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To: Mindy McCarthy, QA/QC Officer

CC: Eric Urban, Water Quality Standards Section Supervisor

From: Michael Suplee, Ph.D., Water Quality Standards Section

Date: 11/14/2013

RE: TECHNICAL MEMORANDUM: Benchmark for nitrate + nitrite in assessing ambient surface water

The Department is currently preparing the rule package for numeric nutrient standards that it will present to the Board of Environmental Review (BER). The Department is not planning to propose adoption of soluble nutrient standards to the BER, it is only going to propose total nutrients. This is because total nitrogen and phosphorus have been shown to provide better overall correlation to eutrophication response than soluble nutrients. Soluble nutrients are rapidly taken up by aquatic organisms (mainly algae, vascular plants, and bacteria), which makes these compounds' concentrations highly variable and therefore difficult to use as ambient surface water criteria.

Nevertheless, the presence of elevated soluble nutrients —if detected during routine surface water assessment—is useful information. Soluble nitrate + nitrite is routinely measured by the Monitoring and Assessment Section; the purpose of this memo is to provide DEQ staff with an assessment benchmark for this soluble measurement. This memo does not address soluble reactive phosphate (SRP), however. SRP concentrations are not routinely measured by the Monitoring and Assessment Section.

A Mechaelis-Menten (i.e., Monod) relationship between soluble nutrient concentrations and uptake rate by stream biota has proven to be a reasonable description of soluble nutrient behavior in streams. For example, O'Brian and Dodds (2008) find that a Michaelis-Menten curve adequately describes N uptake by a stream, and they measured a half-saturation constant (Ks) for the entire study stream of 27 µg N/L. Ks is the

concentration at which the soluble N uptake rate in the stream is half of the maximum (Vmax). In effect, it is a nutrient concentration at which stream primary productivity is still controlled by nutrient concentrations. At approximately five times Ks, nutrients are saturating and further increases in nutrients will not further increase Vmax (Chapra, 1997). A compilation of large number of laboratory and field-derived Ks values for algae (both phytoplankton and benthic algae) provide a median Ks of 67 µg N/L (USEPA, 1985). Multiplying these Ks values by five provides an estimate of soluble N saturation ranging from 135 to 335 µg N/L. However it should be pointed out that some of the above studies use ammonium as the N source, not nitrate. But Rier and Stevenson (2006) specifically studied algal uptake of nitrate, and found a Monod relationship best explained the relationship and reported that growth rates were not N limited above 86 µg N-NO<sub>3</sub>/L and that peak algal biomass was saturated at 308 µg N-NO<sub>3</sub>/L. In the whole-stream nutrient dosing study carried out by the Department (DEQ, 2010), the High-dose Reach (reach which was dosed with enough soluble nutrients that we expected there to be impacts to beneficial uses) received a season-long dose of 119 µg N/L (as nitrate) and we observed increases in algae growth to near-nuisance levels and impacts to dissolved oxygen concentrations which exceeded state standards.

These data indicate that 100  $\mu$ g N-NO<sub>2+3</sub>/L (0.1 mg N-NO<sub>2+3</sub>/L) is a valuable benchmark for assessment purposes and I recommend it be used in routine assessment of ambient surface water-quality data. If concentrations equal to or greater than this concentration are measured during routine stream assessment it can be assumed that the stream is largely saturated for nitrate and detrimental eutrophication impacts may ensue. Similar to total nitrogen and phosphorus, nitrate + nitrite concentrations should be assessed using the binomial test and t-test in the assessment methodology (Suplee and Sada de Suplee, 2011) and using the same parameterization of those statistical tools.

It should be pointed out that the DEQ-7 standards for nitrite (1 mg/L) and nitrate (10 mg/L) are for the protection of human health (i.e., toxicity-based), whereas the 0.1 mg N-NO<sub>2+3</sub>/L benchmark discussed here is for protection of eutrophication impacts and is more akin to the total nutrient standards that will be housed in DEQ-12.

## REFERENCES

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- DEQ (Department of Environmental Quality), 2010. Box Elder Creek Nutrient Addition Study: A Project to Provide Key Information for the Development of Nutrient Criteria in Montana Prairie Streams. Quality Assurance Project Plan.
- O'Brian, J.M, and W.K. Dodds, 2008. Ammonium Uptake and Mineralization in Prairie Streams: Chamber Incubations and Short-term Nutrient Addition Experiments. Freshwater Biology 53: 102-112.
- Rier, S.T., and R. J. Stevenson, 2006. Response of Periphytic Algae to Gradients in Nitrogen and Phosphorus in Streamside Mesocosms. Hydrobiologia 561: 131-147.
- Suplee, M.W., and R. Sada de Suplee, 2011. Assessment Methodology for Determining Wadeable Stream Impairment Due to Excess Nitrogen and Phosphorus Levels. Helena, MT: Montana Dept. of Environmental Quality.
- USEPA (United States Environmental Protection Agency), 1985. Rates, Constants, and Kinetics Formulations in Surface Water Quality Modeling, 2<sup>nd</sup> Edition. Environmental Research Laboratory, document No. EPA/600/3-85/040. June 1985.