on the segmentation of the rating curve

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Abstract

The variability of water chemistry on a daily scale is rarely addressed due to the lack of records. Appropriate tools, such as typologies and dimensionless indicators, which permit comparisons between stations and between river materials, are missing. Such tools are developed here for daily concentrations (*C*), specific fluxes or yields (*Y*) and specific river flow (*q*). The data set includes 128 long term daily records, for suspended particulate matter (SPM), total dissolved solids (TDS), dissolved and total nutrients, totalling 1,236 years of records. These 86 river basins (10^3–10^6 km²) cover a wide range of environmental conditions in semi-arid and temperate regions. The segmentation – truncation of *C* - *q* rating curves into two parts at median flows (*q*) generates two exponents (b_{50inf} and b_{50sup}) that are different for 66% of the analysed rating curves. After segmentation, the analysis of records results in the definition of nine major *C* - *q* types combining concentrating, diluting or stable patterns, showing inflexions, chevron and U shapes. SPM and TDS are preferentially distributed among a few types, while dissolved and total nutrients are more widely distributed. Four dimensionless indicators of daily variability combine median (C_{50}, Y_{50}), extreme (C_{99}, Y_{99}) and flow-weighted (C^*, Y^*) concentrations and yields (e.g., C_{99}/C_{50}, Y^*/Y_{50}). They vary over two to four orders of magnitude in the analysed records, discriminating stations and river material. A second set of four indicators of relative variability [e.g., $(Y^*/Y_{50})/(q^*/q_{50})$], takes into account the daily flow variability, as expressed by q^*/q_{50} and q_{99}/q_{50}, which also vary over multiple orders of magnitude. The truncated exponent b_{50sup} is used to describe fluxes at higher flows accounting for 75% (TDS) to 97% (SPM) of interannual fluxes. It ranges from -0.61 to +1.86 in the database. It can be regarded as the key amplificator (positive b_{50sup}) or reductor (negative b_{50sup}) of concentrations or yields variability. C_{50}, Y_{50}, b_{50sup} can also be estimated in discrete surveys, which provides a new perspective for quantifying and mapping water quality variability at daily scale.

Keywords: daily variability, fluxes, rating curve truncation, indicators, suspended particulate matter, total dissolved solids, nutrients

1. Introduction

The temporal variability of river quality, described in terms of chemical concentrations or of river material fluxes, is of major interest for water users, for river ecology, for a better understanding of river basin hydrology (Hem, 1970; Chapman, 1996; Likens, 2010). It should also be taken into account when estimating river fluxes (Cohn, 1995; Moatar *et al.*, 2006; Mailhot *et al.*, 2008). Ideally, the temporal variability of river water quality and river material fluxes should be captured by means of a continuous record of both concentrations and river flows. In reality, most water quality surveys are based on discrete samples brought to the laboratory for eventual chemical analysis (http://www.gemswater.org). In few surveys, the frequency of sampling is at the daily scale, with implicit assumptions that concentration variations within 24 hours are negligible. Suspended matter is more frequently surveyed at daily scale as in Canada (Ashmore and Day, 1988), USA (Meade *et al.,* 1990), and former USSR (Bobrovitskaya *et al.*, 2003). Research on small representative catchments is often performed using sub-daily records (Gurnell *et al.,* 1994; Jordan *et al.,* 2007).

River water quality analysis is commonly conducted through the analysis of the concentration *vs.* river flow or *C - q* relationship. It is used i) to understand the transportation processes of river material (Müller and Förstner, 1968; Walling and Webb, 1983, 1986; Johnes and Burt, 1991; Nash, 1994; Asselman, 2000), ii) to link river water quality to hydrological variation (Williams, 1989; Gurnell *et al.,* 1994; Heathwaite *et al.,* 1997; Vogel *et al.,* 2003), and iii) to estimate missing concentrations in discrete surveys, particularly for flux calculations (Ferguson, 1986; Cohn *et al.,* 1989; Cohn, 1995; Horowitz, 2003; Johnes, 2007; Crowder *et al.,* 2007; Mailhot *et al.,* 2008). The rating curve, established between measured concentrations and their related flows, is well adapted to the discrete nature of river quality information and corresponds to the general assumption - which is seldom made explicit - that river flow is the major controlling factor of river quality. It is also the common approach to estimate riverine fluxes. However, the *C - q* relationship is often very complex, including hysteresis patterns (Williams, 1989).

Ideally, the variability indicators should be dimensionless permitting comparisons between concentrations of various river materials, major ions, particulate material, nutrients, *etc.,* and/or between their riverine fluxes and river flows. Several indicators of concentration variability at the daily scale have already been proposed, such as the autoregression coefficient (Esterby S, 1996) and the concentration ratios as river flow-weighted average over medians (C^*/C_{50}) and the upper percentile over median (C_{99}/C_{50}). Similar dimensionless ratios allow comparisons between stations and/or river materials for daily specific fluxes. For SPM both concentrations ratios and flux ratios range over three to four orders of magnitude at the global scale (Meybeck *et al*., 2003).

The relationship between the concentration (*C*) and the river flow (*q*) is generally fitted to a *log - log* linear relationship expressed as $C = a\ q^b$. The dimensionless exponent "*b*" expresses the slope of this relationship. The parameter "*a*" has the dimension of a concentration and cannot be used when different types of materials are compared. Both are determined on all available (*C, q*) couples. Typically the exponent "*b*" is generally positive for particulate river material as SPM (Müller and Förstner, 1968) and negative for the dissolved material as TDS (Walling and Webb, 1986). Linear relationships are not always seen, and multiple subtypes have been observed, particularly for individual floods in which hysteresis loops are frequent (Williams, 1989). The *log C – log q* relationship is often not linear and is better defined with second-order or third-order polynomial regressions (Horowitz, 2003). The linear rating curve approach is not always appropriate to describe nutrient behaviour, which is often controlled by biogeochemical processes instead of hydrological processes (Heathwaite *et al.,* 1997, Johnes and Burt, 1991). These may present marked seasonal variations independent of river flow, such as in eutrophic lower river reaches (Van der Weijden and Middelburg, 1989; Allan, 1995; Moatar and Meybeck, 2005).

We have assembled a rare set of multi-year river surveys of daily concentrations and fluxes conducted at 86 stations. To better focus the variability analysis on higher fluxes, the segmentation and the truncation of the rating curve is introduced here. Several types of river material are considered: suspended particulate matter (SPM), total dissolved solids (TDS) as expressed by the electrical conductivity, dissolved nitrate, ammonia, phosphate, total phosphorus, total Kjeldhal nitrogen. They are recorded in medium-to-large basins (10^3 to 10^5 km²) from temperate and semi-arid regions in the USA and Western Europe with limited anthropogenic control on river flows. In order to facilitate interstation comparisons of daily fluxes and flows, riverine fluxes per unit basin area, or yields (*Y*), expressed in kg km^{-2} day^{-1} and specific flow in l s^{-1} km^{-2}, are used throughout this paper. Ratios of concentrations or yields are dimensionless and are used here as indicators of variability at the daily scale. Our objectives are to focus on various materials across a large hydrological gradient, in temperate and semi-arid regions in order to:

i) define dimensionless indicators of daily concentrations and fluxes variability, allowing interstations and/or intermaterials comparisons;
ii) establish a general typology of the concentration *vs.* river flow relationships using the segmentation and the truncation of the classical rating curve;
iii) link the daily variability indicators to a new dimensionless descriptor, the truncated exponent (b_{50sup}) and to hydrological variability;
iv) test whether these indicators can be estimated in discrete water quality surveys, *e.g.* monthly.

2. Definition of indicators of daily variability and presentation of database

2.1. Concentrations and yields ratios

Different quantiles and averages of daily concentrations and fluxes are used here as flow-weighted concentrations (C^*) and yields (Y^*) (see Table 1 for definitions). A first set of dimensionless indicators is considered for expressing the *general variability* of daily concentrations (C^*/C_{50}) and yields (Y^*/Y_{50}). A second set is related to their *extreme variability* (C_{99}/C_{50}) and (Y_{99}/Y_{50}). A third set concerns the *relative variability* of river fluxes compared to river flow: the general relative variability $(Y^*/Y_{50})/(q^*/q_{50})$ and the extreme relative variability $(Y_{99}/Y_{50})/(q_{99}/q_{50})$ (Table 1).

These different indicators are illustrated on figure 1 for total phosphorous in the Grand River (Ohio,USA), from the Lake Erie tributary survey (http://wql-data.heidelberg.edu/index2.html). In this case C^* and C_{50} are much different (figure 1c); this difference is often greater between Y^* and Y_{50} (figure 1d).

Table 1. Dimensionless indicators (bold) of temporal variability of daily concentrations and yields

It should be mentioned that autocorrelation may affect the daily concentration values, but it is assumed that this autocorrelation does not affect parameters and estimation of variability indicators presented in table 1.

2.2. Segmentation and truncation of rating curves at median flows

In the segmentation at median flows, the lower half and upper half of river flows and their related (*C, q*) couples are split, and their "*b*" exponents, b_{50inf} and b_{50sup}, respectively, are calculated separately (Figure 1b). The segmentation generates another set of indicators: b_{50inf}, b_{50sup}, F_{q50} and $W_{50\%}$ (figure 1b).

Figure 1. Example of daily variability of specific river flow (*q*), concentrations (*C*) and yields (*Y*) for total phosphorus in the Grand River (Painesville, OH): a) daily time series of *q* and *C* (2001-2002), b) segmented *C vs. q* relationship, c) distribution of daily concentrations, C_{50}, C_{99}, C^*: median, upper percentile and river flow-weighted values, d) distribution of daily yields, Y_{50}, Y_{99}, Y^*: median, upper percentile and average values

The proportion (%) of river material fluxes discharged in the upper 50% of daily river flows (F_{q50}), which is 98% here, may be different from the flux duration in 50% of the time ($M_{50\%}$). $M_{50\%}$ is determined from the ranking of the upper half of the daily river fluxes, while F_{q50} is the proportion of the river fluxes corresponding to the upper half of daily river flows. Generally, this difference is minor, being less than 2% for 74% of the dataset (maximum 10%).

The interannual variability of riverine fluxes is well known, as for particulate material. For some large rivers the annual fluxes can be very stable, as for the Congo River and for the Mississippi River (Meade *et al*., 2010). For small to medium rivers the interannual variability can exceed two orders of magnitude, particularly for Mediterranean river regimes (Meade and Parker, 1985; Serrat *et al.,* 2001; Syvitsky and Morehead, 1999). In our study, all indicators of temporal variability at the daily scale (Table 1) are determined on pluriannual periods; their interannual variability will be considered in a separate paper.

The dimensionless indicators are station specific and material specific. Three contrasting examples are given in table 2 for basins of similar sizes (5,455 km² to 30,710 km²): for suspended particulate matter in the Eel River (Fort Seward, CA), which is characterised by extreme hydrological and sediment transport variations (Syvitski and Morehead, 1999); for nitrate in the Seine River (Choisy, France; Moatar and Meybeck, 2007), characterised by summer denitrification during low flows (Curie *et al.*, 2009); and for total dissolved solids in the Dolores River (Moab, UT; US Geological Survey database, http://waterdata.usgs.gov/ky/nwis/qw), fed by natural salt springs. In these examples, the variability indicators for concentration (C^*/C_{50}, C_{99}/C_{50}) are much different between stations and river material. Indicators of yield variability (Y^*/Y_{50}, Y_{99}/Y_{50}) are even more variable, ranging over three to four orders of magnitude, while indicators of hydrological variability are much less variable, with q^*/q_{50} ranging from 1.4 in the Seine River to 5.5 in the Eel River. In contrast limited differences are noted for the truncated b exponent: b_{50sup} -0.61 for TDS, -0.03 for nitrate and 1.45 for SPM. The *C - q* types (*c-C, c-S and d-D*) will be discussed further. The other dimensionless indicators of daily variability (F_{q50}, $W_{50\%}$) are much less variable as they are expressed in percent. In the next section we consider the distributions of these indicators between stations and river materials for the temperate and dry regions.

Table 2. Contrasting examples of indicators of daily variability for river concentrations and fluxes and of *C - q* types: suspended particulate matter in the Eel River (Fort Seward, CA), nitrate in the Seine River (Choisy, France) and total dissolved solids in the Dolores River (Moab, UT).

Where to set up the truncation?

The position of truncation should be raised as in some cases; the inflexion of the *C vs. q* relationships does not arise at median river flow. When focusing on one station or on few cascading stations it may be advisable, for a better definition of segmented/truncated rating curves and improved estimations of riverine fluxes, to set up the truncation at the exact inflexion points for each station. In basin-wide surveys or in interbasins comparisons of variability indicators a fixed segmentation is more appropriate for comparisons between stations and/or river materials.

The estimation of truncated exponent in discrete surveys should also be considered. As we have seen b_{50sup} is the main control factor of variability in our analysis: it is crucial that it can be determined in discrete surveys, e.g. monthly, which are very common (Chapman, 1996). The truncation should leave a sufficient number of *C – q* couples for this determination (see section 4). Our tests show that at least 50 (*C, q*) couples are needed. For a monthly survey during 8 years of record a truncation at 50% would generate 48 (*C, q*) couples. A truncation at a narrower position could result in less (*C, q*) couples and higher uncertainty. A truncation at a higher position would require a longer period of record to reach a minimum 50 (*C, q*) couples (e.g., more than 12 years for the 70% truncation) during which the *C - q* relationship might not be stationary.

The proportion of fluxes after truncation also matters. Segmentation at 50% corresponds between 75% (TDS) and 97% (SPM) of the total fluxes depending on the river material (median proportion 90%). If the segmentation is too narrow, *e.g.,* keeping only the upper 30% of flows to calculate b_{70sup}, the associated fluxes may drop to 58% for TDS (79% and 93% for nutrients and SPM, respectively). If the segmentation is too wide, *e.g.,* keeping 70% of (*C, q*) couples, the related truncated b_{30sup} exponent is less contrasted with regards to the integral *b* exponent. In conclusion, the truncation at 50% appears to be an acceptable compromise.

2.3. Daily concentrations and fluxes variability in temperate and semi-arid basins

The data set concerns rivers of temperate regions (USA and west Europe) with some stations in the semi-arid regions (south west USA). We consider 86 stations where long-term records (> 3 years) of daily concentrations are available either for total dissolved solids (TDS), suspended particulate matter (SPM) or nutrients. The selected basins range from 642 km² to 1,061,441 km², with a median of 8,700 km² (Table 3 and Appendices 1 to 3). Within this range of basin areas, it is assumed that SPM, TDS, nutrient concentrations and river flow are relatively constant within a 24-h period. For SPM and TDS, data used come from the US Geological Survey database (http://waterdata.usgs.gov/ky/nwis/qw, http://co.water.usgs.gov/sediment/), in which all information on standardized sampling protocols and data collection can be found (Edwards and Glysson, 1988). The suspended particulate matter is assumed here to be equivalent to the total suspended solids (TSS) as given by the USGS. To remove the influence of reservoirs as much as possible, all the *q* and *C* time series and all the related *C* - *q* patterns have been first visually displayed to check their stationarity and any evidence of river flow regulation, such as marked truncations at lower or higher river flows. As such, approximately 25% of the preliminary set of stations was discarded.

As total dissolved solids (TDS) are not available at the daily scale, the daily electrical conductivity measured by USGS and reported as µS cm^{-1} is used as a proxy for TDS. It is reported in our tables in this unit. Such procedure is common in water quality surveys (Hem, 1970; Chapman, 1996). Because the ionic assemblage does not vary much at most stations, the correlation between conductivity at 25° (in µS cm^{-1}) and the sum of major ions (Σ=Ca^{2+}+Mg^{2+}+Na^{+}+K^{+}+Cl^{-}+SO_4^{2-}+HCO_3^{-}) expressed in meq l^{-1} is generally linear and stable for a given station. Some highly saline rivers, such as the Dolores (Utah), are an exception: Na^{+} - Cl^{-} dominates at low flows, Ca^{2+} - SO_4^{2-} at medium flows and Ca^{2+} - HCO_3^{-} at high flows. In this case conductivity - TDS relationship is likely to vary. However, this ionic assemblage effect remains exceptional and quite limited with regard to the variations of conductivity with river flow. It is therefore not taken into account here. Because most of the indicators used here are dimensionless (see above), the use of conductivity as a TDS proxy is unproblematic. More than one hundred US stations were retained; they include all the hydrological regimes found in the contiguous USA (Meade *et al.,* 1990).

For nutrient fluxes, a second database with daily concentration records over very long periods (generally 10 years) is used. It originates from nine US stations from the Lake Erie tributary survey (http://wql-data.heidelberg.edu/index2.html), from four French sub-basins on the Loire and from the Seine River and the Rhine River at Maxau (Germany). In all sub-data sets the sampling and analytical procedures are standardized during the period of survey at each station. It is not possible to ensure the total harmonization of these procedures between stations: for instance “phosphate concentration” may correspond either to orthophosphate only or to orthophosphate and polyphosphate, depending on the analysis. Since we are focussing here on the variability, as expressed by dimensionless ratios at stations, it is believed that analytical differences between stations do not affect these. Some stations of the Lake Erie data set have been discarded after visual displays of records for obvious odd *C* - *q* patterns for some nutrients. Several types of nutrients were investigated: dissolved nutrients (NO_3^{-},

PO_4^{3-}, NH_4^+) and total nutrients determined on unfiltered samples (total Kjeldahl nitrogen = TKN, and total phosphorus = Ptot).

Overall, our data set includes 47 stations for SPM (55% of station-year data sets), 33 for TDS (18%), and 3 to 12 stations for NO_3^-, PO_4^{3-}, NH_4^+, Ptot and TKN (27%, altogether), totalling 1,236 years of daily records. The SPM stations represent conditions ranging from very clear waters (median SPM 6 mg l^{-1}) to extremely erosive Californian rivers (792 mg l^{-1}), many of which were also used by Nash (1994), and TDS stations include some of the most dilute (36 µS cm^{-1}) and most saline (21 800 µS cm^{-1}) US river waters (Table 3).

The selected stations cover a very wide range of hydrological conditions and mechanical or chemical erosion rates that can be found in temperate regions. Basin sizes range from 600 to 600,000 km² for SPM stations, 600 to 1,000,000 km² for TDS, and 600 to 40,000 km² for nutrients. The survey period length ranges between 3 and 42 years (median 9 years). The median specific river flow is 9.4 l s^{-1} km^{-2} for SPM stations and 11.2 l s^{-1} km^{-2} for nutrient stations, which is typical for temperate regions and very close to the average world value. For the TDS stations, the median river flow is lower (3.3 l s^{-1} km^{-2}) and more representatives of dry temperate regions. This difference between the SPM and TDS river basins results from our objective of covering the widest possible range of concentrations and concentration-river flow relationships. The extreme TDS concentrations are here found in dry and semi-arid conditions, often with evaporites formations, which are common in Texas, Oklahoma, Arizona and Utah. The extreme SPM values used here originate from coastal California (*e.g.*, Eel and Mad Rivers) and from the Colorado Plateau (San Pedro and Paria Rivers). The interannual mean specific river flow (q*) at stations is also very variable, ranging from 0.03 (Canadian R. at Amarillo, TX) to 52.3 l s^{-1} km^{-2} (N. Santiam at Mehana, OR). Similarly, the range of the 99th percentile of specific river flow (q_{99}) is also wide, from 0.39 to 215 l s^{-1} km^{-2}.

Considering such ranges of concentrations and river flows, close to those observed at the global scale for river basins of similar sizes (Walling and Webb, 1983, 1986; Meybeck and Helmer, 1989, Meybeck *et al.*, 2003), it is believed that indicators ranges obtained here (Table 3), are also close to their global distribution.

The ranges and median values of indicators are first presented classically, differentiating various river materials as TDS, SPM, dissolved and total nutrients (Table 3). Some discrepancies between materials are noted on medians, but an important scattering within a given material is also observed: they are related to different rating patterns as defined in the next section.

Table 3: General distribution of dimensionless indicators of daily variability for concentrations, river flows and fluxes (TDS, chloride, dissolved and total nutrients, SPM). See Table 1 for definitions.

3. Analysis and typology of segmented concentration - river flow relationships

Riverine fluxes at higher flows are first analysed, then a segmentation of *C* - *q* records in two parts on the basis of median flow is proposed. The segmented rating curves are described through a general typology of *C* - *q* patterns into nine types on the basis of the segmented b exponents, b_{50inf} and b_{50sup}.

3.1. Focusing on fluxes and concentration patterns at higher flows

The segmentation of rating curves differentiates lower flows from higher flows. Their truncation focuses on the upper half of river flows; the truncated exponent, b_{50sup}, expresses this behaviour. For negative b_{50sup} values fluxes increase less rapidly than river flows, defining a *diluting process*, while for positive values, river fluxes are amplified, defining a *concentrating process*. The distribution of the exponent b_{50sup} in data base (Figure 2a) shows a marked aggregation with the types of river material.

For the total dissolved solids (TDS), b_{50sup} is negative most of the time but can be very slightly positive at some stations ($0 < b_{50sup} < +0.2$), as previously observed by Walling and Webb (1983). For dissolved nutrients, b_{50sup} is generally close to zero for nitrate, negative for ammonia (only three stations in the data base) and slightly positive for phosphates (see also Table 3). For total nutrients, it is always positive. For dissolved and total nutrients, the whole range is -0.4 to +0.67. For suspended particulate matter (SPM), b_{50sup} is always positive and ranges from 0.32 for the Iowa River at Wappelo (IO) to 1.86 for the Paria River at Lees Ferry, Az.

Figure 2. Distribution of the truncated b_{50sup} exponent (a), of the proportion of river material discharge in the upper half of flow (F_{Q50}) (b) and of the general concentration variability (C^*/C_{50}) (c)

Six classes of b_{50sup} are defined to facilitate the description of the concentration-river flow variations at higher flows:

- **[$b_{50sup} < -0.6$]: *very diluting process***; a very rare category, in which river fluxes tend to be constant
- **[$-0.6 < b_{50sup} < -0.2$]**: ***diluting***; most TDS, some phosphate and ammonia downstream of urban sewage inputs
- **[$-0.2 < b_{50sup} < +0.2$]**: ***stable***; some TDS, as in karstic regions, and nutrient seasonal variations, as for nitrate
- **[$+0.2 < b_{50sup} < +0.8$]: *weakly concentrating***; total P and TKN, and SPM in low-relief river basins
- **[$+0.8 < b_{50sup} < +1.4$]: *concentrating*** material; SPM in medium erosive basins
- [**$b_{50sup} > +1.4$]: *very concentrating***; SPM in highly erosive basins

In discrete surveys b_{50sup} is estimated with some uncertainty (see further): adding intermediate classes would not mean significant differences of $C – q$ patterns. However an additional extreme class (b_{50sup} > 2) could be added to describe SPM patterns not present in the database, such for Peace River in Athabasca (Meybeck, 1989). The "very diluted" pattern, found here only for TDS at one station (Dolores, b_{50sup} = -0.64), can be found downstream of major point sources of pollution as for the Seine River downstream of Paris (Chesterikoff *et al.,* 1998).

The proportion of interannual river material flux carried in the upper half of river flows (F_{q50}) ranges between 61% and 99.9% in the database, with a median proportion around 90% (Table 3, Appendices 1 to 3). As this indicator is expressed in %, its distribution is represented here on a probability scale (Figure 2b). For total dissolved solids, F_{q50} ranges from 61% (Gunnison near Grand Junction, CO) to 90% (North Canadian near Yukon, OK) with a median of 75%. Therefore, the greatest part of TDS and nutrient flux is discharged at high flows, even when a marked dilution (b_{50inf} < -0.4) is observed during these events. For dissolved nutrients, the F_{q50} range is slightly shifted towards higher values, starting at 67% for nitrate (Cuyahoga at Independence, OH) and 77% for phosphate (Muskingum at McConnelsville, OH) and reaching 98% (Sandusky near Fremont, OH) for both nutrients. For total nutrients, such as total phosphorus and total Kjeldahl nitrogen (TKN), the F_{q50} range is again shifted to higher values, from 85% (Loire at Orleans, France) to 99 % (Vermilion at Mill Hollow, OH). For SPM, the F_{q50} range is always high, between 85% and 99.9% (Trinity R. at Hoopa, CA), median 97%, with the notable exception of the Rhine River at Maxau (79%), which is greatly influenced by sediment trapping in Swiss lakes.

The distribution of the general variability indicator, the C^*/C_{50} ratio, is presented with a log-scale on Figure 2c. For dissolved solids it is always inferior to unity. For dissolved nutrients and TKN it ranges between 0.76 and 3.26. For total phosphorus and SPM it is always superior to unity and exceeds 100 at few stations. As will be developed further the C^*/C_{50} ratio can also be considered to quantify diluting (C^*/C_{50} < 1) and concentrating (C^*/C_{50} > 1) processes.

3.2. Typology of segmented rating curves and its range of variability indicators

The segmentation defines, for each multiannual record, two C - q subsets with their related segmented b exponents, b_{50inf} and b_{50sup}. These may differ by more than 0.2 for 66% of stations (Figure 3a). Also, for 45% of the data set, the difference between the integral and truncated exponents $|b-b_{50sup}|$ is important: for 34% of the data set, this difference is negative (<-0.2), while for 11%, it is positive (>+0.2) and may eventually reach +0.8. These negative differences between b and b_{50sup} are particularly common for total nutrients (12 records out of 19 for Ptot and TKN) and for suspended particulate matter concentrations (28 records out of 54). Negative or positive differences are less frequent for dissolved solids (2 records out of 33) and dissolved nutrients (9 records out of 22).

Figure 3. Relationships between the b_{50sup} exponent and the b_{50inf} exponent: a) for various riverine materials, b) for different segmented concentration *vs.* river flow patterns (see text for legend of patterns *s-S* to *c-D*).

The b_{50sup} - b_{50inf} population is then split here into different patterns (Figures 3b and 4). These *C - q* patterns have a double symbol with a lowercase symbol first (*c, d or s*), corresponding to patterns observed at lower flows defined by b_{50inf}, and an uppercase symbol (*C, D or S*) corresponding to the higher flows and b_{50sup}. *C* and *c* stand for "concentrating patterns", *i.e.,* significant increases of concentrations with river flow (b_{50sup} or b_{50inf} >+0.2); *D* and *d* stand for "diluting patterns", *i.e.,* a significant decrease of concentration with river flow (b_{50sup} or b_{50inf} <-0.2); and *S* and *s* stand for stable levels (*i.e.* b_{50sup} and b_{50inf} between -0.2 and +0.2). Few *C - q* records present inverted *C - q* relationships at lower flows and upper flows (*U*-pattern and chevron pattern), as illustrated in Figure 4.

The nine main *C – q* patterns found in rivers are fully illustrated in Figure 4 for selected stations:

Type "*s-S*": stable pattern throughout the whole flow range ($-0.2<b_{50inf}<+0.2$ and $-0.2<b_{50sup}<+0.2$), *e.g.,* nitrate in the Great Miami R. below Miamisburg, OH (*b*=0.13, b_{50inf} = 0.1, b_{50sup}=0.06, F_{q50} = 88%)

Type "*d-S*": dilution first, then stabilisation ($b_{50inf}<-0.2$ and $-0.2<b_{50sup}<+0.2$), *e.g.,* PO_4^{3-} in the Great Miami R. below Miamisbourg, OH (*b*= - 0.3, b_{50inf}= -0.58, b_{50sup} = 0.02, F_{q50} = 78%)

Type "*c-S*": concentration first, then stabilisation ($b_{50inf}>+0.2$ and $-0.2<b_{50sup}<+0.2$), *e.g.,* NO_3^- in the Sanduski R. near Fremont, OH (*b*=0.73, b_{50inf}= 1.58, b_{50sup} = 0.03, F_{q50} = 96%)

Type "*s-C*": stable pattern first, then an increase with flow ($-0.2<b_{50inf}<+0.2$ and $b_{50sup}>+0.2$), e.g., SPM in the Seine R., Choisy, France (*b*=0.89, b_{50inf}= 0.05, b_{50sup} = 1.45, F_{q50} = 94 %)

Type "*d-C*" (*U* type): dilution first, then concentration ($b_{50inf}<-0.2$ and $b_{50sup}>+0.2$), *e.g.,* Ptot in the Grand R., Painesville, OH (*b*=0.11, b_{50inf} = -0.23, b_{50sup} = 0.5, F_{q50} = 98%)

Type "*c-C*": concentration throughout the flow range (b_{50inf}> +0.2 and b_{50sup}>+0.2), *e.g.,* SPM in the Trinity R., Hoopa, CA (*b*=1.42, b_{50inf} = 0.87, b_{50sup} = 1.47, F_{q50} = 99.9 %)

Type "*s-D*": stable pattern first, then dilution ($-0.2<b_{50inf}<+0.2$ and $b_{50sup}<-0.2$), *e.g.,* TDS in North Fork Ninnescah, KS (*b*=-0.1, b_{50inf} = 0.06, b_{50sup} = -0.34, F_{q50} = 75 %)

Type "*d-D*": dilution throughout the whole flow range ($b_{50inf}<-0.2$ and $b_{50sup}<-0.2$), *e.g.,* TDS in the Dolores R. near Cisco, UT (*b*=-0.61, b_{50inf} = -0.35, b_{50sup} = -0.64, F_{q50} = 68 %)

Type "*c-D*" (chevron type): concentration first, then dilution (b_{50inf}> +0.2 and $b_{50sup}<-0.2$). The last type is not found in the database, but nitrate levels in the Oise R., France, are very close with b_{50sup} = -0.16 and b_{50inf}=+0.15.

Considering the wide range of b_{50sup} observed for the concentrating patterns, *d-C*, *s-C* and *c-C*, these patterns were also split into sub-types (*d-Cl, d-Cm*, *s-Cl*, *s-Cm*, *s-Ch*, *c-Cl*, *c-Cm*, *c-Ch*) on the basis of their b_{50sup} figure: from 0.2 to 0.8 for the subscript "*l*", 0.8 to 1.4 for the subscript "*m*" and higher than 1.4 for the subscript "*h*". Some of these patterns are illustrated on figure 4 as for SPM in the Trinity River.

Figure 4. Typology of rating curves segmented at median river flow (q_{50}) (log concentrations, mg l^{-1} and µS cm^{-1}, *vs.* log river flow, $m^3 s^{-1}$, relations). See Figure 1 for definitions of indicators and text for details on types and stations used for illustration.

Other types of *C - q* patterns have been reported by previous authors. They are generally based on second-order variations, being described as concave or convex (Asselman, 2000, Crowder *et al.*, 2007), or are defined for individual flood events, such as hysteresis for suspended particulate matter concentrations (Williams, 1989). They are not considered here at this stage, as they require a description with more than two parameters, which makes the typology more complex.

The distribution of variability indicators per *C - q* types is presented in table 4, ranked here in increasing order of b_{50sup}. It must be noted that these types may mix different river materials having common behaviours. Most types are correctly defined, with 5 to 28 *C - q* records (*s-D*, *d-D*, *s-S*, *c-S*, *d-C*, *s-C*, *c-Cl*, *c-Cm*, and *c-Ch*). Because the chevron type (*c-D*) is not represented in the database, the nitrate pattern in the Oise R., which is very close to this one (b_{50inf}=-0.16 instead of -0.2), is used to complement table 4. With the exception of the *s-D* type, which is biased towards drier basins as discussed before, median hydrological characteristics (q^*, q^*/q_{50}, q_{99}/q_{50}, $W_{50\%}$) are very similar from *d-D* to *c-C* types, suggesting that *C - q* types are not much linked to the hydrological variability.

Table 4. Main characteristics of *C - q* patterns and their associated daily variability indicators, ranked in increasing order of truncated exponent (b_{50sup}). r^2, r^2_{50sup}, r^2_{50inf}: regression coefficient of *C - q* relationships, integral and segmented. Median values based on n records.

From the *s-D* type (median b_{50sup}=-0.33) to the C-Ch type (b_{50sup}=+1.70), all indicators of variability of concentrations or fluxes are increasing, which suggests that the truncated b_{50sup} is a control factor of concentration variability, as addressed in the next section.

3.3. Control factors of the truncated exponent, b_{50sup}

Our data set (n=128 record) allowed only a preliminary analysis of some of the control factors for particulate or dissolved materials.

Control of b_{50sup} for river particulate matter

For suspended solids, the truncated exponent, b_{50sup}, is negatively correlated with the median SPM value (C_{50}) at stations: b_{50sup} = -0.4 $C_{50\ SPM}$ + 1.6, (r^2=0.26, n=54 records). The average b_{50sup} is 1.25 for a median SPM concentration around 10 mg l^{-1} and only 0.4 for median SPM values around 200 mg l^{-1}. This pattern confirms an observation made by Müller and Förstner (1968) in their pioneering study: they observed that the integral b exponent was only around 0.4 for a $C_{50\ SPM}$ of approximately 10^4 mg l^{-1}, as for the Yellow River (Huang He) in China.

Control of b_{50sup} for dissolved solids

For dissolved solids, the truncated b_{50sup} is negatively correlated to median TDS: b_{50sup} = - 0.13 $C_{50\ TDS}$ + 0.09, (r^2=0.32, n=37 records, with TDS expressed as the conductivity in µS cm^{-1}). The maximum dilution process is effectively observed in the database for highly saline rivers found in semi-arid regions and/or fed by saline springs. The average b_{50sup} is -0.15 for a median conductivity around 100 µS cm^{-1}, and reaches -0.45 for conductivity around 5,000 µS cm^{1}.

These correlations are limited, suggesting the possibility of other controls on b_{50sup}. The influence of the river basin area for SPM, TDS and nutrients was also tested: there was no significant effect on the exponent. The analysis should require a larger data set covering a wide range of river basin characteristics (climate, morphology, lithology, land cover) to quantify the complex physical and biogeochemical controls in natural or impacted conditions. Such multifactorial analysis has been previously performed for maximum suspended particulate matter (Tramblay *et al.* 2010a, 2010b) and for river water chemistry (Jarvie *et al.*, 2002). It could be made here from discrete surveys provided that key descriptors, b_{50sup}, C_{50} and Y_{50}, can be correctly estimated in such records (see section 5).

4. Linking variability indicators to truncated exponent b_{50sup} and to hydrological variability

The link between variability indicators and $C – q$ types is first explored using the truncated exponent b_{50sup}. Two types of variability indicators are used here: the ratio of the *99^th^* percentile to the median (C_{99}/C_{50} and Y_{99}/Y_{50}) referred to as extreme variability and the ratio of river flow-weighted components to the medians (C^*/C_{50} and Y^*/Y_{50}), referred to as general variability (Table 1). It appears that general and extreme hydrological variability, measured by the q^*/q_{50} and q_{99}/q_{50} ratio, are also necessary to fully understand the distribution of the flux variability indicators. This results in relative variability indicators, as $(Y^*/Y_{50})/(q^*/q_{50})$. All indicators are analysed with truncated exponent. Finally, river material fluxes discharged at higher flows (F_{q50}) are compared to the river flow discharged in 50% of the time ($W_{50\%}$).

4.1. Control of concentration variability indicators by truncated b_{50sup}

The daily variability of concentrations is first addressed through the general variability (C^*/C_{50} ratio). This ratio ranges over three orders of magnitude, from 0.33 (TDS) to 371 (SPM) (Table 1, appendices 1 to 3). For materials that are diluted at high flows (negative b_{50sup}, types *s-D*, *d-D* and *c-D*, Figures 3 and 4), C^*/C_{50} is below unity, whereas for concentrated materials (positive b_{50sup}, types *s-C*, *d-C*, *c-C*), it is above one and can exceed 100. When plotting $log(C^*/C_{50})$ *vs.* truncated b_{50sup} for the various types of river materials (Figure 5a) a direct correlation is noted.

The extreme variability (C_{99}/C_{50} ratio) is then considered for concentrated materials only (b_{50sup}>+0.2), such as SPM and total nutrients. It ranges over two orders of magnitude and is also controlled by b_{50sup} (Figure 5b). In both correlations, a substantial dispersion is however observed, reaching one order of magnitude for SPM. This suggests additional controls on C^*/C_{50} and C_{99}/C_{50}, such as the C – q patterns and the flow variability.

Figure 5. General and extreme variability of concentrations *vs.* truncated exponent b_{50sup}: a) $log(C^*/C_{50})$ *vs.* b_{50sup} (all records, various riverine materials), b) $log(C_{99}/C_{50})$ *vs.* b_{50sup} (for concentrated materials only)

4.2. Control of flux variability indicators by truncated b_{50sup}

It can be demonstrated that flux variability is theoretically linked to the flow variability. Empirical and theoretical figures of variability can therefore be compared.

The extreme flux variability, defined by the Y_{99}/Y_{50} ratio, is addressed first. It ranges in the data base over four orders of magnitude (appendices 1 to 3), discriminating stations and river materials. This indicator is directly linked to the extreme flow variability, q_{99}/q_{50}, through the development of the *C vs. q* relationship:

$$C = a\, q^{b_{50\text{sup}}} \quad (1)$$

$$Y = a\, q^{b_{50\text{sup}}+1} \quad (2)$$

Which implies

$$\log(Y) = \log(a) + (b_{50\text{sup}} + 1)\log(q) \quad (3)$$

Equation 3 can be developed as such:

$$\log(Y_{99}) = \log(a) + (b_{50\text{sup}} + 1)\log(q_{99}) \quad (4)$$

$$\log(Y_{50}) = \log(a) + (b_{50\text{sup}} + 1)\log(q_{50}) \quad (5)$$

Which results in the theoretical Y_{99}/Y_{50}:

$$\left(\log\left(\frac{Y_{99}}{Y_{50}}\right)\right)_{t_h} = (b_{50\text{sup}} + 1)\log\left(\frac{q_{99}}{q_{50}}\right) \quad (6)$$

For each data set, q_{99}/q_{50} is known and b_{50sup} can be estimated, allowing the calculation of theoretical Y_{99}/Y_{50} ratio. The theoretical general variability indicator (Y^*/Y_{50}) can also be calculated. It is however not linearly linked to b_{50sup}:

$$Y^* = \frac{\sum_{i=1}^{n} (q_i\ C_i)}{n} \quad (7)$$

Where n is the number of discrete observation.

From the *C - q* relationship, Y^* can be estimated by:

$$Y^* = \frac{\sum_{i=1}^{n} q_i\ a\ q_i^{b_{50\text{sup}}}}{n} = \frac{a}{n}\sum_{i=1}^{n} q_i^{b_{50\text{sup}}+1} \quad (8)$$

It results that theoretical Y^*/Y_{50} can results from the combination of equations (5) and (8):

$$\left(\frac{Y^*}{Y_{50}}\right)_{th} = \frac{\sum_{i=1}^{n} q_i^{b_{50\text{sup}}+1}}{n\ q_{50}^{b_{50\text{sup}}+1}} \quad (9)$$

The observed indicators of extreme and general variability are compared to theoretical ones for the *C – q* patterns defined in previous sections (figures 6a and 6b). For 128 data points the fit between observed and theoretical values is excellent. There is however a noted discrepancy in both relations for four data points resulting from an underestimated b_{50sup} exponent, for Animas and San Juan

Rivers, or an overestimated b_{50sup} exponent, for San Pedro and Paria Rivers. For these rivers the truncation at 50% should probably be displaced at higher river flows, resulting in a better definition of the *C vs. q* relation at the highest flows.

Figure 6. Material flux variability: a) observed $(Y_{99}/Y_{50})_{obs}$ *vs.* theoretical extreme flux variability $(Y_{99}/Y_{50})_{th}$; b) observed $(Y^*/Y_{50})_{obs}$ *vs.* theoretical general flux variability $(Y^*/Y_{50})_{th}$. Dataset clustered into *C - q* patterns, as defined in figures 3 and 4.

The truncated exponent appears to be the key controlling factor linking general and extreme river material flux variability to river flow variability. This point is clear when plotting the extreme or the general flux variability *vs.* the extreme or the general flow variability for six classes of the truncated exponent b_{50sup} (figure 7a and 7b).

Figure 7. Comparison of material flux variability and flow variability for six classes of truncated b_{50sup} exponent (log – log scales): a) extreme flux variability (Y_{99}/Y_{50}) *vs.* extreme flow variability (q_{99}/q_{50}); b) general flux variability (Y^*/Y_{50}) *vs*. general flow variability (q^*/q_{50}). Thin lines correspond to empirical regressions and dotted lines to theoretical relationship for Y_{99}/Y_{50}.

For each b_{50sup} class empirical relations are highly significant for both extreme variability (figure 7a) and for general variability (figure 7b). For the extreme variability the theoretical relations, derived from equation (6), are represented with thin dotted lines for each b_{50sup} class (centre of classes): they are in good agreement with the empirical observations. For the general variability the theoretical regressions with q^*/q_{50} cannot be established (see equation (9))

4.3. Control of the proportion of river fluxes discharged at higher flows (F_{q50})

The distributions of the concentration *vs.* river flow indicators (Table 4) also suggest a direct correlation between the b_{50sup} exponent, the proportion of fluxes discharged (F_{q50}) at higher flows- expressed in % of total fluxes - and the proportion of total water volume discharged during the 50% higher flows ($W_{50\%}$).

When represented on a probability scale, F_{q50} is positively correlated to b_{50sup} (Figure 8a). It has already been observed that flux or flow duration indicators, expressed in percents, are better represented using probability scales (ASCE Task Committee, 1970; Dunne, 1979; Walling, 1984). However, a large dispersion is observed for a given type of material, as previously noted when considering the various types of river materials (see figure 5). This loose correlation can also be greatly improved when the dataset is represented by b_{50sup} classes, and by plotting the flux duration (F_{q50}) *vs.* the flow duration using a double probability plot (Figure 8b).

Figure 8. Control factors of the proportion (F_{q50}) of the fluxes transported during higher river flows: a) F_{q50} *vs.* the truncated exponent b_{50sup} for different types of riverine materials (all

stations, normal probability scale for F_{q50}); b) F_{q50} vs. $W_{50\%}$, the proportion of inter-annual river flow discharged during higher flows, by classes of b_{50sup} exponent (normal probability scale for both F_{q50} and $W_{50\%}$).

4.4. Developing an integrated typology of relative variability in rivers

The relative daily variability of river concentrations and fluxes refers to river flow variabilities. It is quantified here through a set of four dimensionless ratios: $(C^*/C_{50})/(q^*/q_{50})$ and $(C_{99}/C_{50})/(q_{99}/q_{50})$, $(Y^*/Y_{50})/(q^*/q_{50})$ and $(Y_{99}/Y_{50})/(q_{99}/q_{50})$. These ratios are defined for each *C - q* record, *i.e.*, they are station-specific, river material-specific and record period-specific (see Appendix 1). All ratios related to the average yield (Y^*) and to the extreme yield (Y_{99}) range over three orders of magnitude, while the ratios concerning average concentrations (C^*) and extreme concentrations (C_{99}) ranges over two orders of magnitude. For the eleven *C - q* patterns presented in table 4 the medians of indicators are considered, mixing TDS, SPM, dissolved and total nutrients in common patterns, and plotted *vs.* the median truncated exponent of their class (Figures 9a to 9d). All relative variability indicators are controlled by the truncated exponent.

When the relative variability indicators are lower than unity, the river quality (concentration or fluxes) is less variable than the river hydrology and vice-versa. The point of equal variability is reached for b_{50sup} = 0 for the general (Y^*) and extreme (Y_{99}) flux variability's, and near b_{50sup} = 0.5 for the general (C^*) and extreme (C_{99}) concentrations variability's. These relationships between medians are very regular and near linear for the extreme flux variability $(Y_{99}/Y_{50})/(q_{99}/q_{50})$. In contrast, relationships for extreme concentrations are more scattered, suggesting that for some *C - q* types (*d-C, s-C, c-Cl*), the maximum concentrations are not found in the positions of maximum river flows; a pattern observed for SPM maxima on Californian rivers (Tramblay *et al.*, 2008).

Figure 9. General typology of daily variability controlled by the truncated b_{50sup} exponent: a) general flux variability, b) extreme flux variability, c) general concentration variability, d) extreme concentration variability. Y^*, C^*, q^*: river flow-weighted averages; Y_{50}, C_{50}, q_{50}: medians; Y_{99}, C_{99}, q_{99}: upper percentiles. Medians of indicators as presented in Table 4.

5. Estimates of truncated exponent, median concentrations and yields in discrete surveys

The variability indicators are established on daily records of concentrations, uncommon in regular surveys (Chapman, 1996). However they can be estimated from discrete surveys, as they are linked to river flow variability at the daily scale, to median concentrations and fluxes (C_{50}, Y_{50}), and to the truncated exponent b_{50sup}. This is tested on a subset of the database with 89 records of TDS, nutrients and SPM stations lasting 7 consecutive years. Only six main patterns are present in this subset: *d-D* (mostly TDS), *s-D* (TDS and some total nutrients), *s-S* (dissolved nutrients, some TDS), *c-S* (mostly nutrients), *s-C* (total nutrients, some SPM) and *c-C* (mostly SPM).

Discrete water quality surveys at the monthly frequency were simulated for each group of record through a Monte-Carlo sorting. For each sorting: $b_{50sup}^{\#}$, $C_{50}^{\#}$, $Y_{50}^{\#}$ were determined based on the 7x12=84 (*C, q*) couples and compared to the reference values using the whole daily records (7x365 = 2555 couples) in order to generate the populations of errors for these indicators (*e*). One hundred sorting is generated for each of the 89 records. The biases (e_{50}) and imprecisions (e_{90}-e_{10}) of $b_{50sup}^{\#}$, $C_{50}^{\#}$ and $Y_{50}^{\#}$ estimates are then calculated from the population of errors. They are presented for each *C - q* pattern in order of increasing b_{50sup} on figure 10 for the monthly survey.

For C_{50} and Y_{50} biases are generally very limited (<5%), but imprecision's are increasing with b_{50sup} and can reach 40 to 50% when b_{50sup} > 0.8 (Figure 10 left). For b_{50sup} the estimation performance is variable: for diluting and concentrating *C - q* patterns estimates are satisfactory but for the "stable" *C - q* patterns, as *c-S* and *s-S*, relative imprecisions are maximum, however they correspond to b_{50sup} values close to zero. It can be stated that, in most cases, the three key descriptors can be correctly approached.

Another sorting experiment simulated the weekly surveys. In that case errors ranges are generally divided by a factor of two. Finally uncertainties can be reduced when larger (*C, q*) populations are considered, *i.e.* on records exceeding 7 years, but *C - q* relations must be stationary.

Figure 10. Biases and imprecisions on estimated b_{50sup}, C_{50} and Y_{50} in simulated discrete surveys for six *C - q* patterns. (Monte Carlo sorting, 7 years of record, 100 simulated monthly surveys). N=number of records (TDS, nutrients and SPM) used for each pattern.

6. Conclusions and perspectives

Our analysis of daily variability of river concentrations and fluxes is based on a large database, assembled for medium to large river basins (128 long term daily water quality records covering a history of 1,236 years). As this database covers a very large range of hydrological, chemical and sedimentary characteristics found in semi-arid and temperate conditions, we presume it is representative of these climatic areas.

Truncation-segmentation and *C – q* patterns

The proportion of the annual flux which is left over after a 50% truncation is actually limited, ranging from less than 1% to 35%, with a median of 10%. A discrepancy between truncated and integral rating curves is found in 40% of records. Lower flows and higher flows patterns are different for 66% of the analysed records. The segmentation generates two rating curves with distinct exponents, b_{50inf} and b_{50sup}, on which nine major types of *C - q* patterns are based, combining diluting, stable and concentrating patterns. The segmentation benefit is minimum for the most stable relationships (5% of records) and maximum when *C - q* relationships are inverted between lower and higher flows (U and chevron patterns, 4% of records, often found for nutrients). In the latter case seasonal concentration variability should be investigated, which will add new specific descriptors of water quality temporality.

Role of the truncated exponent b_{50sup}

The diluting and concentrating processes are here defined on the basis of the truncated exponent b_{50sup}. It can be considered as a reductor, when negative, or an amplificator, when positive, of the daily variability with regards to the river flow variability. In the database the b_{50sup} distribution is not centred: the diluting process is limited to | b_{50sup} | < 0.64 while the concentrating process extends much further with | b_{50sup} | exceeding 1.8 for SPM. For example, the median | b_{50sup} | is 0.2 for TDS and 1.07 for SPM. The full range of b_{50sup} for all types of materials and river basins is larger.

The implications of diluting *vs.* concentrating patterns on central values of *C* populations are important. The flow-weighted concentrations (C^*) are superior to the median concentration (C_{50}) when b_{50sup} is positive and inferior when b_{50sup} is negative. Again, this discrepancy is not symmetrically distributed. The minimum C^*/C_{50} reaches 0.4 (median 0.82 for TDS), but the maximum C^*/C_{50} can exceed 100 (median 6 for SPM).

This property explains why the flux calculations methods based on arithmetic means ($\overline{C}$), can be used for most diluted materials but are excluded for the concentrated materials. For the most diluted materials, the use of C_{50} or $\overline{C}$ occasionally leads to a significant overestimation of flow-weighted average concentrations.

Indicators of daily variability

The daily variability of concentrations and river fluxes is described through a set of ratios combining the medians (C_{50}, Y_{50}), upper percentiles (C_{99}, Y_{99}) and river flow-weighted figures (C^*, Y^*) of daily concentrations and fluxes, *e.g.* C^*/C_{50}, Y_{99}/Y_{50}, *etc.* These dimensionless ratios are used to characterise each C – q record. They are highly discriminated between stations and river materials and may range over more than three orders of magnitude. All indicators are jointly controlled by b_{50sup} and by the hydrological variability.

The relative variability indicators, *e.g.* $(Y^*/Y_{50})/(q^*/q_{50})$, compare the variability of concentrations and fluxes to the river flow variability ,as defined by two dimensionless ratios, q^*/q_{50} and q_{99}/q_{50}. The relative variability is only dependant on the truncated exponent b_{50sup}, which appears to be an amplificator, when positive, or a reductor, when negative, of the variability. These indicators also range over several orders of magnitude.

Daily variability indicators in discrete surveys

This analysis of daily variability can be extended to long-term discrete surveys. Simulations showed that three key descriptors - median concentration (C_{50}), median daily yields (Y_{50}) and truncated exponent (b_{50sup}) - can be estimated with very limited bias and acceptable imprecisions from monthly C - q series over a minimum of 7 to 8 years, although the performance of b_{50sup} estimates are poor for stable C - q patterns. Indicators of variability can therefore be estimated in most surveys provided that river flow is known from continuous records. This approach offers very promising perspectives using archived water quality data. The spatial distribution of variability could be studied and mapped, for example at major confluences, when stream orders increase stepwise. Past trends of material fluxes variability (*e.g.,* per decades) could also be investigated, considering human impacts such as dam construction, wastewater collection or treatment and water diversions. Use of discrete surveys data could also allow the in-depth analysis of control factors (hydrology, morphology, land cover) for the $b_{50sup,}$ and for the *C - q* types. The daily variability could become a new field of temporal analysis combining hydrology and water quality.

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Table 1. Dimensionless indicators (bold) of temporal variability of daily concentrations and yields

Symbol	Description and units
A	basin area at stations (km²)
$\mathbf{b}$	integral rating curve exponent established for all daily river flows q (log C= b log q + a)
$\mathbf{b_{50sup}}$	truncated rating curve exponent established for river flows $q > q_{50}$ ($\log C = b_{50sup} \log q + a_{50sup}$)
$\mathbf{b_{50inf}}$	truncated rating curve exponent established for river flows $q < q_{50}$ ($\log C = b_{50inf} \log q + a_{50inf}$)
C_*	flow-weighted mean concentration for material obtained from daily records (mg l^{-1} and µS cm^{-1} for electrical conductivity, a proxy for TDS)
C_{50}, C_{99}	percentiles of daily concentration (mg l^{-1} and µS cm^{-1} for electrical conductivity, a proxy for TDS)
$\mathbf{C_*/C_{50}, C_{99}/C_{50}}$	general and relative concentration variability
$\mathbf{(C_*/C_{50})/(q_*/q_{50})}$, $\mathbf{(C_{99}/C_{50})/(q_{99}/q_{50})}$	general and extreme relative variability of concentration
$q_*, q_{30}, q_{50}, q_{70}$	average, median and deciles for daily specific river flow ($l\ s^{-1}\ km^{-2}$)
$\mathbf{q_*/q_{50}, q_{99}/q_{50}}$	general and extreme flow variability, used as indicators of river flow flashiness
Y_*, Y_{50}, Y_{99}	average, 50th and 99th percentiles of the daily yield distribution for river borne material (kg $km^{-2}\ day^{-1}$); for TDS, these figures are given in conductivity units per km² per day
$\mathbf{Y_*/Y_{50}, Y_{99}/Y_{50}}$	general and extreme flux variability
$\mathbf{(Y_*/Y_{50})/(q_*/q_{50})}$, $\mathbf{(Y_{99}/Y_{50})/(q_{99}/q_{50})}$	general and extreme relative variability of flux
$\mathbf{W_{50\%}}$	proportion of water discharged in the upper 50% of daily river flows (%)
$\mathbf{F_{q50}}$	proportion of river material fluxes discharged in the upper 50% of daily river flows (%)

Table 2. Contrasting examples of indicators of daily variability for river concentrations and fluxes and of *C - q* types: suspended particulate matter in the Eel River (Fort Seward, CA), nitrate in the Seine River (Choisy, France) and total dissolved solids in the Dolores River (Moab, UT).

		q_*/q_{50}	q_{99}/q_{50}	C_*/C_{50}	C_{99}/C_{50}	Y^*/Y_{50}	Y_{99}/Y_{50}	b	b_{50sup}	b_{50inf}	F_{q50}	$W_{50\%}$	Type
Eel	**SPM**	5.5	65.7	158	360	1001	25 720	1.02	1.45	0.4	99%	98%	c-C
Seine	**NO_3^-**	1.4	5.1	1.03	1.4	1.4	4.7	0.14	-0.03	0.41	79%	77%	c-S
Dolores	**TDS**	4.1	41.7	0.3	3.4	1.2	4.8	-0.61	-0.64	-0.35	68%	92%	d-D

Table 3: General distribution of dimensionless indicators of daily variability for concentrations, river flows and fluxes (TDS, chloride, dissolved and total nutrients, SPM). See Table 1 for definitions.

	yrs	A	q_*	q_*/q_{50}	q_{99}/q_{50}	C_*	C_*/C_{50}	C_{99}/C_{50}	Y_*	Y^*/Y_{50}	Y_{99}/Y_{50}	b	b_{50sup}	b_{50inf}	$b_{50sup}-b_{50inf}$	$W_{50\%}$	F_{q50}
TDS																	
min	4	743	0.03	1.0	2.4	32	0.33	1.14	5.9	1.00	2.17	-0.61	-0.64	-0.40	-0.22	66.5	61.4
max	27	1 061 441	52.3	4.1	46.6	3867	0.98	3.37	395.3	2.50	26.51	0.00	-0.04	0.08	0.47	95.3	90.4
median	8	13 177	3.7	1.7	11.9	643	0.82	1.48	146.6	1.36	6.12	-0.23	-0.24	-0.16	0.16	81.8	74.7
SPM																	
min	3	660	0.2	1.1	2.5	29	1.4	4.9	12.6	1.6	10.7	0.36	0.32	-0.08	-0.47	65.4	79.2
max	42	251 149	46.0	5.8	80.8	92138	321	558	7309	1604	32594	2.00	1.86	2.21	1.50	97.9	100.0
median	12	8 060	11.1	1.8	11.7	207	6	24	166	11	178	0.84	1.07	0.48	0.51	85.6	97.2
Nitrate																	
min	3	679	7.2	1.4	5.0	2.84	0.76	1.29	3.7	1.23	3.82	-0.51	-0.42	-0.55	-1.59	77.1	67.3
max	22	30 710	15.1	3.3	40.4	27.08	1.81	5.03	26.0	5.16	68.15	0.80	0.32	1.68	0.31	95.2	97.1
median	9.5	8 468	10.9	1.8	10.6	20.25	1.20	2.57	16.4	2.18	15.51	0.16	0.06	0.30	-0.26	85.0	88.5
P-PO4																	
min	5	1 777	8.4	1.5	8.6	0.03	0.93	2.30	0.01	1.62	10.06	-0.30	0.00	-0.58	-0.55	84.1	78.1
max	21	36 970	15.0	3.1	25.9	0.48	3.26	11.40	0.17	8.87	112.23	0.60	0.52	0.65	0.42	94.0	97.6
median	9	6 954	11.1	1.8	12.5	0.13	1.11	3.61	0.05	3.37	34.30	0.16	0.17	0.10	-0.45	85.4	88.9
Ptot																	
min	3	679	8.4	1.5	6.8	0.13	1.17	2.44	0.14	1.84	13.55	-0.09	0.19	-0.61	0.23	81.6	85.5
max	22	36 970	15.1	3.3	40.4	0.42	4.54	9.67	0.42	18.54	330.56	0.41	0.67	0.29	0.99	95.2	98.9
median	9	5 100	11.3	1.8	11.9	0.30	1.71	4.98	0.28	3.32	39.48	0.14	0.49	-0.16	0.54	85.2	90.3
TKN																	
min	3	679	8.4	1.6	6.8	0.74	1.23	2.56	0.75	2.10	16.40	0.05	0.23	-0.38	0.15	81.6	85.5
max	22	19 218	15.1	3.3	40.4	1.77	2.00	4.00	1.67	7.15	112.82	0.22	0.42	0.12	0.80	95.2	97.6
median	9	3 245	11.2	1.8	12.5	1.15	1.42	3.32	1.31	2.82	29.65	0.12	0.31	-0.04	0.32	85.4	89.4

Table 4. Main characteristics of C – q patterns and their associated daily variability indicators, ranked in increasing order of truncated exponent (b_{50sup}). r^2, r^2_{50sup}, r^2_{50inf}: regression coefficient of *C - q* relationships, integral and segmented. Median values based on n records.

	type s-D	type d-D	*type c-D*	type d-S	type s-S	type c-S	type d-C	type s-C	type c-Cl	type c-Cm	type c-Ch
b_{50sup}	**-0.33**	**-0.29**	***-0.16***	**-0.09**	**-0.05**	**0.14**	**0.42**	**0.50**	**0.49**	**1.12**	**1.70**
n (records)	**17**	**8**	***1***	**8**	**12**	**7**	**5**	**22**	**12**	**28**	**8**
A (km²)	16972	14545	*16972*	3438	12710	16395	6954	2699	16047	7773	4553
q* ($l\ s^{-1}\ km^{-2}$)	1.76	6.39	*7.24*	12.10	10.24	11.10	12.23	10.91	7.76	12.61	18.22
q^*/q_{50}	1.87	1.57	*1.37*	1.82	1.63	2.46	1.80	2.12	1.82	1.66	3.04
q_{99}/q_{50}	12.49	8.54	*4.97*	11.25	9.28	17.83	12.50	16.08	11.52	8.62	28.84
C^*/C_{50}	0.74	0.83	*0.99*	0.92	0.98	1.37	1.39	2.10	2.76	5.74	145.06
$(C^*/C_{50})/(q^*/q_{50})$	0.39	0.51	*0.72*	0.53	0.66	0.57	0.77	1.01	1.54	2.78	32.67
C_{99}/C_{50}	1.48	1.93	*1.29*	2.40	1.52	2.94	2.85	5.60	10.16	22.46	334.83
$(C_{99}/C_{50})/(q_{99}/q_{50})$	0.10	0.20	*0.26*	0.25	0.20	0.19	0.24	0.53	1.09	2.03	6.89
Y^*/Y_{50}	1.35	1.23	*1.29*	1.72	1.73	3.14	2.82	5.52	5.98	9.23	421.25
$(Y^*/Y_{50})/(q^*/q_{50})$	0.71	0.79	*0.95*	0.95	0.98	1.28	1.57	2.34	2.74	5.91	150.01
Y_{99}/Y_{50}	7.50	4.46	*3.82*	10.28	12.34	25.43	32.17	69.35	62.84	145.09	8720.52
$(Y_{99}/Y_{50})/(q_{99}/q_{50})$	0.48	0.58	*0.77*	0.90	0.96	1.48	2.57	4.04	5.11	13.42	303.08
b	-0.22	-0.35	*0.02*	-0.21	-0.01	0.49	0.07	0.24	0.67	0.88	1.24
b_{50inf}	-0.11	-0.33	*0.15*	-0.36	0.02	0.57	-0.35	0.03	0.64	0.59	0.44
$b_{50sup}-b_{50inf}$	-0.20	0.03	*-0.31*	0.22	-0.05	-0.44	0.80	0.48	-0.14	0.49	1.06
r^2	0.50	0.71	*0.01*	0.33	0.15	0.31	0.05	0.24	0.37	0.43	0.79
r^2_{50sup}	0.06	0.40	*0.15*	0.29	0.03	0.16	0.16	0.01	0.10	0.06	0.22
r^2_{50inf}	0.48	0.46	*0.26*	0.11	0.06	0.02	0.37	0.38	0.17	0.43	0.71
$W_{50\%\ (\%)}$	82.5	79.4	*77.4*	85.1	84.5	91.1	85.1	89.1	85.5	83.5	91.3
$F_{q50\ (\%)}$	74.7	69.2	*77.3*	78.6	85.2	94.3	88.6	96.2	94.6	96.3	99.9

Figure 1. Example of daily variability of specific river flow (*q*), concentrations (*C*) and yields (*Y*) for total phosphorus in the Grand River (Painesville, OH): a) daily time series of *q* and *C* (2001-2002), b) segmented *C vs. q* relationship, c) distribution of daily concentrations, C_{50}, C_{99}, C^*: median, upper percentile and river flow-weighted values, d) distribution of daily yields, Y_{50}, Y_{99}, Y^*: median, upper percentile and average values

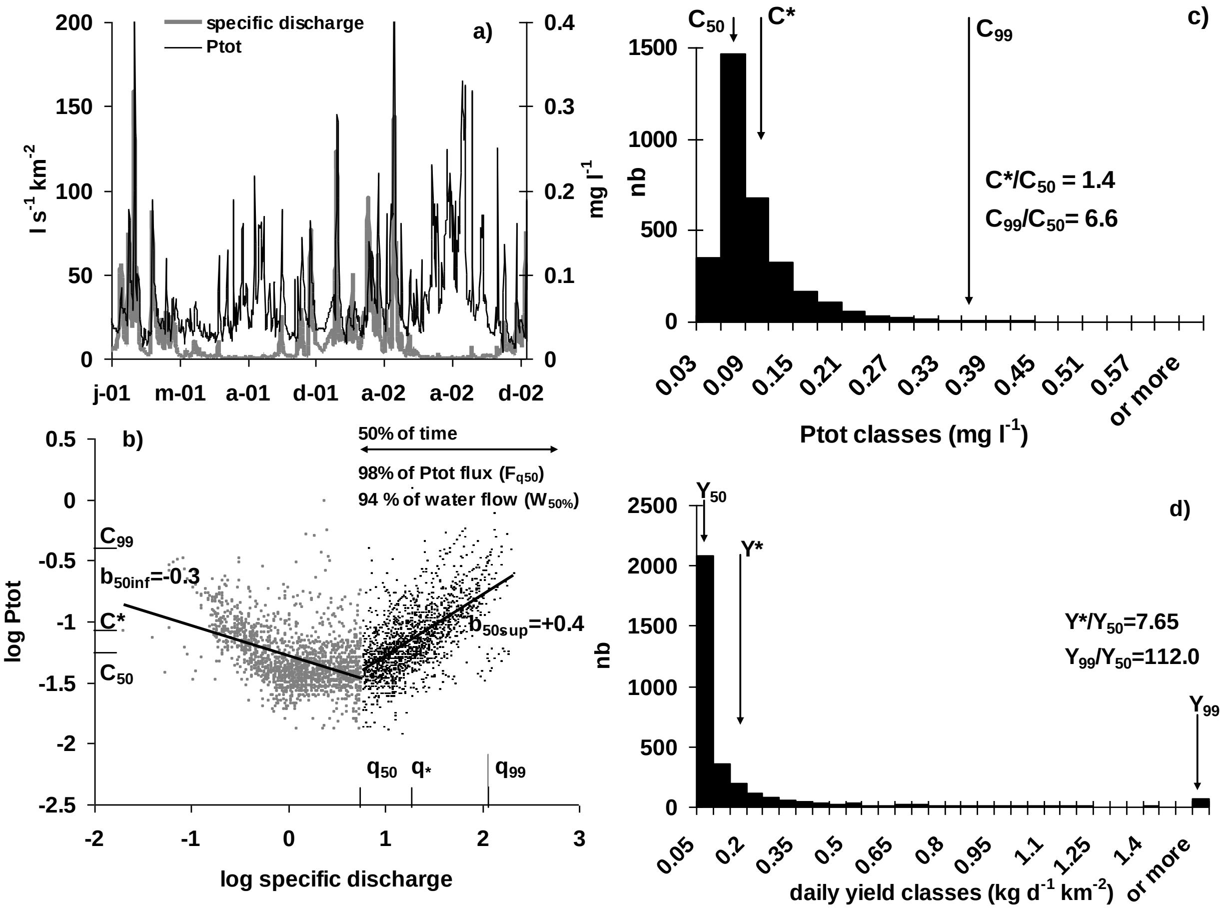


Figure 2. Distribution of the truncated b_{50sup} exponent (a), of the proportion of river material discharge in the upper half of flow (F_{Q50}) (b) and of the general concentration variability (C^*/C_{50}) (c)

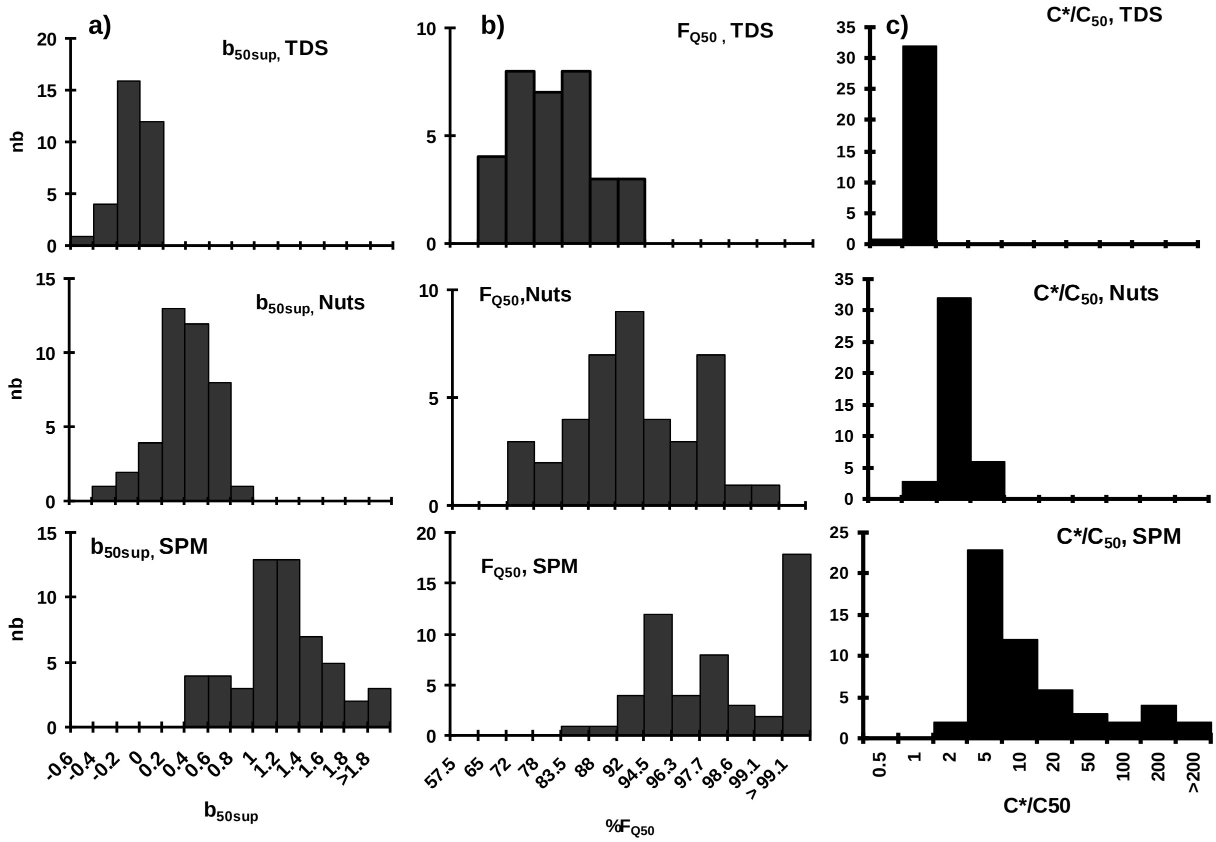


Figure 3. Relationships between the b_{50sup} exponent and the b_{50inf} exponent: a) for various riverine materials, b) for different segmented concentration *vs.* river flow patterns (see text for legend of patterns *s-S* to *c-D*).

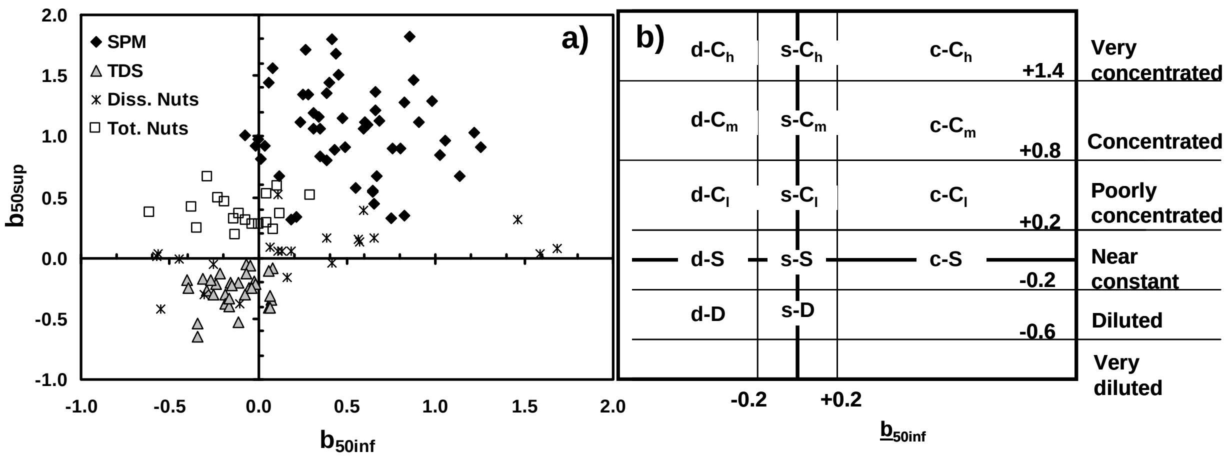


Figure 4. Typology of rating curves segmented at median river flow (*q_{50}*) (log concentrations, mg l^{-1} and µS cm^{-1}, *vs.* log river flow, m^3 s^{-1}, relations). See Figure 1 for definitions of indicators and text for details on types and stations used for illustration.

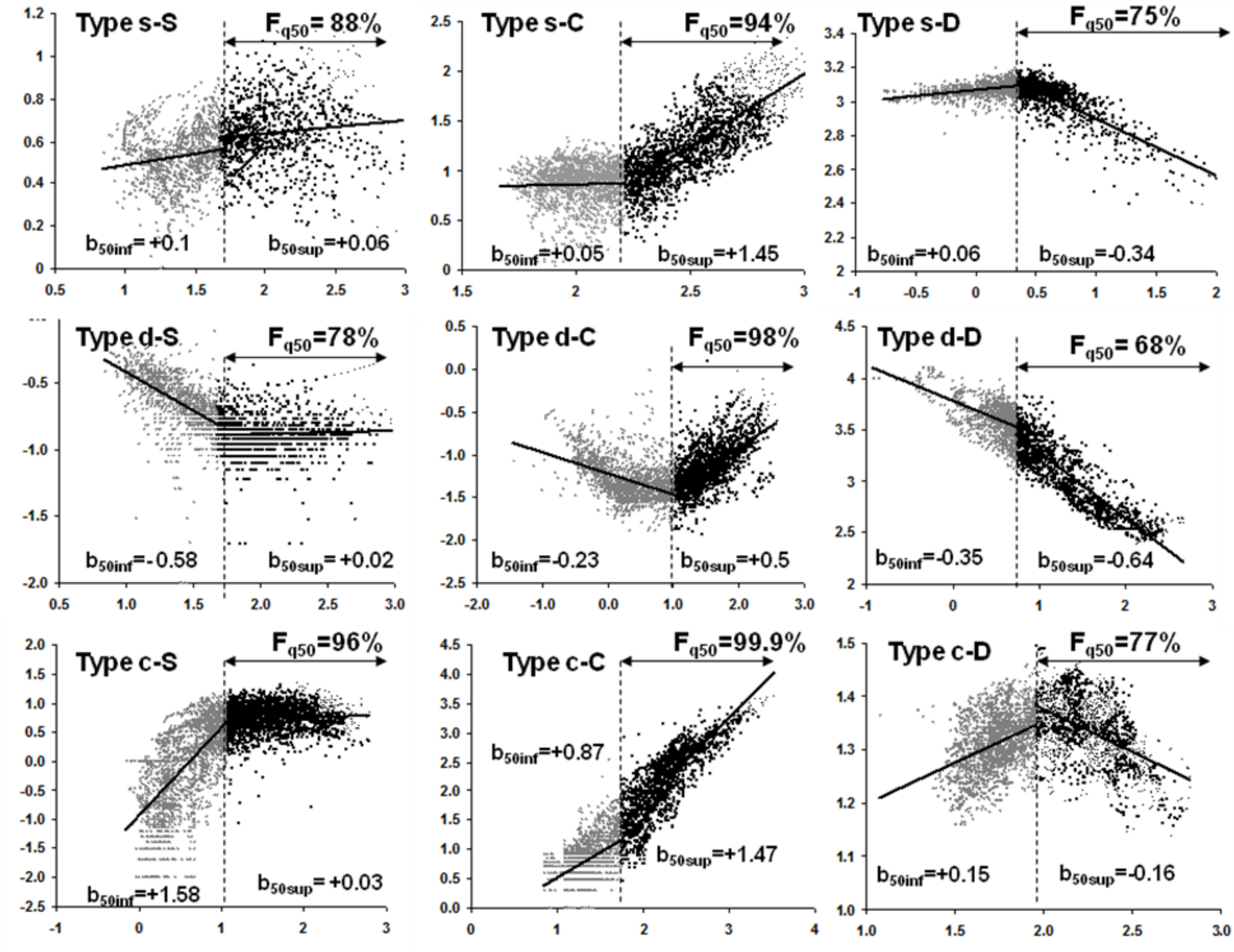


Figure 5. General and extreme variability of concentrations *vs.* truncated exponent b_{50sup}: a) $log(C^*/C_{50})$ *vs.* b_{50sup} (all records, various riverine materials), b) $log(C_{99}/C_{50})$ *vs.* b_{50sup} (for concentrated materials only)

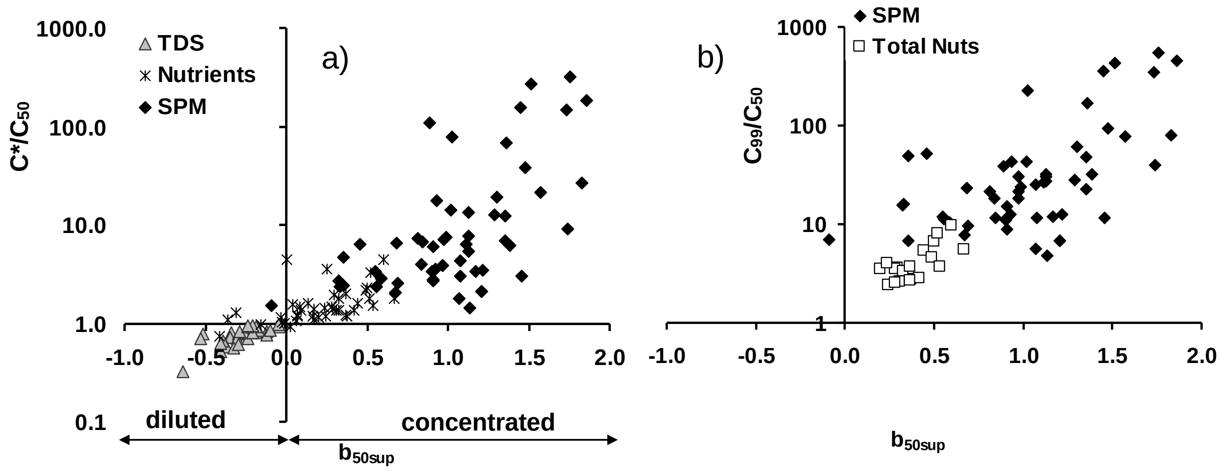


Figure 6. Material flux variability: a) observed $(Y_{99}/Y_{50})_{obs}$ *vs.* theoretical extreme flux variability $(Y_{99}/Y_{50})_{th}$; b) observed $(Y^*/Y_{50})_{obs}$ *vs.* theoretical general flux variability $(Y^*/Y_{50})_{th}$. Dataset clustered into *C - q* patterns, as defined in figures 3 and 4.

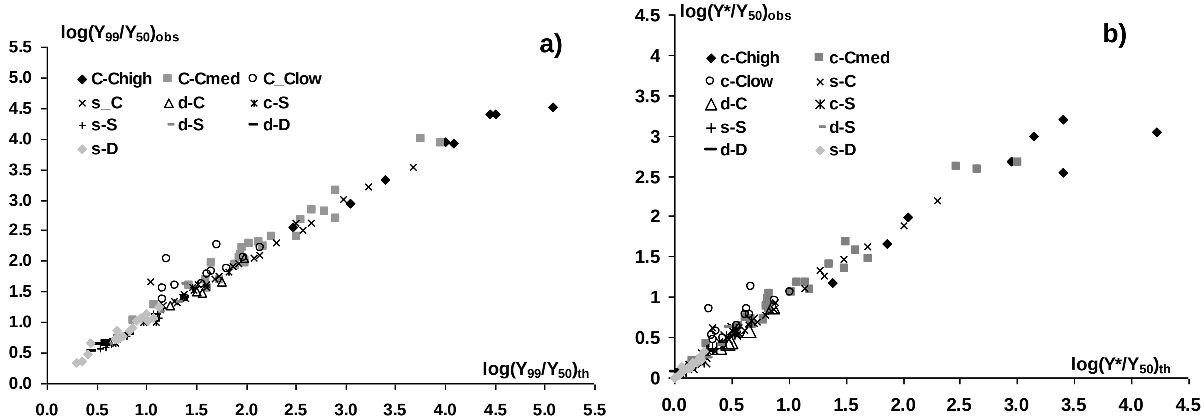


Figure 7. Comparison of material flux variability and flow variability for six classes of truncated *b_{50sup}* exponent (log – log scales): a) extreme flux variability *(Y_{99}/Y_{50}) vs.* extreme flow variability (q_{99}/q_{50}); b) general flux variability *(Y^*/Y_{50}) vs.* general flow variability *(q^*/q_{50}).* Thin lines correspond to empirical regressions and dotted lines to theoretical relationship for *Y_{99}/Y_{50}*.

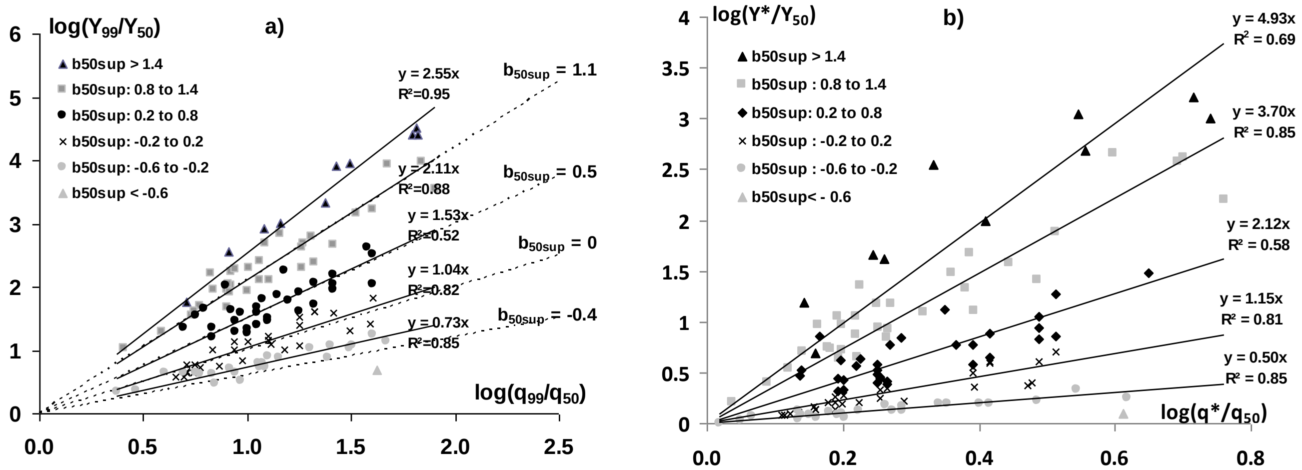


Figure 8. Control factors of the proportion (*F_{q50}*) of the fluxes transported during higher river flows: a) *F_{q50}* vs. the truncated exponent b_{50sup} **for different types of riverine materials (all stations, normal probability scale for *F_{q50}*); b) *F_{q50}* vs. *$W_{50\%}$*, the proportion of inter-annual river flow discharged during higher flows, by classes of *b_{50sup}* exponent (normal probability scale for both *F_{q50}* and *$W_{50\%}$*).**

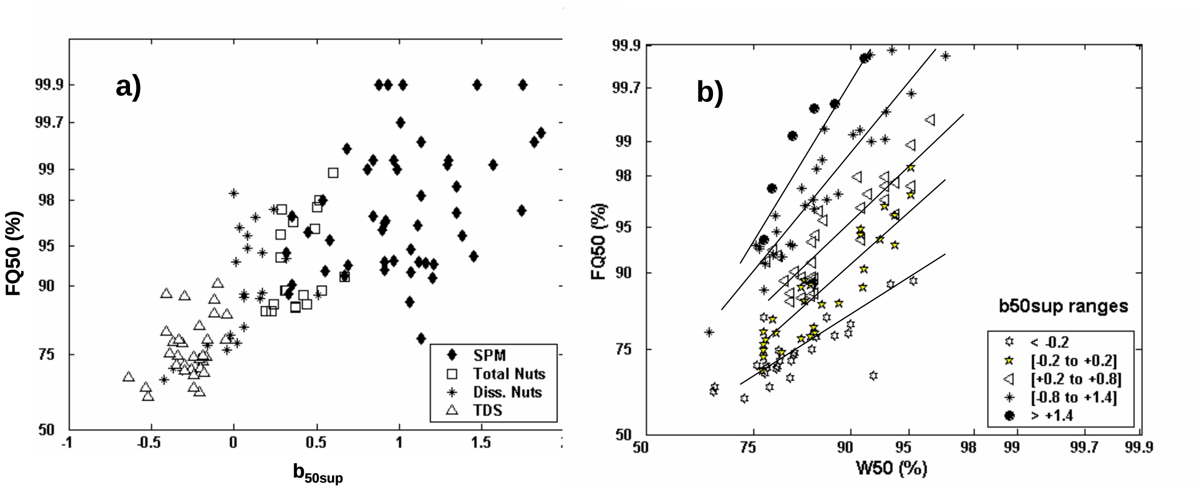


Figure 9. General typology of daily variability controlled by the truncated b_{50sup} exponent: a) general flux variability, b) extreme flux variability, c) general concentration variability, d) extreme concentration variability. Y^*, C^*, q^*: river flow-weighted averages; Y_{50}, C_{50}, q_{50}: medians; Y_{99}, C_{99}, q_{99}: upper percentiles. Medians of indicators as presented in Table 4.

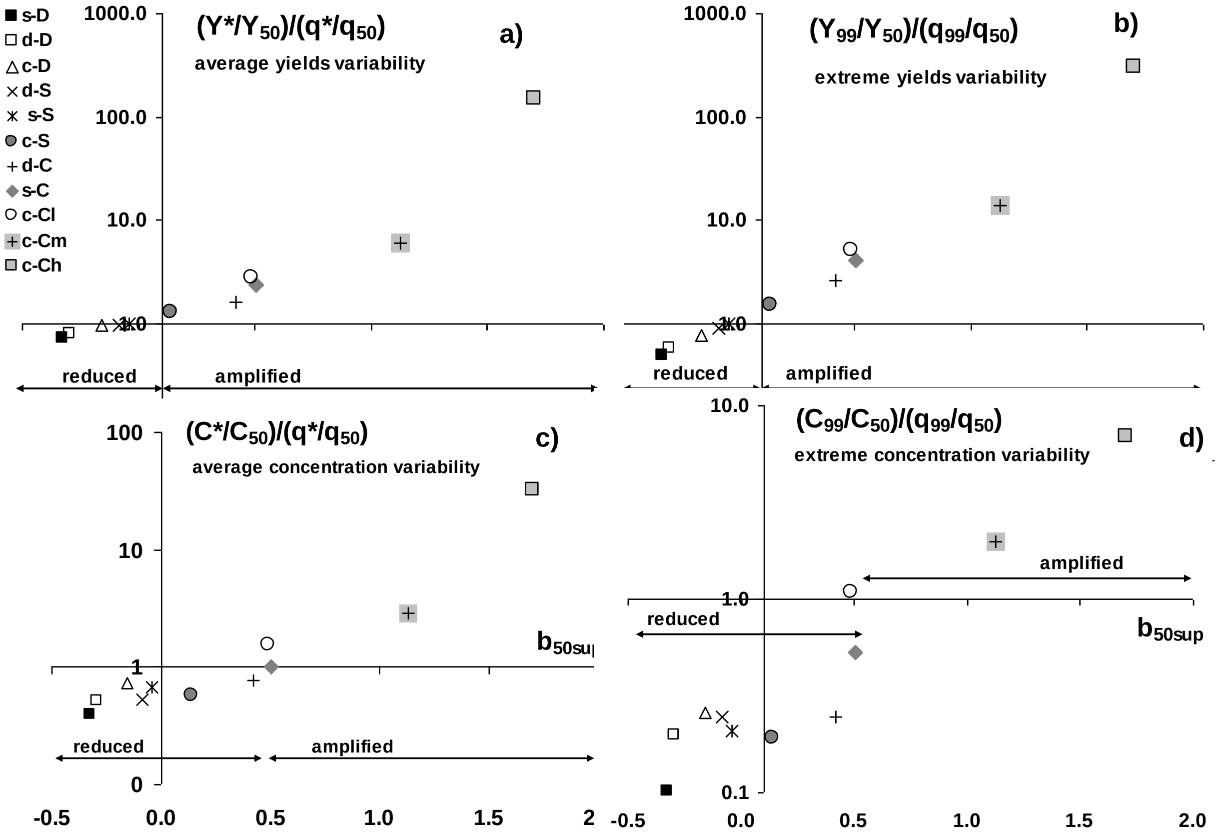
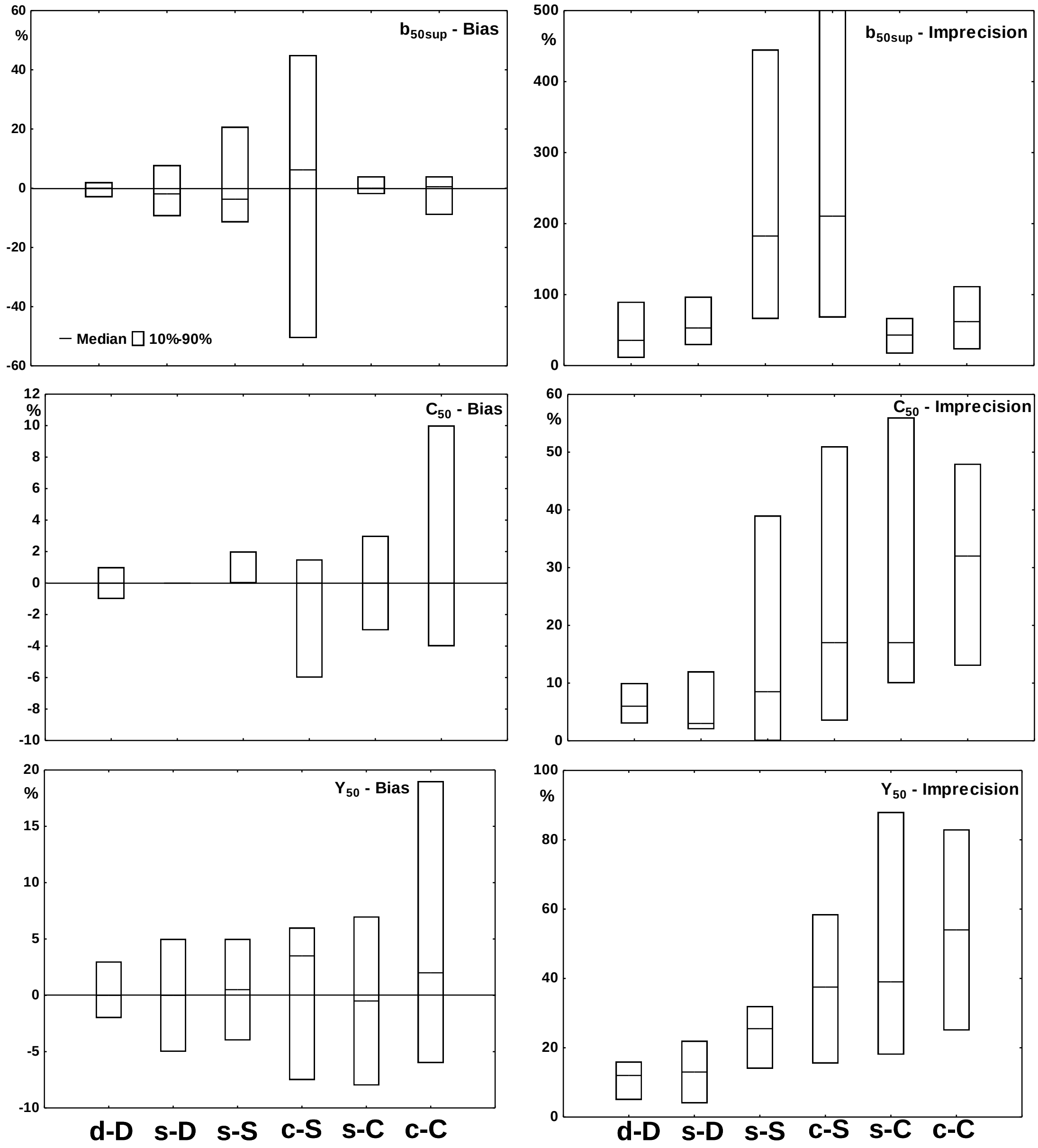


Figure 10. Biases and imprecisions on estimated b_{50sup}, C_{50} and Y_{50} in simulated discrete surveys for six C - q patterns. (Monte Carlo sorting, 7 years of record, 100 simulated monthly surveys). N=number of records (TDS, nutrients and SPM) used for each pattern.



Appendices 1. Indicators of daily variability of concentrations and fluxes at stations: suspended particulate matter, symbols listed in table 1. r^2, $r^2 50inf$, $r^2 50sup$: regression coefficients for integral and truncated logC vs. logQ relation

River, Location, State		yrs	period		A km²	q_* $l\ s^{-1}\ km^{-2}$	$q_*/q50$	q_{99}/q_{50}	C_* $mg\ l^{-1}$	C_*/C_{50}	C_{99}/C_{50}	Y_* $kg\ d^{-1}\ km^{-2}$	Y^*/Y_{50}	Y_{99}/Y_{50}	b	b_{50inf}	b_{50sup}	r2	$r2_{50inf}$	$r2_{50sup}$	$W_{50\%}$	F_{q50}	type
Tradewater at Olney, KY	**SPM**	6	1967	1972	660	14.5	4.47	37.71	39	6.6	23	50	30	430	0.36	0.11	0.68	0.38	0.03	0.38	96.2	99.4	**s-Cl**
Vermilion at Mill Hollow, OH	**SPM**	3	2001	2003	679	11.2	3.26	40.36	148	14.4	44	144	76	1668	0.37	-0.08	1.01	0.25	0.01	0.45	95.2	99.7	**s-Cl**
Redwood C at Orick, CA	**SPM**	14	1971	1984	717	39.1	3.60	30.87	1053	131.6	310	3557	488	9039	1.03	0.43	1.68	0.79	0.27	0.75	96.0	100.0	**c-Ch**
Muddy C nr Vaughn, MT	**SPM**	12	1971	1982	730	4.5	1.86	8.43	714	7.0	23	277	15	173	0.77	0.24	1.35	0.41	0.02	0.45	83.5	97.4	**c-Cm**
Brandywine C at Wilmington, DE	**SPM**	33	1947	1979	813	17.3	1.39	8.10	110	9.2	40	165	15	365	0.81	0.26	1.72	0.30	0.02	0.45	78.5	97.5	**c-Ch**
Cuyahoga Old Portage, OH	**SPM**	8	1973	1980	1 046	14.3	1.50	6.92	66	3.9	22	81	6	91	0.83	1.05	0.97	0.36	0.17	0.25	81.6	93.5	**c-Cm**
Mad at Arcata, CA	**SPM**	7	1967	1973	1 256	34.4	4.92	47.59	1589	69.1	171	4725	379	8640	1.00	0.38	1.36	0.84	0.13	0.82	97.3	100.0	**c-Cm**
Conococheague C at Fairview, MD	**SPM**	13	1967	1979	1 279	16.4	1.66	10.24	89	6.4	27	126	11	202	0.75	0.61	1.10	0.31	0.07	0.30	84.0	96.6	**c-Cm**
Siuslaw at Mapleton, OR	**SPM**	7	1968	1974	1 522	46.0	2.79	20.52	82	13.6	33	325	38	639	0.60	0.23	1.13	0.52	0.04	0.64	93.4	99.5	**c-Cm**
Rappahannock R at Remington, VA	**SPM**	41	1952	1992	1 605	11.7	1.68	12.21	138	12.6	48	140	22	476	0.68	0.27	1.35	0.40	0.06	0.46	86.5	98.5	**c-Cm**
Santa Clara R at Los Angeles-Ventura Co Line, CA	**SPM**	9	1969	1977	1 618	1.2	3.95	33.63	16409	109.4	40	1667	459	1427	1.07	0.75	0.90	0.45	0.08	0.36	91.9	99.9	**c-Cm**
Grand at Painesville, OH	**SPM**	12	1979	1990	1 773	17.5	2.40	18.27	142	7.5	24	215	22	417	0.45	0.00	0.98	0.40	0.00	0.52	92.1	99.0	**s-Cm**
Cuyahoga Independence, OH	**SPM**	22	1982	2003	1 834	15.1	1.56	8.82	230	6.7	31	301	11	189	0.91	0.47	1.15	0.39	0.04	0.30	82.0	93.5	**c-Cm**
Upper Iowa at Dorchester, IA	**SPM**	5	1976	1980	1 993	6.3	1.82	14.33	822	21.6	79	450	42	1028	1.13	0.07	1.57	0.40	0.00	0.44	82.1	99.1	**s-Ch**
Coal at Alum Creek, AZ	**SPM**	4	1975	1978	2 162	16.0	2.29	18.69	400	12.9	28	552	30	482	0.98	0.82	1.28	0.63	0.20	0.63	90.2	99.1	**c-Cm**
Fisher at Libby, MT	**SPM**	8	1968	1975	2 169	7.5	2.43	14.47	174	19.4	61	113	48	694	1.25	0.97	1.30	0.67	0.09	0.60	86.9	99.2	**c-Cm**
River Raisin at Monroe, MI	**SPM**	5	1967	1971	2 698	0.2	1.79	12.71	94	3.6	13	63	9	129	0.42	-0.02	0.93	0.21	0.00	0.34	87.1	96.9	**s-Cm**
San Pedro R at Charleston, AZ	**SPM**	11	1964	1974	3 195	0.4	3.51	64.89	10579	320.6	558	342	1107	32594	1.44	0.41	1.80	0.63	0.06	0.68	91.2	99.9	**c-Ch**
Sandusky nr Fremont, OH	**SPM**	12	1989	2000	3 245	11.1	3.06	25.74	223	7.3	22	214	26	456	0.62	0.38	0.81	0.50	0.09	0.43	93.3	99.0	**c-Cm**
Animas R at Farmington, NM	**SPM**	38	1951	1988	3 521	6.7	2.24	15.07	847	6.4	53	493	13	183	0.73	0.65	0.46	0.26	0.10	0.06	86.0	96.1	**c-Cl**
Paria R at Lees Ferry, AZ	**SPM**	27	1949	1975	3 651	0.2	2.15	26.81	92138	184.3	456	1597	354	8402	2.00	2.21	1.86	0.52	0.15	0.41	88.2	99.6	**c-Ch**
Green at Mudfordville, KY	**SPM**	11	1967	1977	4 331	20.2	1.85	11.51	152	4.0	18	266	8	129	0.64	0.34	0.84	0.39	0.04	0.25	88.5	97.2	**c-Cm**
Eel R at Fort Seward, CA	**SPM**	9	1967	1975	5 455	27.5	5.51	65.77	1744	158.5	360	4135	1001	25720	1.02	0.40	1.45	0.87	0.28	0.86	97.9	100.0	**c-Ch**
East Fork White R at Seymour, IN	**SPM**	13	1967	1979	6 061	12.8	1.86	14.02	158	2.9	11	174	6	73	0.50	0.54	0.58	0.33	0.14	0.20	86.6	95.5	**c-Cl**
Dan at Paces, VA	**SPM**	12	1969	1980	6 602	13.5	1.38	8.37	206	3.4	12	240	5	103	0.81	0.34	1.16	0.44	0.03	0.57	76.2	93.2	**c-Cm**
Pecos at Santa Rosa, NM	**SPM**	22	1963	1984	6 861	0.4	5.03	69.49	4691	78.2	230	151	416	9710	1.18	1.21	1.04	0.60	0.22	0.47	93.8	99.9	**c-Cm**
Trinity at Hoopa, CA	**SPM**	9	1970	1978	7 386	19.2	2.57	23.66	763	38.1	95	1264	100	2126	1.42	0.87	1.47	0.85	0.26	0.69	91.4	99.9	**c-Ch**
Eel R at Scotia, CA	**SPM**	20	1960	1979	8 060	28.3	5.20	62.19	2988	272.7	438	7309	1604	25591	1.13	0.45	1.51	0.84	0.20	0.79	97.5	100.0	**c-Ch**
Iowa at Iowa city, IA	**SPM**	18	1969	1986	8 468	8.5	1.57	6.21	149	2.7	16	109	4	46	0.37	0.18	0.32	0.19	0.03	0.03	85.5	94.3	**s-Cl**
Pembina R at Walhalla, ND	**SPM**	13	1963	1975	8 674	1.0	5.77	80.78	1360	17.9	44	122	159	3524	0.47	0.03	0.93	0.49	0.00	0.66	97.0	99.9	**s-Cm**
Juniata R at Newport, PA	**SPM**	38	1951	1988	8 684	13.6	1.78	11.52	63	7.9	28	74	15	255	0.86	0.60	1.13	0.49	0.11	0.38	85.8	98.2	**c-Cm**
Scioto at Chillicothe, OH	**SPM**	7	1997	2003	9 982	10.7	1.84	10.00	115	3.4	11	106	7	88	0.73	0.43	0.90	0.48	0.05	0.43	85.4	96.3	**c-Cm**
Marne at Neuilly, France	**SPM**	10	1995	2004	12 710	9.5	1.58	5.93	55	3.1	12	45	5	50	0.87	0.31	1.07	0.58	0.03	0.46	79.3	94.6	**c-Cm**
Des Moines at Saylorville, IA	**SPM**	7	1969	1975	15 122	5.7	1.93	11.82	518	3.5	12	257	7	65	0.71	0.64	0.55	0.68	0.32	0.24	90.8	98.0	**c-Cl**
Maumee at Waterville, OH	**SPM**	20	1982	2001	16 395	9.4	2.48	18.37	208	4.2	12	167	13	201	0.44	0.01	0.82	0.35	0.00	0.50	91.0	99.2	**s-Cm**
Oise at Mery, France	**SPM**	10	1995	2004	16 972	7.2	1.37	4.97	38	2.1	8	23	3	23	0.82	0.66	0.68	0.51	0.14	0.19	77.4	91.5	**c-Cl**
Delaware at Trenton, NJ	**SPM**	14	1968	1981	17 553	20.5	1.46	6.68	56	6.2	32	99	9	161	0.88	0.66	1.37	0.31	0.05	0.31	79.1	95.9	**c-Cm**
Klamath R at Orleans, CA	**SPM**	12	1967	1978	21 943	12.1	1.75	11.94	376	26.9	80	392	45	859	1.36	0.85	1.82	0.80	0.24	0.73	85.5	99.5	**c-Ch**
Seine at Choisy, France	**SPM**	10	1995	2004	30 710	7.6	1.44	5.07	30	3.0	12	20	5	57	0.89	0.05	1.45	0.55	0.00	0.61	77.1	93.9	**s-Ch**
Iowa at Wappelo, IA	**SPM**	10	1979	1988	32 358	8.3	1.37	5.64	287	2.4	11	206	3	35	0.81	0.64	0.56	0.34	0.09	0.09	79.6	92.2	**c-Cl**
San Juan R at Shiprock, NM	**SPM**	31	1955	1985	33 400	1.7	1.46	7.85	3812	4.8	50	552	7	107	0.59	0.82	0.35	0.13	0.12	0.02	82.5	90.2	**c-Cl**
Rio Grande at Otowi Bridge, NM	**SPM**	33	1956	1988	37 025	1.1	1.66	9.33	1429	2.4	16	132	4	40	0.63	0.75	0.33	0.18	0.06	0.04	80.7	88.8	**c-Cl**
Minnesota R at Mankato, OH	**SPM**	27	1968	1994	38 579	3.4	2.32	15.69	271	2.4	7	82	6	60	0.39	0.21	0.35	0.49	0.10	0.16	91.8	97.2	**c-Cl**
Mississippi at Anoka, MN	**SPM**	19	1976	1994	49 448	5.2	1.32	5.42	30	2.2	7	13	3	36	0.76	0.31	1.20	0.39	0.04	0.42	77.1	91.3	**c-Cm**
Rhin at Maxau, Germany	**SPM**	19	1974	1992	50 196	25.6	1.09	2.54	29	1.4	5	64	2	11	0.98	0.68	1.13	0.34	0.05	0.24	65.4	79.2	**c-Cm**
Tennessee Chattawooga, TN	**SPM**	7	1935	1941	55 402	15.9	1.52	7.94	188	3.5	13	257	5	90	1.07	0.66	1.22	0.38	0.02	0.44	76.0	93.0	**c-Cm**
Seine at Poses, France	**SPM**	3	1983	1985	65 000	7.4	1.20	4.08	38	1.8	6	24	3	19	0.93	0.35	1.07	0.60	0.03	0.50	77.1	87.4	**c-Cm**
Sacramento at Freeport, CA	**SPM**	9	1980	1988	65 403	11.0	1.56	5.56	82	2.8	12	78	4	40	1.06	1.25	0.91	0.66	0.29	0.45	75.5	93.3	**c-Cm**
Green R nr Jensen , UT	**SPM**	30	1949	1978	76 795	1.6	1.58	8.10	1289	5.5	31	175	9	111	0.92	0.90	1.13	0.34	0.11	0.28	82.1	93.3	**c-Cm**
Tennessee at Savannah, TN	**SPM**	7	1935	1941	85 796	15.9	1.67	8.04	88	2.8	9	121	5	48	0.83	0.49	0.91	0.33	0.02	0.34	78.8	92.3	**c-Cm**
Tennessee at Paducah, KY	**SPM**	6	1936	1941	104 073	15.1	1.68	8.42	124	2.6	10	162	4	42	0.88	1.13	0.68	0.39	0.09	0.21	78.7	92.9	**c-Cl**
Arkansas R at Arkansas city, KS	**SPM**	13	1962	1974	113 180	0.5	2.08	20.86	1203	6.0	16	51	12	245	0.88	0.79	0.91	0.45	0.09	0.40	85.2	96.8	**c-Cm**
Green R at Green , UT	**SPM**	42	1942	1983	116 124	1.4	1.66	8.26	2309	4.4	26	283	7	84	0.96	0.59	1.07	0.32	0.03	0.29	80.3	92.1	**c-Cm**
Mississippi R at St Louis, MO	**SPM**	42	1949	1990	251 149	21.1	1.23	3.88	720	2.1	8	13	3	19	1.03	1.02	0.85	0.43	0.16	0.17	74.0	89.0	**c-Cm**

Appendices 2. Indicators of daily variability of concentrations and fluxes at stations: nutrients, symbols listed in table 1. r², r²50inf, r²50sup: regression coefficients for integral and truncated logC vs. logQ relation

River, Location, State		yrs	period		A	q_*	q_*/q_{50}	q_{99}/q_{50}	C_*	C_*/C_{50}	C_{99}/C_{50}	Y_*	Y_*/Y_{50}	Y_{99}/Y_{50}	b	b_{50inf}	b_{50sup}	r2	$r2_{50inf}$	$r2_{50sup}$	$W_{50\%}$	F_{q50}	type
					km²				mg l^{-1}			kg d^{-1} km^{-2}											
Vermilion at Mill Hollow, OH	No3	3	2001	2003	679	11.2	3.3	40.4	16.4	1.64	5.03	15.89	5.16	68.1	0.58	0.57	0.14	0.39	0.16	0.05	95.2	97.1	**c-S**
Grand at Painesville, OH	No3	9	1995	2003	1 777	15.0	2.6	20.8	2.8	1.46	3.86	3.66	3.94	42.0	0.16	0.06	0.10	0.11	0.01	0.01	94.0	95.9	**s-S**
Cuyahoga at Independence, OH	No3	22	1982	2003	1 834	15.1	1.6	8.8	7.7	0.76	2.52	10.09	1.23	4.5	-0.51	-0.55	-0.42	0.65	0.39	0.30	81.6	67.3	**d-D**
Raisan at Monroe, MI	No3	21	1983	2003	2 699	8.4	1.8	11.2	20.0	1.81	4.03	14.60	3.06	25.0	0.78	1.46	0.32	0.58	0.53	0.18	85.1	93.7	**c-Cl**
Sandusky nr Fremont, OH	No3	12	1989	2000	3 245	11.1	3.1	25.9	27.1	1.59	3.61	25.96	4.07	38.3	0.73	1.58	0.03	0.46	0.45	0.00	93.3	96.5	**c-S**
Great Miami below Miamisburg, OH	No3	6	1998	2003	6 954	12.2	1.8	12.5	20.5	1.22	2.63	21.63	2.16	16.9	0.13	0.10	0.06	0.13	0.02	0.01	84.9	88.2	**s-S**
Scioto at Chilicothe, OH	No3	7	1997	2003	9 982	10.7	1.8	10.0	19.3	1.18	2.16	17.93	2.21	14.1	0.15	0.13	0.06	0.17	0.03	0.02	85.4	88.8	**s-S**
Marne at Neuilly, France	No3	8	1997	2004	12 710	9.7	1.5	5.6	22.1	1.06	1.64	18.62	1.62	6.1	0.16	0.18	0.06	0.20	0.04	0.02	78.8	81.9	**s-S**
Maumee at Waterville, OH	No3	21	1982	2002	16 395	9.5	2.5	17.8	26.7	1.37	2.94	21.96	3.14	25.4	0.80	1.68	0.09	0.44	0.44	0.02	91.1	94.8	**c-S**
Oise at Mery, France	No3	10	1995	2004	16 972	7.2	1.4	5.0	21.2	0.99	1.29	13.23	1.29	3.8	0.02	0.15	-0.16	0.01	0.15	0.26	77.4	77.3	**s-S**
Muskingum at McConnelsville, OH	No3	9	1995	2003	19 218	11.8	1.6	6.8	8.0	1.18	2.05	8.13	1.88	10.2	0.35	0.56	0.16	0.23	0.11	0.07	83.5	87.8	**c-S**
Seine at Choisy, France	No3	10	1995	2004	30 710	7.6	1.4	5.1	25.7	1.03	1.39	16.96	1.38	4.7	0.14	0.41	-0.03	0.23	0.31	0.01	77.1	79.2	**c-S**
Marne at Neuilly, France	nh4	10	1995	2004	12 710	9.5	1.6	5.9	0.1	1.01	3.71	0.11	1.24	4.2	-0.30	-0.31	-0.29	0.20	0.03	0.14	79.3	70.0	**d-D**
Oise at Mery, France	nh4	10	1995	2004	16 972	7.2	1.4	5.0	0.2	1.09	4.33	0.14	1.35	4.5	-0.20	-0.11	-0.37	0.06	0.00	0.09	77.4	70.8	**s-D**
Seine at Choisy, France	nh4	10	1995	2004	30 710	7.6	1.4	5.1	0.1	1.10	3.00	0.07	1.47	6.0	-0.04	-0.26	-0.05	0.00	0.02	0.00	77.1	76.1	**d-S**
Grand at Painesville, OH	P-po4	9	1995	2003	1 777	15.0	2.6	20.8	0.0	1.05	11.40	0.01	4.13	41.6	-0.20	-0.57	0.03	0.11	0.29	0.00	94.0	93.4	**d-S**
Raisan at Monroe, MI	P-po4	21	1983	2003	2 699	8.4	1.8	11.2	0.1	1.76	5.80	0.02	3.37	38.2	0.16	0.10	0.52	0.02	0.00	0.09	85.1	88.6	**s-Cl**
Sandusky nr Fremont, OH	P-po4	12	1989	2000	3 245	11.1	3.1	25.9	0.1	3.26	8.21	0.04	8.87	112.2	0.60	0.59	0.40	0.35	0.10	0.10	93.3	97.6	**c-Cl**
Great Miami below Miamisburg, OH	P-po4	6	1998	2003	6 954	12.2	1.8	12.5	0.5	0.93	2.94	0.17	1.78	14.5	-0.30	-0.58	0.02	0.32	0.30	0.00	84.9	78.1	**d-S**
Scioto at Chilicothe, OH	P-po4	7	1997	2003	9 982	10.7	1.8	10.0	0.4	1.00	3.61	0.12	1.77	10.1	-0.19	-0.45	0.00	0.11	0.10	0.00	85.4	80.2	**d-S**
Maumee at Waterville, OH	P-po4	21	1982	2002	16 395	9.5	2.5	17.8	0.2	1.41	3.44	0.05	3.61	34.3	0.41	0.38	0.17	0.17	0.04	0.02	91.1	94.3	**c-S**
Loire at Orleans, France	P-po4	5	1981	1985	36 970	11.3	1.5	8.6	0.1	1.11	2.30	0.10	1.62	10.3	0.49	0.65	0.17	0.31	0.13	0.05	84.1	88.9	**c-S**
Vermilion at Mill Hollow, OH	ptot	3	2001	2003	679	11.2	3.3	40.4	0.3	4.54	9.67	0.26	18.54	330.6	0.29	0.11	0.60	0.40	0.05	0.45	95.2	98.9	**s-Cl**
Grand at Painesville, OH	ptot	9	1995	2003	1 777	15.0	2.6	20.8	0.1	2.34	6.61	0.17	7.65	113.7	0.11	-0.23	0.50	0.08	0.19	0.37	94.0	97.7	**d-Cl**
Cuyahoga at Independence, OH	ptot	22	1982	2003	1 834	15.1	1.6	8.8	0.3	1.59	5.40	0.42	2.79	29.6	0.11	-0.19	0.46	0.02	0.02	0.13	81.6	86.8	**s-Cl**
Raisan at Monroe, MI	ptot	21	1983	2003	2 699	8.4	1.8	11.2	0.2	1.82	5.56	0.14	3.85	46.8	0.16	-0.29	0.67	0.06	0.06	0.38	85.1	91.3	**d-Cl**
Sandusky nr Fremont, OH	ptot	12	1989	2000	3 245	11.1	3.1	25.9	0.4	3.35	8.10	0.36	11.26	159.4	0.41	0.29	0.52	0.48	0.11	0.41	93.3	98.0	**c-Cl**
Great Miami below Miamisburg, OH	ptot	6	1998	2003	6 954	12.2	1.8	12.5	0.4	1.21	2.79	0.41	2.75	32.2	-0.09	-0.61	0.37	0.05	0.64	0.36	84.9	86.5	**d-Cl**
Scioto at Chilicothe, OH	ptot	7	1997	2003	9 982	10.7	1.8	10.0	0.3	1.19	2.44	0.30	2.41	18.7	0.00	-0.35	0.24	0.00	0.16	0.19	85.4	86.8	**d-Cl**
Maumee at Waterville, OH	ptot	21	1982	2002	16 395	9.5	2.5	17.8	0.4	2.19	4.56	0.34	6.05	81.3	0.25	0.02	0.49	0.41	0.00	0.56	91.1	96.4	**s-Cl**
Muskingum at McConnelsville, OH	ptot	9	1995	2003	19 218	11.8	1.6	6.8	0.2	1.52	3.75	0.19	2.66	22.7	0.20	0.05	0.53	0.23	0.01	0.41	83.5	89.3	**s-Cl**
Loire at Orleans, France	ptot	5	1981	1985	36 970	11.3	1.5	8.6	0.3	1.17	3.50	0.26	1.84	13.5	0.01	-0.13	0.19	0.00	0.03	0.08	84.1	85.5	**s-S**
Vermilion at Mill Hollow, OH	tkn	3	2001	2003	679	11.2	3.3	40.4	1.5	1.96	3.62	1.40	7.15	112.8	0.13	0.05	0.29	0.29	0.04	0.35	95.2	97.6	**s-Cl**
Grand at Painesville, OH	tkn	9	1995	2003	1 777	15.0	2.6	20.8	0.8	1.51	3.52	1.03	4.52	52.3	0.07	0.00	0.28	0.08	0.00	0.21	94.0	96.0	**s-Cl**
Cuyahoga at Independence, OH	tkn	22	1982	2003	1 834	15.1	1.6	8.8	1.2	1.44	4.00	1.51	2.10	19.2	0.12	0.08	0.23	0.06	0.01	0.08	81.6	85.5	**s-Cl**
Raisan at Monroe, MI	tkn	21	1983	2003	2 699	8.4	1.8	11.2	1.2	1.38	3.32	0.84	2.56	25.2	0.13	-0.14	0.32	0.09	0.03	0.25	85.1	89.4	**s-Cl**
Sandusky nr Fremont, OH	tkn	12	1989	2000	3 245	11.1	3.1	25.9	1.7	2.00	3.75	1.67	6.86	91.0	0.22	0.12	0.36	0.37	0.04	0.44	93.3	96.9	**s-Cl**
Great Miami below Miamisburg, OH	tkn	6	1998	2003	6 954	12.2	1.8	12.5	1.2	1.39	2.85	1.31	2.82	29.7	0.07	-0.38	0.42	0.02	0.14	0.40	84.9	88.6	**d-Cl**
Scioto at Chilicothe, OH	tkn	7	1997	2003	9 982	10.7	1.8	10.0	1.1	1.36	2.61	1.06	2.64	21.6	0.13	-0.07	0.31	0.13	0.01	0.28	85.4	89.3	**s-Cl**
Maumee at Waterville, OH	tkn	21	1982	2002	16 395	9.5	2.5	17.8	1.8	1.42	2.56	1.45	3.86	41.7	0.08	-0.04	0.28	0.11	0.01	0.39	91.1	93.8	**s-Cl**
Muskingum at McConnelsville, OH	tkn	9	1995	2003	19 218	11.8	1.6	6.8	0.7	1.23	2.70	0.75	2.13	16.4	0.05	-0.11	0.36	0.02	0.03	0.25	83.5	86.1	**s-Cl**

Appendices 3. Indicators of daily variability of concentrations and fluxes at stations: total dissolved solids, symbols listed in table 1. r², r²50inf, r²50sup: regression coefficients for integral and truncated logC vs. logQ relation

River, Location, State		yrs	period		A	q*	q^*/q_{50}	q_{99}/q_{50}	C*	C^*/C_{50}	C_{99}/C_{50}	Y_*	Y^*/Y_{50}	Y_{99}/Y_{50}	b	b_{50inf}	b_{50sup}	r2	$r2_{50inf}$	$r2_{50sup}$	$W_{50\%}$	Fq_{50}	type
					Km²	$ls^{-1}km^{-2}$			μScm^{-1}														
Brandywine at Chadds Ford, PA	TDS	8	1974	1981	743	18.9	1.32	7.27	200	0.88	1.36	328	1.24	5.71	-0.18	-0.16	-0.19	0.41	0.27	0.21	77.1	72.8	**s-S**
Jackson at Falling Spring, VA	TDS	9	1976	1984	1 061	13.8	1.95	15.09	151	0.81	1.59	180	1.66	10.50	-0.23	-0.32	-0.17	0.71	0.60	0.36	85.5	79.0	**d-S**
Arkansas at Granite, CO	TDS	13	1994	2006	1 105	9.6	1.93	11.40	105	0.84	1.70	87	1.46	6.23	-0.28	-0.25	-0.21	0.67	0.18	0.49	82.3	73.6	**d-D**
Rappahannock at Remington, VA	TDS	10	1974	1983	1 603	13.3	1.67	12.89	63	0.93	1.59	72	1.62	12.71	-0.07	-0.07	-0.04	0.18	0.12	0.02	86.6	84.9	**s-S**
N Santiam at Mehama, OR	TDS	6	2001	2006	1 694	52.3	1.37	5.67	32	0.89	1.33	145	1.21	4.44	-0.19	-0.12	-0.20	0.57	0.13	0.39	75.7	70.8	**s-D**
Clackamas at Estacada, OR	TDS	4	2002	2005	1 737	37.6	1.29	5.53	45	0.90	1.42	147	1.21	4.41	-0.31	-0.40	-0.18	0.82	0.76	0.32	76.9	69.4	**d-S**
NF Ninnescah, KS	TDS	8	1999	2006	1 846	1.8	1.45	12.18	972	0.82	1.23	148	1.15	5.46	-0.10	0.07	-0.34	0.20	0.19	0.66	79.7	74.7	**s-D**
Peace at Zolfo Springs, FL	TDS	5	1972	1976	2 138	5.7	1.87	11.53	316	0.74	1.40	155	1.34	5.41	-0.33	-0.18	-0.35	0.80	0.30	0.66	81.8	72.0	**s-D**
Bird C nr Catoosa, OK	TDS	6	2000	2005	2 646	6.3	3.01	30.83	269	0.85	1.86	146	2.50	20.84	-0.13	-0.22	-0.12	0.34	0.15	0.27	88.7	85.1	**d-S**
Medina at San Antonio, TX	TDS	12	1988	1999	3 410	2.4	2.19	24.99	650	0.72	1.16	133	1.56	12.03	-0.22	-0.06	-0.24	0.71	0.05	0.66	82.5	74.2	**s-D**
S F Shenandoah at Front Royal, VA	TDS	8	1969	1976	4 230	12.0	1.54	9.38	231	0.86	1.56	239	1.36	6.89	-0.23	-0.27	-0.18	0.51	0.28	0.23	80.3	74.3	**d-S**
Sun nr Vaughn, MT	TDS	7	1988	1994	4 787	3.7	1.67	11.90	559	0.80	1.52	179	1.33	6.12	-0.27	-0.19	-0.30	0.67	0.21	0.58	79.9	72.0	**s-D**
Wichita at Wichita Falls, TX	TDS	5	1997	2001	8 129	0.5	2.52	31.86	3134	0.59	1.42	140	1.58	12.09	-0.30	-0.19	-0.37	0.50	0.11	0.48	88.2	78.3	**s-D**
Wichita nr Charlie, TX	TDS	5	1997	2001	8 903	0.8	2.26	20.16	2784	0.70	1.48	189	1.56	10.85	-0.23	0.06	-0.31	0.34	0.01	0.39	85.7	78.1	**s-D**
Dolores nr Cisco, UT	TDS	8	1952	1959	11 857	1.9	4.08	41.67	963	0.33	3.37	156	1.24	4.83	-0.61	-0.35	-0.64	0.84	0.30	0.79	92.3	67.9	**d-D**
Marne at Neuilly, France	TDS	10	1995	2004	12 710	9.5	1.58	5.93	484	0.98	1.18	395	1.57	5.50	-0.02	-0.05	-0.05	0.04	0.02	0.12	79.3	78.8	**s-S**
Virgin at Littlefield, AZ	TDS	10	1973	1982	13 177	0.6	1.93	14.28	1936	0.66	1.24	102	1.31	7.56	-0.32	-0.17	-0.39	0.78	0.33	0.70	85.1	75.1	**s-D**
Arkansas nr Avondale, CO	TDS	20	1986	2005	16 380	1.6	1.51	8.26	664	0.82	1.57	89	1.27	5.23	-0.33	-0.30	-0.26	0.75	0.46	0.43	79.5	70.5	**d-D**
Oise at Mery, France	TDS	8	1995	2002	16 972	7.7	1.30	4.50	557	0.95	1.23	372	1.21	3.76	-0.09	-0.02	-0.19	0.30	0.01	0.33	77.1	74.7	**s-S**
Delaware at Trenton, NJ	TDS	11	1982	1992	17 553	18.1	1.42	6.78	151	0.85	1.41	235	1.22	4.12	-0.29	-0.26	-0.30	0.78	0.41	0.58	77.7	70.2	**d-D**
Gunnison nr Gd Junction, CO	TDS	10	1992	2001	20 525	3.8	1.37	6.99	643	0.80	1.51	213	1.09	3.03	-0.48	-0.11	-0.52	0.69	0.02	0.63	73.1	61.4	**s-D**
Sheyenne at Lisbon, ND	TDS	7	1965	1971	21 203	0.3	2.96	38.69	648	0.78	1.39	16	2.35	26.51	-0.13	-0.07	-0.12	0.48	0.07	0.31	91.3	87.7	**s-S**
Potomac nr. Wash, DC, MA	TDS	10	1989	1998	29 927	13.3	1.83	12.49	241	0.80	1.60	278	1.50	8.01	-0.18	-0.16	-0.22	0.60	0.39	0.36	87.1	82.4	**s-D**
Seine at Choisy, France	TDS	10	1995	2004	30 710	7.6	1.44	5.07	443	0.98	1.14	292	1.38	4.38	0.00	0.08	-0.08	0.00	0.07	0.23	77.1	82.4	**s-S**
North Canadian nr Yukon, OK	TDS	8	1999	2006	34 129	0.2	2.47	17.78	988	0.87	1.46	19	2.31	11.97	-0.02	0.06	-0.10	0.01	0.02	0.03	91.5	90.4	**s-S**
Arkansas at Las Animas, CO	TDS	8	1993	2000	37 324	0.3	3.07	31.15	1492	0.58	1.75	40	1.66	10.56	-0.32	-0.17	-0.33	0.76	0.12	0.69	89.8	78.8	**s-D**
Canadian nr Amarillo, TX	TDS	6	2001	2006	50 341	0.0	4.15	46.60	1944	0.53	1.89	6	1.80	13.51	-0.07	0.05	-0.41	0.07	0.04	0.43	95.3	88.8	**s-D**
Red nr Burkburnett, TX	TDS	8	1995	2002	53 253	0.9	3.50	40.02	3867	0.61	1.78	315	2.13	17.54	-0.19	-0.08	-0.30	0.43	0.06	0.42	93.7	88.3	**s-D**
San Juan nr Bluff, UT	TDS	6	1965	1970	59 544	1.0	1.16	4.03	699	0.93	2.15	62	1.18	4.47	-0.38	-0.40	-0.24	0.59	0.46	0.10	77.3	68.5	**d-D**
Colorado nr Cisco, UT	TDS	21	1983	2003	62 392	3.3	1.59	9.28	761	0.71	1.48	219	1.15	3.31	-0.49	-0.35	-0.53	0.87	0.40	0.83	78.0	64.5	**d-D**
Arkansas at Ralston, OK	TDS	9	1970	1978	141 003	1.1	2.61	24.29	1044	0.64	1.83	99	1.56	7.50	-0.25	0.06	-0.41	0.42	0.01	0.49	90.0	80.8	**s-D**
Columbia nr Quincy, OR	TDS	9	1998	2006	665 084	9.3	1.12	2.36	134	0.97	1.26	108	1.08	2.17	-0.17	-0.02	-0.21	0.26	0.00	0.12	66.5	63.2	**s-D**
Missouri at Nebraska City, NE	TDS	27	1951	1977	1 061 441	1.0	1.04	2.93	681	0.96	1.24	57	1.00	2.29	-0.09	-0.04	-0.24	0.13	0.03	0.24	66.8	64.7	**s-D**