# Draft - Derivation of Site-specific Numeric Nutrient Criteria for Selected Streams in the Upper Clark Fork Basin

## Addendum A to "*Scientific and Technical Basis of the Numeric Nutrient Criteria for Montana's Wadeable Streams and Rivers: Update 1*"

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# ACRONYMS

| Acronym | Definition |
|---|---|
| DEQ | Department of Environmental Quality (Montana) |
| HUC | Hydrologic Unit Code |
| MBMG | Montana Bureau of Mines and Geology |
| PL | Prediction Limit |
| SRP | Soluble Reactive Phosphate |
| TMDL | Total Maximum Daily Load |
| TN | Total Nitrogen |
| TP | Total Phosphorus |
| TPA | TMDL Planning Area |

# 1.0 INTRODUCTION

On the 2012 303(d) List there are ten tributaries[1] to the Clark Fork River located within the Upper Clark Fork Total Maximum Daily Loads (TMDL) Planning Area (TPA) and the Central Clark Fork Tributaries TPA which are listed for nutrient impairments, and while nutrient sources are frequently documented in the lower portions of these basins, elevated phosphorus concentrations have been observed in headwater areas of some impaired streams with no identifiable anthropogenic sources. This suggests that natural background of total phosphorus (TP) in these basins is higher than for other regional streams where the Middle Rockies level-III ecoregion TP criterion (30 µg TP/L) is recommended.

Suplee and Watson (2013) use three major lines of information to derive regional nutrient criteria; regional dose-response studies (nutrient concentrations as dose, effect on stream beneficial uses as response), regional reference sites, and nutrient ratios (Redfield, 1958). Of these three factors, dose response studies are the most important and in the Middle Rockies level III ecoregion dose response studies suggest TP should be 20-40 µg/L (30 µg TP/L was recommended as the criterion). However cases arise where the natural background TP may be higher than 30 µg TP/L and in such cases site-specific criteria are warranted.

This addendum outlines our considerations and the methods used to investigate and then develop site-specific numeric nutrient criteria for select tributaries to the upper Clark Fork River, where phosphorus concentrations may be naturally elevated when compared to the Middle Rockies TP criterion of 30 µg/L.

# 2.0 VOLCANIC GEOLOGY AND PHOSPHORUS IN STREAMS

Apatite is the most common phosphate mineral and is found most notably in granite pegamatites (Sorrell, 1973). Apatite is principally calcium orthophosphate and may also contain fluoride, hydroxide or chloride ions and is widespread in igneous rock (volcanics) and marine sediments (Hem, 1985). Using ecoregion boundaries, it was found that reference streams in the Absaroka-Gallatin Volcanic Mountains Level IV ecoregion contain natural phosphorus at concentrations significantly greater than other areas of the Level III Middle Rockies ecoregion (Varghese and Cleland, 2008); this is most likely due to the high proportion of volcanic geology there. Volcanics are a large source of P (Dillon and Kirchner, 1975), and pyroclastics (erupted volcanic material) are usually unconsolidated materials containing large quantities of volcanic glass which shows the least resistance to chemical weathering (Shoji et al., 1993). Pyroclastics are common in the Absaroka-Gallatin Volcanic Mountains ecoregion (Woods et al., 2002).

To investigate the potential influence of volcanics on background phosphorus concentrations in the Middle Rockies level-III ecoregion, all surficial volcanic geology was mapped (**Figure 2-1**). The Upper Clark Fork TMDL planning area (TPA) and the Level IV Absaroka-Gallatin Volcanic Mountains are also displayed to provide context. Surficial geology layers were downloaded from the Montana Bureau of Mines and Geology (MBMG) website (http://www.mbmg.mtech.edu/gis/gis-products.asp) and were a

[1] The streams are Silver Bow Creek, Hoover Creek, Willow Creek, Peterson Creek, Gold Creek, Dunkleberg Creek, Dempsey Creek, Lost Creek, Tenmile Creek, and Rattler Gulch. The last two are located within the Central Clark Fork Tributaries TPA and the rest are within the Upper Clark Fork TPA.

combination of MBMG and United States Geological Survey (USGS) digital products. For the purposes of this investigation, volcanic geology was defined to include all layers that contained:

- Andesite
- Basalt
- Dacite
- Rhyolite
- Trachyandesite
- Trachyte
- Tuff
- Volcanic rock

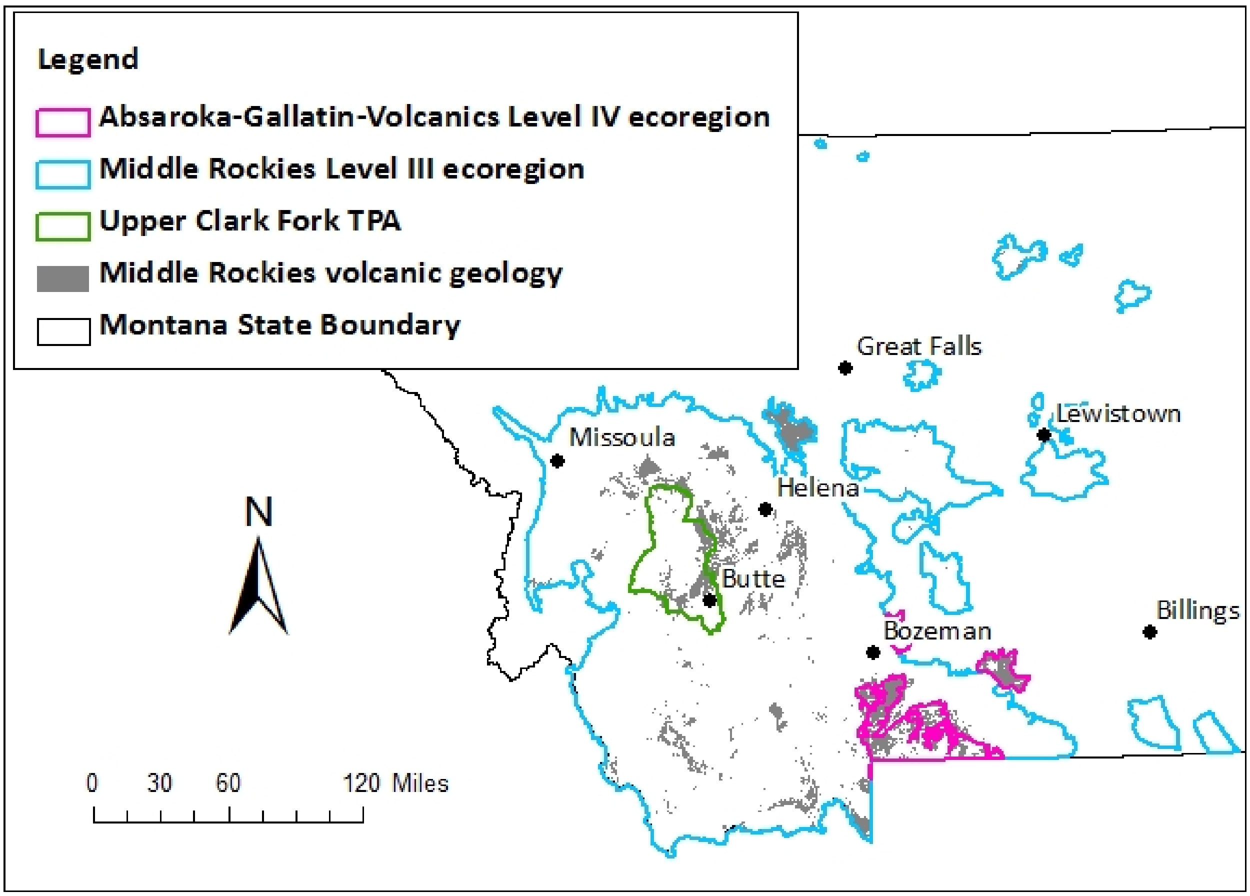


**Figure 2-1. Volcanic Geology within the Level III Middle Rockies Ecoregion in Montana.**

Within the Middle Rockies Level III ecoregion in Montana, there are several areas of volcanic intrusions most notably in the area between Helena and Butte, MT and in the area south of Bozeman, MT in the Gallatin National Forest and the lands bordering Yellowstone National Park. There are also numerous outcroppings throughout southwestern Montana. In **Figure 2-1**, it is apparent that volcanic geology is not exclusive to the Level IV ecoregion Absaroka-Gallatin Volcanic Mountains where phosphorus concentrations have been documented to be significantly higher than for other areas in the Middle Rockies.

## 2.1 Department of Environmental Quality (DEQ) Reference Stream Sites Influenced by Volcanic Geology

In many areas of the state, the Department's stream reference sites (n = 185) are sufficiently numerous to be able to characterize locally-elevated nutrient concentrations, for example the high phosphorus concentrations in the Absaroka-Gallatin Volcanic Mountains Level IV ecoregion. However, in the Upper Clark Fork basin extensive mining in and around the Boulder batholith resulted in widespread environmental degradation throughout much of the watershed making the identification and monitoring of water quality reference sites difficult. As a result there is an almost complete lack of reference sites in the north-central portion of the Middle Rockies ecoregion in Montana around Helena and Butte where there is also a large concentration of surficial volcanic geology (**Figure 2-2**). Prior to 2013, there was only one reference site with water quality data available in the upper Clark Fork basin. The site is located on Twin Lakes Creek, a small tributary in the headwaters of Warm Springs Creek west of Anaconda, and there was no volcanic geology influence in its watershed. However, a reference site on Baggs Creek (8.5 air miles east of Deer Lodge) was established by the Department's Reference Stream Project in the summer 2013 and sampled the same season. A complete assessment indicated that Baggs Creek rates as tier 1, i.e. natural condition (Suplee et al., 2005) and, most importantly, the site is highly influenced by local volcanic geology (at least 29% of the watershed area). In **Figure 2-2**, Baggs Creek is shown as the green dot directly north of Butte.

All DEQ reference sites in the Middle Rockies ecoregion were reviewed to determine if surficial volcanic geology was contributing to their respective watersheds. In **Figure 2-2**, a subset of the Middle Rockies reference sites was selected based on site proximity to volcanic geology which included these filters:

- Site is downstream of volcanic geology.
- Site is not in a position in the basin where contributions from portions of the basin not underlain by volcanics may have a dilution effect and potentially reduce the volcanics signature.

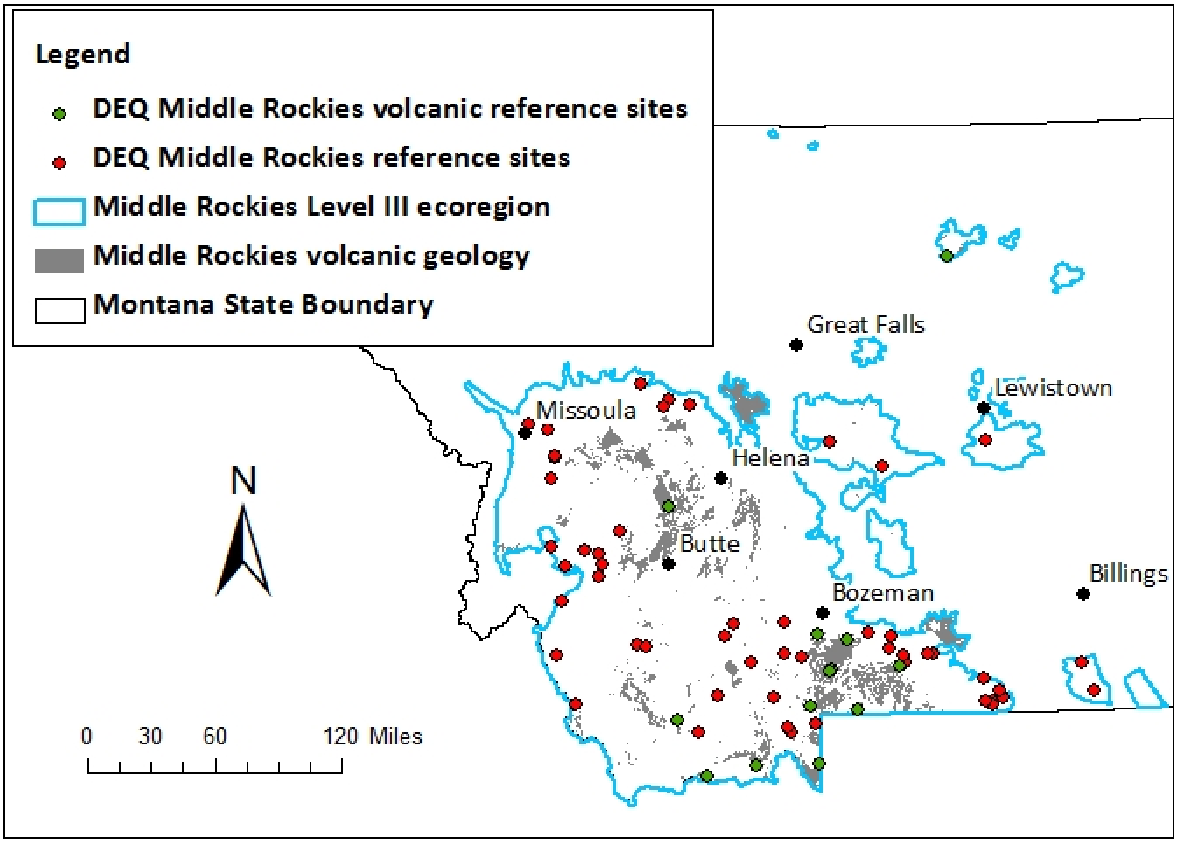


**Figure 2-2. Department of Environmental Quality reference sites as of 2013 in the Middle Rockies Level III ecoregion. Those shown in green are influenced by volcanic geology.**

A total of 13 reference stream sites were selected in the Middle Rockies Level III ecoregion based on contributing area underlain by volcanics (**Figure 2-2**). Four sites are within the Level IV ecoregion Absaroka-Gallatin Volcanic Mountains and 1 is located in the Bears Paw Mountains in north-central Montana.

## 2.2 Empirical Site-specific Modeling of Total Phosphorus Based on the Scientific Literature

In addition to considering reference data from Middle Rockies streams influenced by volcanic geology, we also took advantage of a site-specific modeling approach that was recently published in the scientific literature (Olson and Hawkins, 2013). Olson and Hawkins (2013) use the nonparametric Random Forest model to predict how baseflow concentrations of Total Phosphorus (TP) and Total Nitrogen (TN) varied among western U.S. streams in response to continuous variation in nutrient sources, sinks and other processes affecting nutrient concentrations. Background TN and TP concentrations were modeled based on 27 physical, chemical and geologic attributes and used an extensive dataset of grab samples collected across the western United States. The 95$^{th}$ percentile of the empirical distribution from the model output was chosen as the upper prediction limit.

The authors acknowledged several shortcomings in the models. The models were not very precise (TP model, $r^2$= 0.46; TN model, $r^2$= 0.23) and tended to over-predict TP and under-predict TN at higher concentrations. Although the $r^2$ values were low results of a signal-to-noise analysis indicated that the model explained most of the spatial variation in nutrient concentrations. The model is also unable to account for streams with geothermal inputs. The Upper Clark Fork basin includes several tributaries with known hot springs (Warm Springs Creek near Phosphate, Warm Springs Creek near Anaconda, Gregson Creek [Fairmont Hot Springs]). However, during model development Olson and Hawkins did find that volcanic rocks were a more important predictor of stream TP than % rock P. Further model analysis found that most of the explanatory power of volcanic rocks is related to their P content and a minor amount is related to their relatively younger age and faster weathering rates compared with other rock types found in the western U.S. (Olson and Hawkins, 2013).

Based on the importance of volcanic geology in the model prediction, which was consistent with the Department's own findings in the Absaroka-Gallatin Volcanic Mountains ecoregion, the authors were contacted and they ran the model simulation for a number of 12 digit Hydrologic Unit Codes (HUCs) in the Middle Rockies level-III ecoregion in order to determine predicted TP background concentrations (**Table 2-1**). They used the volcanic geology extent layer for the Middle Rockies Level III ecoregion in Montana that was created by the Department for this effort.

**Table 2-1. Site-specific TP criteria recommendations based on the model of Olson and Hawkins (2013).**

| 12-digit HUC | Watershed name | TP prediction (µg/L) | % volcanic geology | Upper Clark Fork watershed (Y/N) |
|---|---|---|---|---|
| 170102010806 | Gold Creek | 40.5 | 0.0% | Y |
| 170102010205 | Silver Bow Creek-McCleery Gulch | 48.3 | 30.3% | Y |
| 170102010401 | Warm Springs (nr Anaconda) | 46.9 | 0.3% | Y |
| 170102010207 | Willow Creek | 57.4 | 42.8% | Y |
| 170102010403 | Lower Lost Creek | 60.9 | 23.1% | Y |
| 170102010810 | Clark Fork River-Dunkleberg Creek | 41.6 | 3.1% | Y |
| 170102010704 | Peterson Creek | 56.2 | 38.8% | Y |
| 170102010402 | Upper Lost Creek | 28.7 | 29.3% | Y |
| 170102010209 | Silver Bow Creek-White Pine Creek | 59.9 | 28.5% | Y |
| 170102010204 | Silver Bow Creek-Butte | 61.3 | 4.1% | Y |
| 170102010808 | Hoover Creek | 43.5 | 26.0% | Y |
| 170102010701 | Dempsey Creek | 31.0 | 0.0% | Y |
| 100700020202 | Upper Big Creek | 50.9 | 79.4% | N |
| 100200041302 | Lower Willow Creek | 43.3 | 0.0% | N |
| 100700020203 | Lower Big Rock Creek | 41.2 | 77.5% | N |
| 170102010706 | Cottonwood Creek | 51.6 | 29.2% | Y |
| 100200041301 | Upper Willow Creek | 29.7 | 0.0% | N |

For those basins with <5% volcanic geology the model predicted background TP concentrations from 29.7 µg/L to 61.3 µg/L with a mean of 42.0 µg/L and a standard deviation of 9.8 µg/L. For those basins with >20% volcanic geology (23%-79%) the model predicted background TP concentrations from 28.7 µg/L to 60.9 µg/L with a mean of 49.9 µg/L and a standard deviation of 9.4 µg/L. There is no significant difference ($\alpha$=0.05) between the TP predictions for those basins with <5% volcanic geology and those with greater percentages of volcanic geology. For the purposes of site-specific nutrient target development in the Upper Clark Fork River, the findings of the Olson and Hawkins model (2013) are a valuable independent data source although the model runs did not yield the anticipated differences between basins with known volcanic geologies and those with none or minimal mapped volcanic formations. However, it must be born in mind that volcanic geology is only one of 27 predictor variables in the model affecting the outcome.

# 3.0 Analysis of the Effect of Volcanic Geology on Middle Rockies Reference-stream Phosphorus Levels and Development of Site-specific Nutrient Criteria

**Section 2.0** provided the background information on the importance of volcanic geology in stream phosphorus levels and included a recent approach in the scientific literature for deriving site-specific nutrient criteria. In keeping with the multiple-lines-of-evidence methods utilized by Suplee and Watson (2013) to develop numeric nutrient criteria, we considered the available information and posed the following questions:

1. *Do Middle Rockies reference streams influenced by volcanic geology have phosphorus concentrations higher than Middle Rockies reference streams as a whole?*
2. *If descriptive statistics for Middle Rockies reference streams influenced by volcanic geology are generated, should the Absaroka-Gallatin Volcanic Mountains data be included or excluded?*

Question 1 was intended to see if there is empirical support for the idea that within the Middle Rockies ecoregion there are volcanically-influenced reference streams which have naturally higher phosphorus levels. Question 2 addresses a concern we had based on the observation that TP and soluble reactive phosphate (SRP) concentrations in Absaroka–Gallatin Volcanic Mountains reference streams appeared to be very high compared to other volcanically-influenced reference streams in the Middle Rockies.

## 3.1 Phosphorus Levels in Reference Streams of the Middle Rockies

**Table 3-1** provides descriptive statistics for all Middle Rockies reference streams from the all-observations dataset (Suplee and Watson, 2013) and also shows descriptive statistics for Middle Rockies reference streams influenced by volcanic geology. Middle Rockies reference stream sites influenced by volcanic geology have naturally higher TP concentrations which are significantly greater than the Middle Rockies reference streams as a whole (Mann-Whitney test[2], $p < 0.001$). Middle Rockies reference streams influenced by volcanic geology but outside of the Absaroka-Gallatin Volcanic Mountains also have significantly higher TP (Mann-Whitney test, $p < 0.001$) compared to reference streams from the Middle Rockies as a whole. These data demonstrate that volcanic geology is a reasonable sub-stratification tool within the Middle Rockies that helps explains the higher TP concentrations observed in reference streams under volcanic-geology influence.

[2] This statistical test is a non-parametric test analogous to the t-test and determines if the median of two populations is different. For datasets such as these, for which the probability distributions are rarely normal and are frequently heavily skewed to the right, non-parametric tests have better power than parametric tests (Conover, 1999).

**Table 3-1. Descriptive Statistics for TP Concentrations in Reference Streams of the Middle Rockies Level III Ecoregion.**

| Dataset | Nutrient | Number of Reference Sites | Number of Samples | Min (µg/L) | Max (µg/L) | Average (µg/L) | Median (µg/L) |
|---|---|---|---|---|---|---|---|
| Middle Rockies (all-observations dataset) from Suplee and Watson (2013) | TP | 61 | 245 | 0.5 | 840 | 26 | 10 |
| All Middle Rockies reference sites influence by volcanic geology | TP | 13 | 52 | 5 | 240 | 51 | 32 |
| Middle Rockies reference sites influence by volcanic geology, not including the Absaroka-Gallatin Volcanic Mountains | TP | 9 | 36 | 5 | 240 | 38 | 30 |

As mentioned earlier, we noted that the reference streams of the Absaroka-Gallatin Volcanic Mountains had particularly high TP (and SRP) concentrations and their removal (n=4 sites) from the volcanic-influenced Middle Rockies dataset substantially lowered the average concentration of the volcanic-influenced streams (see 2nd and 3rd rows, **Table 3-1**). This led us to believe that not all volcanic geology may be the same, and that some volcanic rocks may weather faster than others. For example Olson and Hawkins (2013) observe that streams draining the relatively young volcanic rocks of the Gila Mountains (New Mexico) had very high TP concentrations which they attribute to the fast chemical weathering rates of that particular formation. In Montana, descriptions of the Absaroka-Gallatin Volcanic Mountains ecoregion note that the ecoregion is under laid by Tertiary pyroclastic material and that these air-fall volcanics readily weather to clay (Woods et al., 2002).

We carried out an empirical test to see if the Absaroka-Gallatin Volcanic Mountains ecoregion potentially has higher phosphorus weathering rates than other volcanically-influenced areas. We calculated the SRP:TP ratio of stream water samples for two populations: (1) reference streams of the Absaroka-Gallatin Volcanic Mountains ecoregion and (2) all other Middle Rockies reference streams influenced by volcanic geology. Chemical weathering is the only means by which rock-bound P becomes available for uptake by stream flora and other microorganisms (Smeck, 1973; Froelich, 1988) and therefore if the Absaroka-Gallatin Volcanic Mountains ecoregion has a naturally higher phosphorus weathering rate we would expect to see —all things being equal[3]—higher SRP:TP ratios there.

The analysis showed that reference streams in the Absaroka-Gallatin Volcanic Mountains ecoregion had significantly higher SRP:TP ratios (Mann-Whitney test, $p = 0.0016$) than other volcanically-influenced Middle Rockies reference streams. The Absaroka-Gallatin Volcanic Mountains had a median SRP:TP ratio of 0.89 (for the other volcanics it was 0.46); this means that nearly 90% of the total phosphorus measured in streams of the Absaroka-Gallatin Volcanic Mountains is actually soluble, available P. These results, in conjunction with the high weathering rates described by Woods et al. (2002) led us to

[3] We restrained our analysis to streams in the Middle Rockies ecoregion, where we generally expect stream water temperatures and light levels to be approximately equivalent regionally for growth of aquatic flora. Therefore, there is no reason to expect that Middle Rockies streams outside of the Absaroka-Gallatin Volcanic Mountains ecoregion would have stream flora that could take up SRP to a greater extent than flora in the Absaroka-Gallatin Volcanic Mountains ecoregion.

conclude that phosphorus data from the Absaroka-Gallatin Volcanic Mountains ecoregion should not be included in our compilation of volcanic-influenced Middle Rockies reference data, because the higher weathering rates there have led to particularly high P concentrations which would not necessarily be representative of what we would expect to see in the upper Clark Fork Basin volcanic areas.

## 3.2 Derivation of Site-specific Nutrient Criteria for Volcanic-influenced Streams in the Upper Clark Fork Basin

In keeping with the multiple-lines-of-information approach used by Suplee and Watson (2013) to develop numeric nutrient criteria, we restate here the information which is available and which pertains to Middle Rockies streams in the upper Clark Fork River basin influenced by volcanic geology:

1. There is a single reference site (Baggs Creek) located in the area which has at least 29% of its watershed comprised of volcanic geology. The single available TP sample from the stream during summer baseflow was 12 µg/L, while SRP was non-detect;
2. we have compiled nutrient data from Middle Rockies reference streams sites influenced by volcanic geology (Baggs Creek included), but excluding the data from the Absaroka-Gallatin Volcanic Mountains level IV ecoregion; and
3. there are site-specific TP criteria developed for a number of streams in the upper Clark Fork basin using the model developed by Olson and Hawkins (2013).

Each of these pieces of information was given careful consideration in developing the following criteria recommendations.

When the natural background concentration of a nutrient exceeds a regionally-applicable criterion (e.g., 30 µg TP/L in the Middle Rockies), the 75$^{th}$ percentile of the natural background concentration has been used as a starting point for the new criterion (see Section 4.0; Suplee and Watson, 2013).The 75$^{th}$ percentile of the volcanic-influence reference sites excluding the Absaroka-Gallatin Volcanic Mountains is 34 µg TP/L (higher than the Middle Rockies criterion); the 80$^{th}$ percentile is 39 µg TP/L, and the 90$^{th}$ percentile is 50 µg TP/L.

Data from Baggs Creek (TP = 12 µg/L) suggests that TP concentrations need not necessarily be high in the presence of upper Clark Fork basin volcanic geology, however this is a single sample and there is variability in summer TP concentrations when more samples are accumulated. For example, the volcanic-influenced reference site on Elk Springs Creek (ElkSprin_037_C) has measured TP ranging from 7 to 22 µg/L (n = 6). Baggs Creek is our best, most locally-applicable reference site in the upper Clark Fork basin, but our data size is limited. We at least know that the concentration measured there falls within the range of other volcanic-influenced reference streams.

The work of Olson and Hawkins (2013) provides site-specific criteria but only some of the streams mentioned in **Section 1.0** have a volcanic-geology influence. Gold Creek, Dempsey Creek, and Dunkleberg Creek have zero or negligible volcanic geology in their watersheds (**Table 2-1**) and therefore the considerations outlined in this document do not apply to them. Lost Creek has some volcanic-geology influence, however the stream loses significant flows in an alluvial fan just about where the volcanic geology is located and further downstream the system is highly influenced by groundwater recharge from areas up gradient (not by the volcanics directly in its watershed). We do not believe that our process should apply to it either. At this point, we are not sufficiently convinced that the model results from Olson and Hawkins (2013) should be used to set criteria without consideration of other lines of evidence and, as such, Gold Creek, Dempsey Creek, Dunkleberg Creek, and Lost Creek should continue to be covered by the Middle Rockies ecoregional criteria (30 µg TP/L, 300 µg TN/L).

For four of the remaining streams (Silver Bow Creek, Hoover Creek, Willow Creek, and Peterson Creek, and also Browns Gulch, which drains to Silver Bow Creek and has a very high percentage of volcanic geology), the results from Olson and Hawkins provide a range of potential criteria (**Table 2-1)**. For the streams in **Table 2-1** there is poor correlation between Olson and Hawkins TP values and percent volcanic geology ($r^2$= 0.06, not significant) but this is not entirely unexpected as there are 26 other variables in their model leading to the predicted values. Predicted TP values for the four streams range from 27 to 43 µg TP/L, with 95$^{th}$ percentile upper-prediction concentrations ranging from 44 to 60 µg TP/L. Olson and Hawkins (2013) state that "The prediction and 95% Prediction Limit (PL) could be used as thresholds, with values above the prediction triggering close monitoring and values above the 95% PL triggering immediate regulatory action."

Giving consideration to all these lines of information, we recommend 40 µg TP/L for Silver Bow Creek (downstream of the Browns Gulch confluence), Hoover Creek, Willow Creek, Peterson Creek, and for Browns Gulch. We also recommend that this criterion be applied to Tenmile Creek and Rattler Gulch (both located in the Central Clark Fork Tributaries TPA) , as they are both influenced by volcanic geology (45% and 18% of their watersheds, respectively) of the Clark Fork River drainage and nutrient TMDLs are required for these streams (**Table 3-2**).

**Table 3-2. Endpoint Coordinates for Streams to which Site-specific Criteria in this Document apply.**
The criteria should apply from the headwaters to the endpoints for all but Silver Bow Creek. For Silver Bow Creek, the criteria should apply from the confluence with Browns Gulch to the endpoint shown.

| Stream Name | Endpoint Description | NAD 83 Coordinates of Endpoints (decimal degrees) | |
|---|---|---|---|
| | | Latitude | Longitude |
| TENMILE CREEK | mouth (at Bear Creek-Clark Fork River) | 46.7605 | -113.3533 |
| RATTLER GULCH | terminus, just above (north) of the Clark Fork, West of Drummond | 46.6974 | -113.2215 |
| WILLOW CREEK | mouth (at Mill Creek) | 46.1161 | -112.8054 |
| PETERSON CREEK | mouth (at Clark Fork River) | 46.3891 | -112.7369 |
| SILVER BOW CREEK | Warm Springs Creek (Clark Fork River) | 46.1869 | -112.7718 |
| BROWNS GULCH | mouth (at Silver Bow Creek) | 46.0033 | -112.7029 |
| HOOVER CREEK | mouth (at Clark Fork River) | 46.5962 | -113.0101 |

Forty micrograms TP per liter equates to the 81$^{st}$ percentile of the volcanic-influence reference sites in the Middle Rockies (again, excluding the Absaroka-Gallatin Volcanic Mountains ecoregion). By setting the TP criterion at the 81$^{st}$ percentile of the applicable reference distribution, we can approximate that the affected streams will pass future assessments (once TMDLs have been met) using methods in Suplee and Sada de Suplee (2011) which allow for a 20% exceedance of a criterion using the binomial test. Forty micrograms per liter falls within the prediction range (27 to 43 µg TP/L) for these streams based on Olson and Hawkins work, but below the upper-prediction range (44 to 60 µg TP/L) they would suggest should trigger regulatory action. We also gave consideration to the fairly low TP measured in Baggs Creek (12 µg/L), and although the data there is extremely limited Baggs Creek is still our best, most applicable reference site for localized volcanic geology effects in the upper Clark Fork basin.

When setting a new TP criterion, consideration must also be given to the nitrogen criterion. The scientific literature generally suggests that for these streams 40 µg TP/L is saturating or nearly so, and therefore N-limitation is what is probably keeping reference streams with these elevated phosphorus concentrations from becoming choked with algae. As a result, the TN criterion should be somewhat lowered from the ecoregional value, down to 260 µg TN/L, which provides a new criteria N:P ratio of 6.5, i.e., N and P co-limited but leaning slightly towards N limitation.

To recap, the recommended criteria (40 µg TP/L and 260 µg TN/L) should apply from headwaters to mouth for Browns Gulch, Hoover Creek, Willow Creek, Peterson Creek, Rattler Gulch, and Tenmile Creek. For Silver Bow Creek the criteria should apply from the Browns Gulch confluence downstream to its confluence with the Clark Fork River.

# 4.0 CONCLUSION

Analysis showed that there is a subset of reference sites within the Middle Rockies ecoregion which are influenced by volcanic geology. This volcanic geology in turn promotes higher phosphorus concentrations than what is typically seen in Middle Rockies ecoregion streams as a whole. The Department is required to complete nutrient TMDLs on a number of impaired streams in the Clark Fork River basin and it is known that they too are influenced by volcanic geology in some cases. We used data from Middle Rockies reference streams influenced by volcanic geology along with some site-specific modeling approaches recently published in the scientific literature (Olson and Hawkins, 2013) to develop site-specific nutrient criteria for several upper Clark Fork River basin streams. The recommended criteria are 40 µg TP/L and 260 µg TN/L and should apply from the headwaters to the mouth in Browns Gulch, Hoover Creek, Willow Creek, Peterson Creek, Rattler Gulch, and Tenmile Creek. For Silver Bow Creek, the criteria should apply from the Browns Gulch confluence downstream to its confluence with the Clark Fork River (**Table 3-2**). As for other Middle Rockies streams, these nutrient criteria should apply from July 1$^{st}$ to September 30$^{th}$ each year.

# 5.0 REFERENCES

Conover, William J. 1999. Practical Nonparametric Statistics, 3rd. ed., New York: John Wiley & Sons.

Dillon, Peter J. and W. B. Kirchner. 1975. The Effects of Geology and Land Use on the Export of Phosphorus From Watersheds. *Water Research.* 9(2): 135-148.

Froelich, Phillip N. 1988. Kinetic Control of Dissolved Phosphate in Natural Rivers and Estuaries: A Primer on the Phosphate Buffer Mechanism. *Limnology and Oceanography.* 33(No. 4 Part 2): 649-668.

Hem, John D. 1985. Study and Interpretation of the Chemical Characteristics of Natural Water. U.S. Geological Survey Water-Supply Paper 2254.

Olson, J. R. and Charles P. Hawkins. 2013. Developing Site-Specific Nutrient Criteria From Empirical Models. *Freshwater Science.* 32(3): 719-740.

Redfield, Alfred C. 1958. The Biological Control of Chemical Factors in the Environment. *American Scientist.* 46: 205-221.

Shoji, S., M. Nanzyo, and R. A. Dahlgren. 1993. Volcanic Ash Soils — Genesis, Propeties and Utilization, Amsterdam: Elsevier.

Smeck, Neil E. 1973. Phosphorus: an Indicator of Pedogenetic Weathering Processes. *Soil Science.* 115: 199-206.

Sorrell, C. A. 1973. Minerals of the World, A Guide to Field Identification, New York: Golden Press.

Suplee, Michael W. and Rosie Sada de Suplee. 2011. Assessment Methodology for Determining Wadeable Stream Impairment Due to Excess Nitrogen and Phosphorus Levels. Helena, MT: Montana Department of Environmental Quality Water Quality Planning Bureau. WQPMASTR-01.

Suplee, Michael W., Rosie Sada de Suplee, David L. Feldman, and Tina Laidlaw. 2005. Identification and Assessment of Montana Reference Streams: A Follow-Up and Expansion of the 1992 Benchmark Biology Study. Helena, MT: Montana Department of Environmental Quality.

Suplee, Michael W. and Vicki Watson. 2013. Scientific and Technical Basis of the Numeric Nutrient Criteria for Montana's Wadeable Streams and Rivers—Update 1. Helena, MT: Montana Department of Environmental Quality.

Varghese, Arun and Joshua Cleland. 2008. Updated Statistical Analyses of Water Quality Data, Compliance Tools, and Changepoint Assessment for Montana Rivers and Streams. Fairfax, VA.

Woods, Alan J., James M. Omernik, John A. Nesser, Jennifer Shelden, Jeffrey A. Comstock, and Sandra J. Azevedo. 2002. Ecoregions of Montana, 2nd ed., Reston, VA: United States Geographical Survey.