

PERSPECTIVES

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Misuse of inorganic N and soluble reactive P concentrations to indicate nutrient status of surface waters

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Abstract. Dissolved inorganic N (DIN) and soluble reactive P (SRP) have been used by some to indicate the trophic status of waters, and concentration ratios (DIN:SRP) to indicate nutrient deficiency. The utility of such measurements should be questioned, particularly based on well-known problems associated with determination of the concentration of SRP, which is commonly assumed to represent PO_4^{3-} . Another potential problem with using inorganic nutrient pools to represent trophic state and nutrient availability ratios arises because concentration values are in units of mass per unit volume, and cannot be used with certainty to estimate supply (i.e., turnover rate of the nutrient pool, expressed either in mass per unit volume per unit time or simply as per unit time) to organisms without information on uptake and remineralization. Two data sets with lotic water-column nutrient values were explored, a large, continental-scale data set with analyses and collections done by many laboratories, and a more limited data set collected and analyzed by the same laboratory. In concert, the data sets indicated that at high total N (TN) (i.e., >5 mg/L) and total P (TP) (i.e., >2 mg/L) concentrations, $>60\%$ of the nutrient is usually made up of dissolved inorganic forms, but at low levels the ratio of dissolved inorganic to total nutrients is highly variable. Last, DIN:SRP is a weak surrogate for TN:TP and thus should be used with caution to indicate nutrient limitation.

Key words: ammonium, dissolved reactive phosphorus, inorganic nutrients, nitrate, nutrient limitation, phosphate, water-quality monitoring.

Nutrients such as N and P are required for organisms and can control ecosystem production. The most commonly limiting nutrients in fresh waters are N and P (Elser et al. 1990, Dodds 2002). Measurements of nutrient concentrations may be used to indicate trophic state, and ratios of values for nutrients can be used to indicate if a particular nutrient is limiting (Dodds 2002). Measurements of total N (TN) and total P (TP) are useful for determining trophic state because they present the total nutrient content actually in biomass or available for incorporation into active biomass. Likewise, the TN to TP ratio (TN:TP) is commonly used to indicate nutrient deficiency because it correlates well with other measures of nutrient deficiency such as growth-based bioassays (e.g., Dodds and Prisco 1990). Dissolved organic nutrients

(e.g., ions such as NH_4^+ , NO_3^- and PO_4^{3-}) are the form of nutrients that many microbes and plants utilize. It is easier to measure dissolved inorganic N (DIN) and soluble reactive P (SRP) than TN and TP concentrations because determinations of total nutrients require an additional digestion step to convert nutrients to the dissolved inorganic form. Thus, there may be a tendency to use DIN and SRP values to indicate how nutrient-rich an aquatic habitat is. My paper considers how useful common measures of DIN and SRP may be for indicating trophic state and nutrient limitation (i.e., can DIN and SRP values serve as surrogates for TN and TP?).

SRP and DIN are commonly measured and reported in water-quality data sets, presumably as a measure of trophic status (i.e., relative nutrient availability) or to indicate eutrophication problems. By extension, if DIN and SRP are indicative of trophic status (relative nutrient avail-

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ability), then DIN:SRP can serve as an indicator of nutrient deficiency for aquatic primary producers. However, there are important caveats to such uses related to how well SRP measures actual PO_4^{3-} concentrations, and generally how well inorganic nutrient levels (standing stock) indicate actual nutrient availability (supply rates). Potential problems exist with interpreting inorganic nutrient assays when they may represent a poorly defined chemical fraction (e.g., SRP may not be a reliable indicator of PO_4^{3-}). Problems may also arise when it is assumed that standing stocks of SRP and DIN are always indicative of nutrient supply. Although there are many examples of situations where such problems may arise, I will not cite them directly unless they appear in my own work. Thus, readers can assess their own data and those of others effectively without my specifically mentioning papers that may have misused these data in the past.

Researchers commonly include dissolved inorganic nutrient values (e.g., SRP or DIN) to characterize nutrients at a site (e.g., Dodds and Castenholz 1988, Dodds et al. 2000). These kinds of data can only provide limited information about system characteristics because inorganic nutrients can be under high demand and turnover rapidly (i.e., pattern does not necessarily describe process). Thus, even though concentrations may be low, supply may be high. It is well documented that nutrient regeneration supplies nutrients as they are removed by biota, and the balance between uptake and remineralization rates determines actual concentrations of inorganic nutrients (e.g., Dodds 1993). Low dissolved inorganic nutrient concentrations could mean high turnover related to high remineralization and uptake rates, and the system could be very productive. Alternatively, nutrient supply could be limiting and system productivity very low. These alternatives have not been explicitly explored over a wide variety of aquatic systems.

A problem more specific to inorganic P measurements is the uncertainty over what SRP values represent. These problems could complicate using SRP as a surrogate for TP as well as the use of DIN:SRP to indicate N or P limitation. Colorimetric assays are most often used for determination of SRP. It has been known for >35 y that SRP assays do not measure only PO_4^{3-} . Since the work of Rigler (1966) using radioiso-

topic tracers of PO_4^{3-} , it has been evident that free PO_4^{3-} is often not a major component of SRP. These observations have been confirmed repeatedly (e.g., Bentzen and Taylor 1991, Dodds et al. 1991). More recently, Hudson et al. (2000) surveyed 14 lakes and demonstrated that PO_4^{3-} made up <1% of SRP in all the lakes. What the SRP measurement represents has not been well documented in spite of its continued use in virtually all water-quality assessment programs that include nutrient analyses.

Standard acidic SRP assays hydrolyze condensed PO_4^{3-} (pyro-, meta-, and other polyphosphates; APHA 1995) in addition to directly reacting with PO_4^{3-} . In a critique of the SRP technique, Chamberlain and Shapiro (1973) noted that several factors hinder the ability of the assay to indicate PO_4^{3-} , including 1) interference by natural color, 2) interference by arsenate, 3) hydrolysis of organic compounds such as ATP and PO_4^{3-} esters, and 4) reaction with acid labile particulate inorganic P compounds such as FePO_4 . It is not evident how much the condensed PO_4^{3-} , or the other listed interferences contribute to the SRP pool, and if this proportion varies spatially and temporally.

There are 2 pieces of information that can provide insight into how PO_4^{3-} :SRP or PO_4^{3-} :TP may change in natural waters. Hudson et al. (2000) demonstrated that the relative proportion of PO_4^{3-} in TP decreases as TP increases. Dodds (1995) demonstrated that the biologically available PO_4^{3-} (the maximum amount of PO_4^{3-} as determined by a ^{32}P bioassay) to SRP ratio decreased as P deficiency increased. These 2 observations suggest that it cannot be assumed that SRP is proportional to PO_4^{3-} unless additional information on the biology or chemistry of the system is available.

It could be argued that SRP is ultimately biologically available, so measuring it is useful. However, most organic P and polyphosphates are also biologically available. The degree of availability is variable. Thus, the SRP assay reacts to a poorly defined subset of all P-containing compounds that are biologically available, and no experimental data are currently published (that I am aware of) to establish a relationship between biological availability of SRP and TP values. If such a relationship existed, it would probably not remain constant temporally or spatially in aquatic systems.

Given the continued use of SRP and DIN

measurements, I will consider what the standing amount of a dissolved inorganic nutrient pool can indicate in general. I also explore the use of SRP data in concert with DIN values to indicate nutrient deficiency. I obtained data from 2 sources to address these issues: 1) a large compilation of stream and river nutrient data taken from >600 sampling stations across the United States, to examine how nutrient values may vary in many different types of waters in samples analyzed by different laboratories, and 2) data taken from a single site, where collection, analysis, recovery efficiencies, and statistical techniques were the same for all samples.

Methods

The 1st set of nutrient data was taken from a compilation of the United States Geological Survey (USGS) National Stream Water-Quality Monitoring Networks (WQN) (Alexander et al. 1996). This data set provides a very general picture, but differences in sample collection methods, analytical techniques, recovery efficiencies on water with different chemistry levels, and statistical treatment of data make it difficult to apply results to any specific site. The data set was sorted to include all sampling dates where values above detection were available for NH_4^+ , NO_3^- , SRP, TN, and TP. DIN was calculated by summing NO_3^- and NH_4^+ . In most cases, NO_2^- values were small relative to NO_3^- . Samples were removed where reported SRP was >TP, or where DIN was >TN. These cases could have been a result of analytical error (contamination or incomplete digestion) or data entry error. Such cases were rare, representing <0.1% of the data set. The final data set had 7863 values from individual sampling episodes.

A 2nd data set was used to characterize within-site relationships among nutrient measurements (and acted as a control for any cross-laboratory or cross-site effects that may have been present in the USGS data). These data were taken from the water-quality record at Kings Creek, Konza Prairie Biological Station, Kansas. The geology, hydrology, ecology, and nutrient dynamics at the site have been described in detail (Gray et al. 1998, Gray and Dodds 1998, Dodds et al. 2000). Briefly, low nutrient levels characterize this prairie stream. It drains relatively pristine tallgrass prairie, and periphyton in the stream can be limited by N, P, or both,

depending on position in the landscape and season (Tate 1990). The watershed is moderately impacted by row crop agriculture in the lower reaches (Kemp and Dodds 2001).

Samples were collected at a variety of sites in Kings Creek including 4 small (~100 ha) prairie watersheds, 2 mid-reach sites, and 1 downstream site (see Kemp and Dodds 2001 for a map of stream sampling sites and details of watershed management). Nutrient samples were regularly collected from the middle of the channel in acid-washed bottles and returned to the laboratory where they were refrigerated or frozen until analysis. Inorganic samples were generally analyzed within a day. Samples not to be analyzed within 3 d, were frozen until analysis. Frozen inorganic nutrient samples were analyzed within 2 wk of sampling. All glassware was kept scrupulously clean (i.e., acid washed, no PO_4^{3-} detergents, care was taken to cover stored clean glassware) and standard solutions were run with every assay.

External standards and internal spikes used at the time of analysis assessed reliability and recovery efficiencies of the assays. NH_4^+ was analyzed by a spectrophotometric indo-phenol blue method, $\text{NO}_3^- + \text{NO}_2^-$ (hereafter referred to as NO_3^-) by Cd reduction followed by diazo dye formation. SRP concentrations were determined by the ammonium-phosphomolybdate method (APHA 1995). Assays were run on a Technicon Auto Analyzer II (Technicon Auto-analyzer 1973). TN and TP samples were digested by a perchlorate-autoclave method (Ameel et al. 1993) and analyzed for NO_3^- and SRP as described above. Efficiency of digestion was assessed using urea and ATP for N and P internal standards, respectively. Method detection limits (99% certainty values were >0) were 0.7 $\mu\text{g NO}_3^- - \text{N/L}$, 1.2 $\mu\text{g NH}_4^+ - \text{N/L}$, 2.0 $\mu\text{g SRP-P/L}$, 3.6 $\mu\text{g TN-N/L}$, and 10.1 $\mu\text{g TP-P/L}$. Detection limits for total nutrients were higher because of dilution by the digestion solution. Only samples collected in 1998 with detectable amounts for all nutrients were used in the analysis (a total of 373 complete sets of values).

Results

The ability of SRP to serve as a surrogate for TP was questionable in the broader USGS data set. The amount of SRP in TP was variable

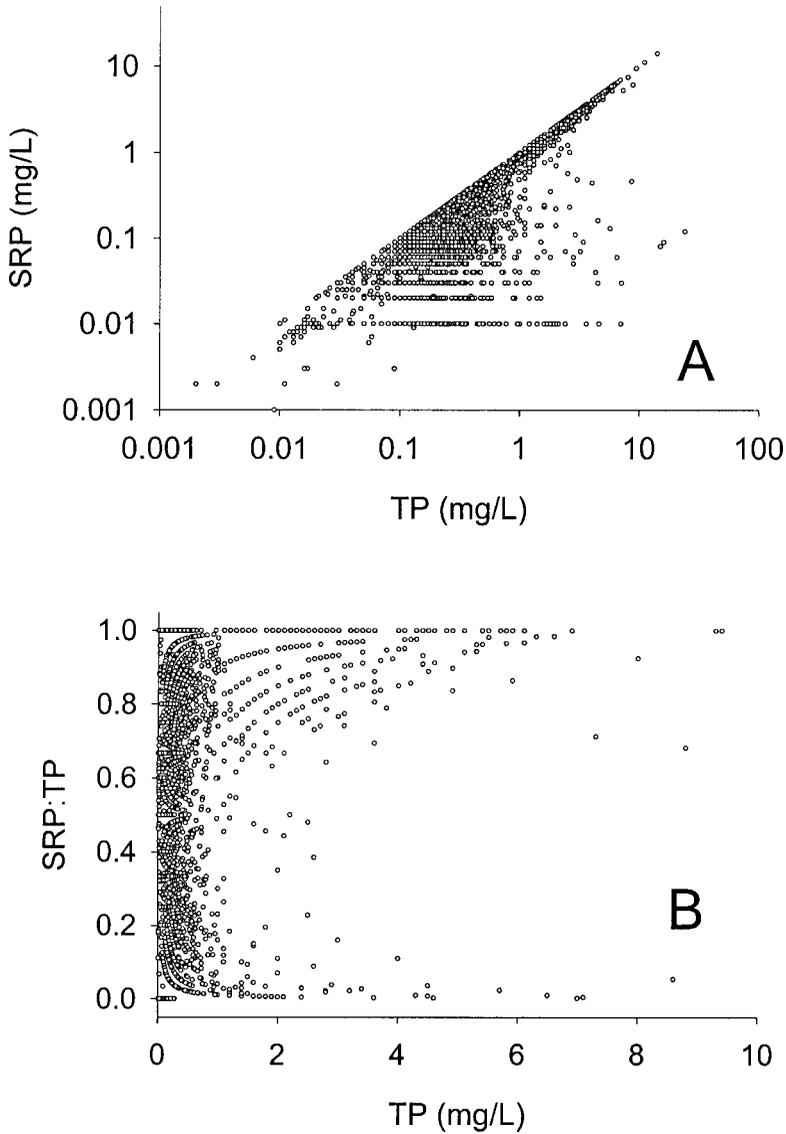


FIG. 1. Relationships between soluble reactive P (SRP) and total P (TP) (A), SRP:TP and TP (B), dissolved inorganic N (DIN) and total N (TN) (C), and DIN:TN and TN (D) from a large US Geological Survey river data set.

across many rivers that have been sampled in the United States (Fig. 1A). This effect was evident at values of TP < 2 mg/L but was most pronounced at values of TP < 0.1 mg/L, where SRP ranged from <1% to almost 100% of reported TP (Fig. 1A). A way to more effectively visualize how well SRP can be used to predict TP is to plot SRP:TP as a function of TP (Fig. 1B). Above 2 mg/L TP, SRP generally made up >80% of the TP, but in a few cases it made up

a very small portion of the TP. Below 0.5 mg/L TP, SRP could not be used to predict TP.

A similar picture emerged when considering the ability to use DIN as a surrogate for TN across a variety of systems. Above TN values of 5 mg/L, $\geq 60\%$ of the TN was usually made up of DIN (Fig. 1C). Below ~ 5 mg TN/L, DIN made up almost any proportion of TN (Fig. 1D).

Data from one year, within one watershed, analyzed by one laboratory with consistent

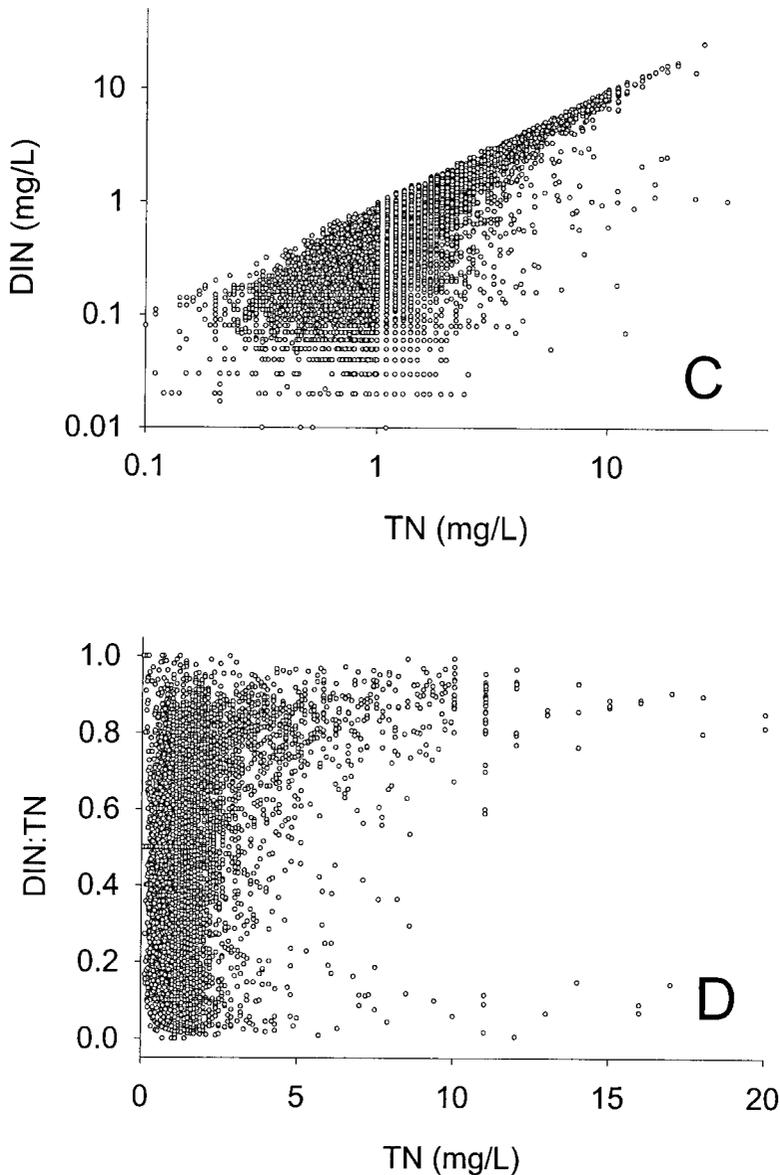


FIG. 1. Continued.

methods, were very similar to those of the larger data set. Values were low in the relatively pristine prairie stream watershed of Kings Creek relative to many in the USGS data set, and the absolute amount of SRP relative to TP and DIN relative to TN was extremely variable (Fig. 2A, C). Likewise the proportion of SRP:TP and DIN:TN to TP and TN, respectively, was highly variable at the low values of TP and TN that characterized this data set (Fig. 2B, D).

DIN:SRP appears to be a weak predictor of TN:TP. In the USGS set, DIN:SRP correlated closely to TN:TP at DIN:SRP < 1, but there was substantial scatter at intermediate levels (Fig. 3A). The relationship between TN:TP and DIN:SRP resulted in an $\sim 1:1$ relationship, but there was a substantial amount of variance in the relationship (i.e., the 95% prediction bands were almost \pm one order of magnitude). In the more restricted Kings Creek data set, there was a weak relationship between

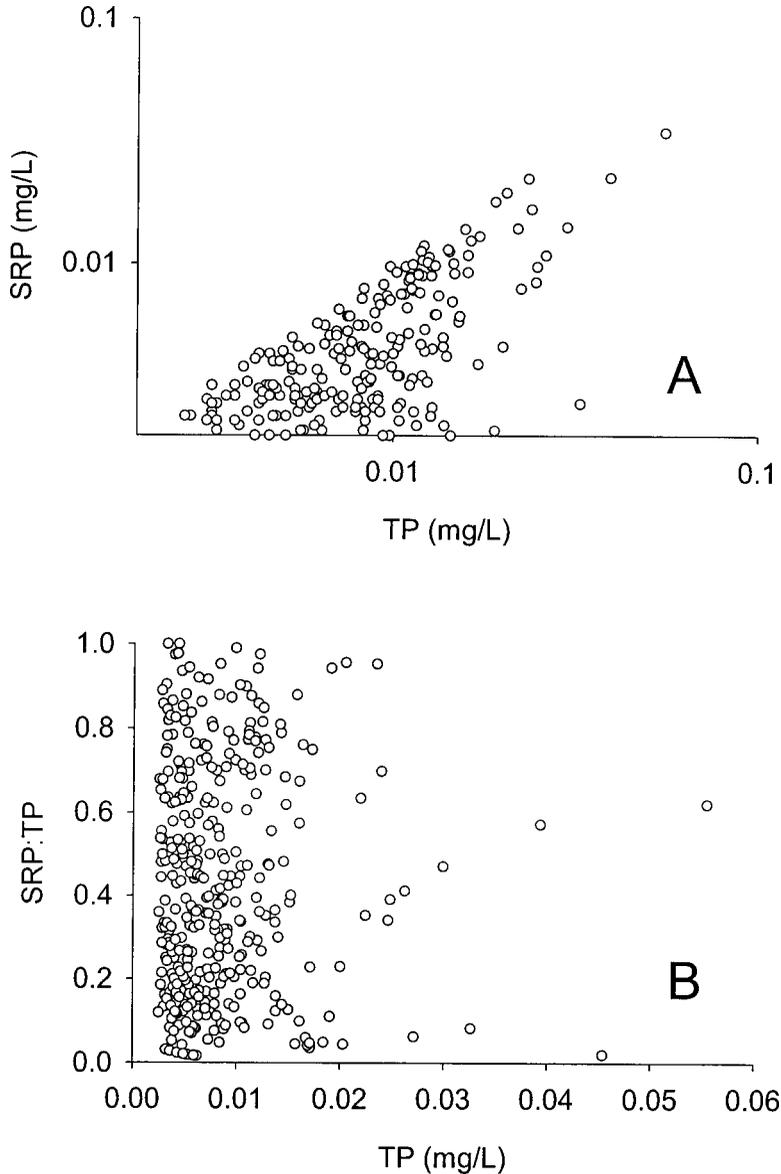


FIG. 2. Relationships between soluble reactive P (SRP) and total P (TP) (A), SRP:TP and TP (B), dissolved inorganic N (DIN) and total N (TN) (C), and DIN:TN and TN (D) from the Kings Creek watershed in 1998.

DIN:SRP and TN:TP, with very broad 95% prediction bands (Fig. 3B). Also, DIN:SRP values were generally $1/10^{\text{th}}$ of TN:TP values.

Discussion

Are SRP and DIN measurements useful for determining trophic state?

Trophic state or nutrient demand cannot be determined solely from inorganic nutrient con-

centrations when dissolved inorganic nutrient values are low. Concentrations cannot indicate supply because a large biomass of primary producers may have a very high nutrient demand and render inorganic nutrient concentrations low or below detection. Pattern (nutrient concentration) should not be confused with process (nutrient turnover rate, or supply), which may be particularly true in streams where inorganic nutrients can turnover very rapidly. For exam-

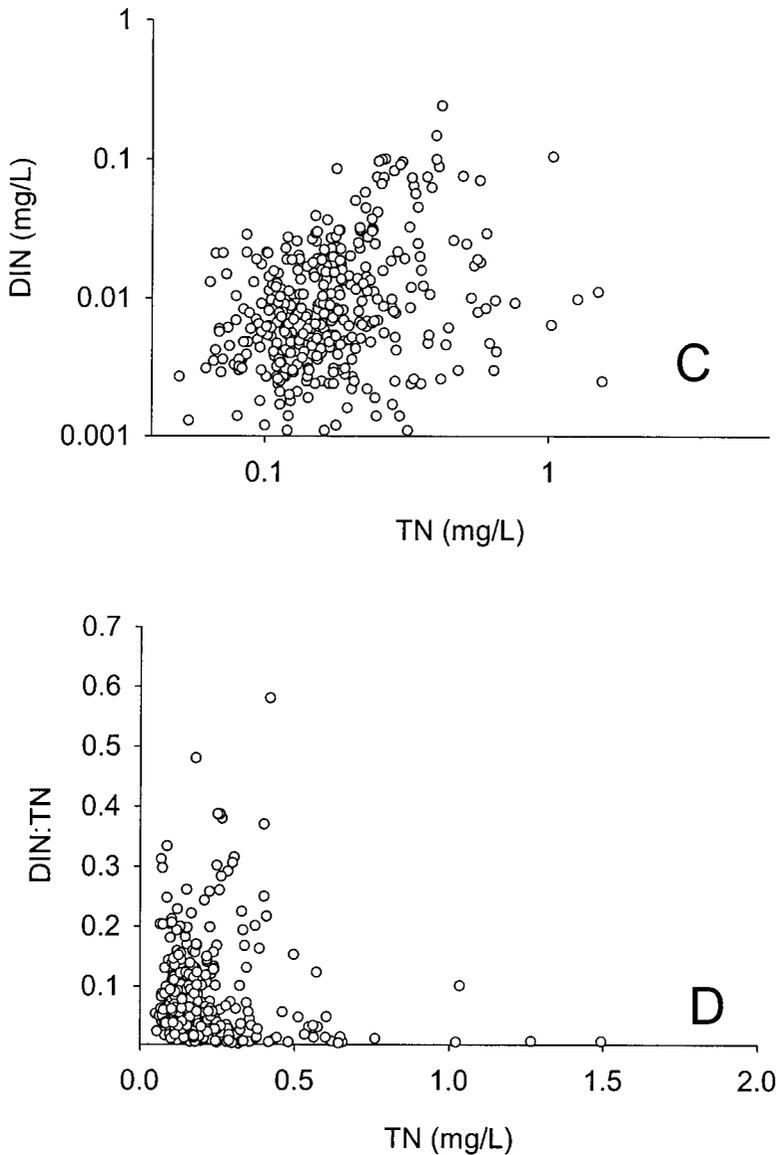


FIG. 2. Continued.

ple, stream NH_4^+ pools can be completely replaced by remineralization in as little as 6 min (Dodds et al. 2000).

As an example of how trophic state is not necessarily related to inorganic nutrients from planktonic systems, the SRP values in eutrophic Milford Reservoir (Dodds 1995) are only 4 times higher than those in oligotrophic Flathead Lake (Dodds et al. 1991). Flathead Lake planktonic chlorophyll levels are $\sim 1/30^{\text{th}}$ those in Milford

Reservoir (Dodds and Prisco 1990, Dodds 1995).

The ineffectiveness of using dissolved inorganic nutrient concentrations to make predictions about trophic state is supported by both lake and river data. Dissolved inorganic nutrients are not as strongly correlated with benthic algal biomass across a variety of streams as are TN or TP (Dodds et al. 1997). Likewise, classification of trophic state in lakes and eutrophi-

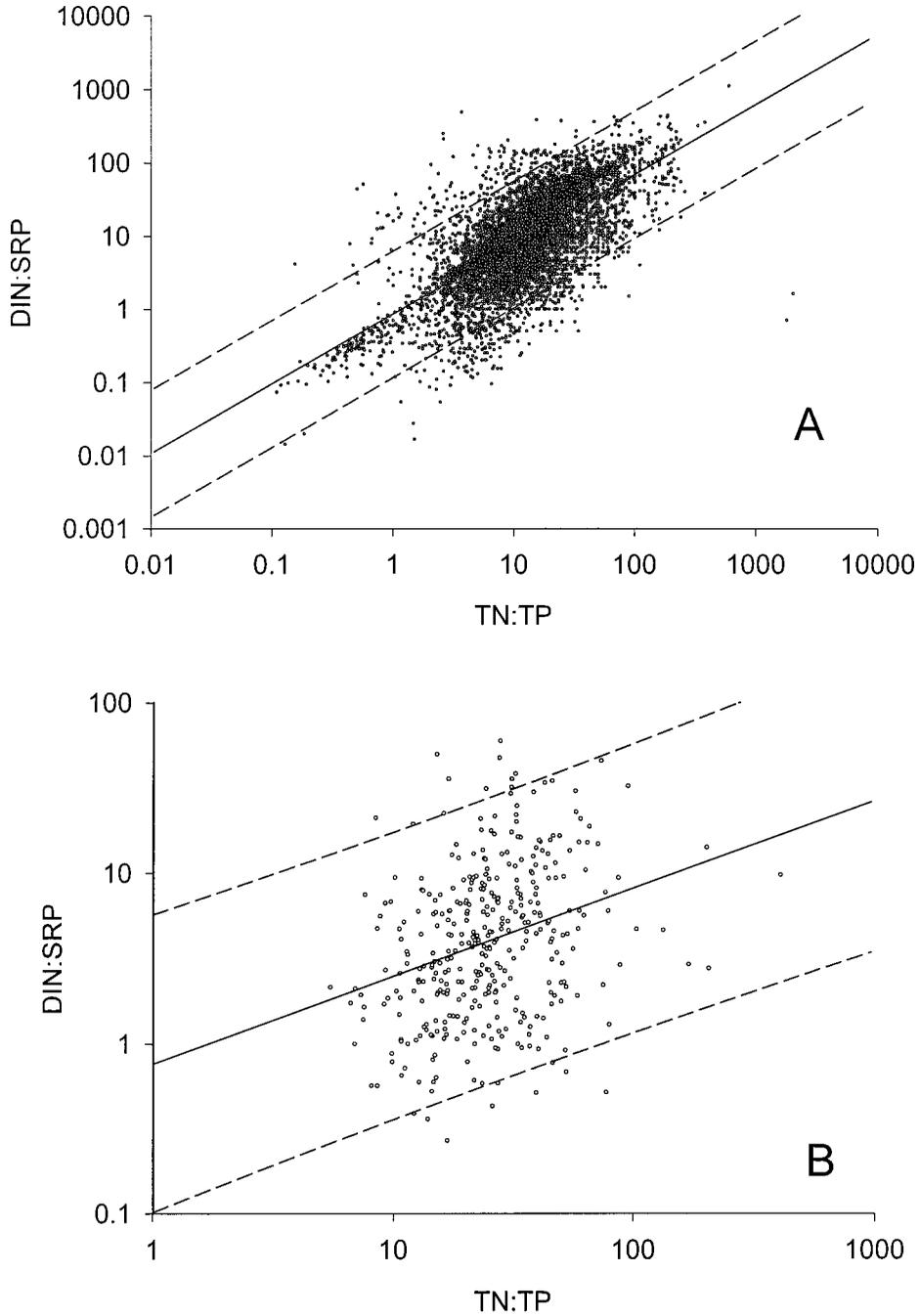


FIG. 3. Relationship of dissolved inorganic N (DIN):soluble reactive P (SRP) to total N (TN):total P (TP) for a large US Geological Survey river database (A) and the Kings Creek watershed (B). Dashed lines represent the 95% prediction bands. Both regression equations were significant ($p < 0.005$).

cation management generally focus on TN and TP in the water column, not DIN and SRP, because DIN and SRP are not able to predict algal biomass as accurately (e.g., Ryding and Rast 1989).

However, dissolved inorganic nutrients may be useful in trophic state determinations where values are high. If SRP values are very high (>0.1 mg/L), then they likely make up much of the TP and indicate a very P-enriched system (e.g., in sewage effluent). Likewise, if DIN values exceed 1 mg/L, then a system is very unlikely to be limited by N.

Do DIN assays have the same type of problems as SRP?

The problems with SRP measurement as an indicator of PO_4^{3-} concentrations are well known, but it is not certain if NO_3^- or NH_4^+ assays similarly overestimate the amounts of available DIN. Attempts to use $^{15}\text{N}-\text{NO}_3^-$ and NH_4^+ in uptake experiments under a variety of nutrient concentrations (e.g., Dodds et al. 1991) have not revealed an effect such as Rigler (1966) observed in his ^{32}P experiments (i.e., that SRP substantially overestimates PO_4^{3-} concentration). The greatest SRP overestimates of PO_4^{3-} occur under very low SRP conditions, when true $\text{PO}_4^{3-}-\text{P}$ values are ~ 0.1 $\mu\text{g}/\text{L}$. It is technically very demanding, and maybe not possible, to use ^{15}N as a true tracer under conditions where DIN concentrations are in the ng/L range. Very small amounts of stable isotope tracer, concentration methods, and very large-volume incubations would be required to make estimates of N incorporation at low ambient levels of DIN. Such assays would be very sensitive to contamination and isotopic discrimination problems. Radioactive N tracers (^{13}N) would allow uptake measurements to be made at very low DIN concentrations and may tell a different story for waters with colorimetric NH_4^+ or NO_3^- concentrations at or near analytical detection limits, but radioisotope experiments with N are very difficult (see Suttle et al. 1990) and are rarely done.

Does DIN:SRP correlate with TN:TP?

TN:TP has often been used to indicate relative nutrient deficiency based on the observation of Redfield (1958) that algal cells have a N:P by mass of 7:1 (16:1 by moles) under balanced

growth. Researchers since then have used TN:TP in water to indicate nutrient deficiency in phytoplankton (Smith 1982, Hecky and Kilham 1988). Growth-based bioassays confirm that TN:TP is a reliable indicator of the relative limitation of N and P in natural mixed-species assemblages (Dodds and Prisco 1990). However, TN and TP values are not always available. Thus, when DIN and SRP values are available, there is the temptation to argue that the ratio of these biologically available nutrient pools can be used to estimate nutrient deficiency.

There is a positive relationship between DIN:SRP and TN:TP across many systems (Fig. 3A), but the relationship is highly variable. For any value of DIN:SRP in the middle of the range (e.g., 10, by mass), TN:TP could vary from 1 to 100 (across a gradient from strong N to strong P deficiency). Smith (1982) cited evidence that N is limiting when TN:TP by mass is <10 , and by P when it is >17 . It is worth noting that the 95% prediction bands for the relationships between DIN:SRP and TN:TP exceed this range (7) in both the USGS and the Konza data sets. It is further worth noting that, although regression analysis of the USGS data set resulted in close to a 1:1 relationship between DIN:SRP and TN:TP, the Konza data had DIN:SRP values that were $\sim 1/10^{\text{th}}$ of the TN:TP. These data suggest that for Konza Prairie streams DIN:SRP values must be ≤ 1 to indicate N deficiency and ≥ 200 to indicate P deficiency.

Can DIN:SRP be used to assess nutrient limitation?

I have already discussed the problems with SRP measurement, and these problems are also important in assessing the relative value of DIN:SRP determination; if it is not known exactly what SRP assays measure, an equal uncertainty surrounds DIN:SRP. Additional problems may arise because it cannot be assumed that the level of DIN or SRP is necessarily indicative of supply. For example, measurements of uptake kinetic parameters for plankton in Flathead Lake indicate half-saturation constants of 0.5–3 μg $\text{PO}_4^{3-}-\text{P}$ /L, 14–140 μg $\text{NO}_3^- -\text{N}$ /L, and 14–600 μg $\text{NH}_4^+ -\text{N}$ /L across seasons. Maximum uptake rates of NO_3^- and PO_4^{3-} were roughly equivalent, and both were ~ 10 times less than for NH_4^+ , which means, in this lake at low nutrient concentrations, affinity for PO_4^{3-} is always

much greater at a given concentration than that for NO_3^- or NH_4^+ . Thus, even if PO_4^{3-} concentrations are 1/10th those of NH_4^+ or NO_3^- , the actual rate of uptake of PO_4^{3-} may equal or exceed that of DIN.

DIN:SRP must be coupled with knowledge of absolute amounts to be at all useful. If DIN:SRP is extremely high (e.g., 100:1), then N deficiency is unlikely because it is probable that DIN is not in short supply. Likewise, if DIN:SRP $\ll 1$, then it is unlikely that P is limiting. It is at intermediate DIN:SRP that there is a problem because DIN and SRP could both be very high, with no nutrient limitation whatsoever, or DIN:SRP could still indicate limitation by one of the nutrients. For example, if there are 1 mg/L DIN and 2 mg/L SRP, a DIN:SRP = 0.5 would suggest N deficiency even though neither nutrient is likely to be limiting at such high levels. Alternatively, DIN and SRP could be 0.1 and 0.2 $\mu\text{g/L}$, the DIN:SRP also equals 0.5, but both nutrients could be strongly limiting.

Given all these problems, it is not surprising that a number of investigators have been unable to link nutrient deficiency bioassays to DIN:SRP. For example, DIN:SRP did not predict limiting nutrients in 6 streams flowing into the north shore of Lake Superior where seasonal growth-based bioassays on periphyton were performed (Wold and Hershey 1999). Francoeur et al. (1999) used growth-based bioassays to estimate nutrient limitation in 12 New Zealand streams and found nutrient limitation was not predicted by DIN:SRP. No correlation occurred between DIN:SRP and nutrient limitation of both fungi and algae in growth bioassays conducted at 10 streams across North America (Tank and Dodds 2003). Although it is possible that DIN:SRP could predict N or P limitation in some cases, it is unwise to assume that it will in all cases.

Final Comments

It is easier to measure DIN and SRP than to measure TN and TP because the latter 2 measurements require a digestion step. Investigators continue to routinely measure SRP because it is easy, not because of the quality of information such measurements provide. For example, I administer the monitoring project on Kings Creek described in this paper, and we continue to measure SRP, in part because reviewers ask for this information when assessing submitted pa-

pers, and in part because it is easy. The main value of SRP measurement came early in my involvement in this monitoring program: SRP values frequently exceeded TP values, indicating problems with the TP digestion method.

The data considered in this paper suggest that SRP measurements are not useful in most waters that are not heavily polluted with nutrients. There are probably some examples of using such values in a predictive fashion, but these examples are likely to be rare, given the data presented here. Measurement of NH_4^+ and NO_3^- may be defensible in many cases because the assays apparently really measure NH_4^+ and NO_3^- , these inorganic nutrients can be toxic at high concentrations, and their concentrations may be indicative of relative rates of N-cycling processes such as nitrification and remineralization. However, DIN:SRP probably does not reliably provide an ecologically sound and general measure of nutrient limitation. The best values to use for indication of trophic state and nutrient limitation are TN and TP.

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