

GUIDANCE FOR DEVELOPING SITE-SPECIFIC MINERALS CRITERIA

IN SUPPORT OF OAC 785:45 APPENDIX F
AND
THE AGRICULTURE BENEFICIAL USE IN OKLAHOMA'S
WATER QUALITY STANDARDS

OWRB TECHNICAL REPORT TR2001-2



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EXECUTIVE SUMMARY

Oklahoma's Water Quality Standards contain historically derived segment-specific averaged criteria found in Appendix F of OAC 785:46 for chlorides, sulfates and total dissolved solids (TDS) to protect the Agricultural Beneficial Use. These values cannot be modified unless no value is given and historical data did not exist for a particular segment. However, site-specific criteria may be calculated for those segments without criteria and for tributary segments that do not contain chloride, sulfate, and TDS concentrations consistent with segment default values. This document provides guidance to facilitate the site-specific criteria development process in these segments.

This document will be incorporated into Oklahoma's Continuing Planning Process Document.

GUIDANCE FOR DEVELOPING SITE-SPECIFIC MINERALS CRITERIA

INTRODUCTION

Mineral criteria in Oklahoma's Water Quality Standards (OAC 785:45) are intended to protect the Agriculture Beneficial Use and are expressed as yearly mean standards (YMS) and sample standards (SS) for chlorides, sulfates and TDS. The yearly mean standard is the arithmetic mean of historical data from USGS gauging stations between October 1976 to September 1983 plus one standard deviation from the mean. The sample standard is the mean of these same data plus two standard deviations. Yearly mean standards and sample standards are listed for USGS monitoring station locations by water quality management segments in OAC 785:45 Appendix F. See Figure 1.

Historical data are used to derive segment-specific criteria found in Appendix F which are used to insure that increased mineral loads do not adversely affect livestock or crop irrigation practices in a particular region. Due to ambient mineral concentrations, mineral criteria in western Oklahoma are much higher than criteria in eastern Oklahoma. Since mineral criteria implementation is based upon historical ambient concentrations, site-specific criteria development for minerals is different than for toxicants. Site-specific criteria development for toxicants is designed to consider local conditions when developing permit limits while still protecting the Fish and Wildlife Propagation beneficial use. Site-specific criteria development for minerals is designed to keep minerals in receiving water at historical levels while supporting existing agricultural practices for a given stream reach. Because water quality management segments are so large, average concentrations obtained at a few USGS stations often do not represent historical mineral concentrations for all waterbodies within a segment. If new data are developed in an area where no gauges exist and the SS and the YMS of those data are significantly different from the segment average due to naturally occurring events or conditions, the new data are more representative of mineral quality in that segment than segment averages. Therefore, site-specific criteria for minerals are developed to make criteria for chlorides, sulfates and TDS more representative of smaller, more local segments. This document provides appropriate guidance for developing mineral criteria for small segments within segments published in Oklahoma's Water Quality Standards (OAC 785:46 Appendix F) where historical mineral concentrations are significantly different from segment averaged concentrations.

OKLAHOMA WATER QUALITY STANDARDS

Numerous references to the Agriculture Beneficial Use can be found throughout the Standards. One of the first is the declaration of the B.U. found in OAC 785:45-5-13(a). It states "*The surface waters of the State shall be maintained so that toxicity does not inhibit continued ingestion by livestock or irrigation of crops*".

The first mention of the possibility of site-specific criteria comes later in this same section where it states "(f) *The data from sampling stations in each segment are averaged, and the mean chloride, sulfate, and total dissolved solids at 180°C are presented in Appendix F of this Chapter. **Segment averages shall be used unless more appropriate data are available***" (emphasis added).

Appendix F contains stream segment averages derived from USGS gauging station data taken from October 1976 through September 1983. Revisions to these numbers are not permitted as per OAC 785:46-9-2(a) which states "*Historical values for chlorides, sulfates and TDS for water*

quality segments identified in OAC 785:45 Appendix F will not be updated". (This has been interpreted to include the averages listed within each segment with multiple station entries.) It does not mean that historical data cannot be changed if it becomes apparent that the original calculations of yearly mean standard and sample standard were done incorrectly. This same section goes on to say "Data from surrounding segments shall be used by the permitting authority to develop yearly mean standards and sample standards for those segments with inadequate historical data". There are currently only two listings in Appendix F that come from a time frame outside of that originally stated in the Standards and they are noted as being from a recent site-specific study. A sample from Appendix F is shown below (Figure 1). The "segment number" is taken from water-quality-management basin maps. "Monitoring station" is the USGS gauging station in abbreviated form. Remember "Yearly mean standard" is defined as "...the arithmetic mean of historical data from October 1976 to September 1983 plus one standard deviation of the mean". The "sample standard" is defined as "...the arithmetic mean of historical data from October 1976 to September 1983 plus two standard deviations of the mean". These figures are derived by processes that are based on those detailed in **Standard Methods for Examination of Water and Wastewater**. It is important to note that the TDS concentration must be derived at 180°C.

SEGMENT	MONITORING STATION	CHLORIDE (mg/l)		SULFATE (mg/L)		TOTAL DISSOLVED SOLIDS AT 180°C (mg/L)	
		YEARLY MEAN STANDARD	SAMPLE STANDARD	YEARLY MEAN STANDARD	SAMPLE STANDARD	YEARLY MEAN STANDARD	SAMPLE STANDARD
120400	1945	563	794	126	165		
	1946	313	412	91	116		
	AVG	472	656	113	147		
120410	16557	649	843	145	179	998	1168
120420	1644	774	1014	150	180		
	1645	695	881	150	183		
	1650	703	934	173	220		
	AVG	708	905	152	186	1398*	1743*

Figure 1: Sample of OAC 785:45 Appendix F, Statistical Values of The Historical Data for Mineral Constituents of Water Quality

CURRENT USES OF MINERAL CRITERIA

Appendix F is currently used for multiple purposes. One is in Use Support Assessment Protocols (USAP) to determine if the Agriculture Beneficial Use is being supported. OAC 785:46-15-8(b) requires "the Agriculture beneficial use shall be deemed to be fully supported with respect to chlorides, sulfates and TDS if the mean...do not exceed the yearly mean standard... and no more than 10% of the sample concentrations...exceed the sample standard...". Another use is in permitting point source discharges for minerals. OAC 785:45-5-13 establishes the limits by "For chlorides, sulfates and total dissolved solids at 180°C (see Standard Methods), the arithmetic mean of the concentration of the samples taken for a year in a particular segment shall not exceed the historical "yearly mean standard" determined from the table following subsection (g) of this Section and 785:45-1-2 calculated for

that segment. For permitting purposes, the long-term average concentration shall not exceed the yearly mean standard. Yearly mean standards shall be implemented by the permitting authority using long-term average flows and complete mixing of effluent and receiving water. Furthermore, not more than one (1) in twenty (20) samples randomly collected at a site shall exceed the historical value of the "sample standard" calculated for that segment. For permitting purposes, the short-term average concentration shall not exceed the sample standard. Sample standards shall be implemented by the permitting authority using short term average flows and complete mixing of effluent and receiving water".

However, this same section goes on to say "...e) Increased mineralization from other elements such as calcium, magnesium, sodium and their associated anions shall be maintained at or below a level that will not restrict any beneficial use". **Therefore, it is important that the metal cations normally associated with chlorides, sulfates and TDS (such as sodium, magnesium and calcium) be controlled as part of the overall minerals strategy.**

ORGANIZATION OF GUIDANCE DOCUMENT

General. This guidance document illustrates the general process of developing site-specific criteria for minerals. The document is organized as follows to meet this goal:

1. Is a Site-specific Approach Appropriate? Before deciding that a site-specific criterion is the best option you should read this section.
2. Data Availability? Before expending resources on data collection you should read this section.
3. What is the General Process for Developing Site-specific Criteria? The process for developing site-specific mineral criteria is designed to ensure that historical mineral concentrations are maintained while still protecting existing downstream uses for that segment.
4. How Should the Field Sampling Program be Designed? The design of the field-sampling plan will affect the success of the study. This section discusses details of the sampling process.
5. How Should Laboratory Tests Be Conducted? Defensible data must support a site-specific criterion. These data depend on properly conducted laboratory tests that follow appropriate quality control procedures. This section provides information to help interpret the results.
6. How are Site-Specific Criteria Developed? This section provides the methodology for use of collected data in site-specific criteria development.
7. The Final Report. Final reports must justify site-specific criteria and be presented at an informal Standards hearing.

1. Is a Site-specific Approach Appropriate?

Development of a Site-specific Criterion Costs Money.

The site-specific process includes developing a work plan that is acceptable to the Oklahoma Water Resources Board (OWRB) and consistent with this guidance document. After a work plan is developed, an extensive field sampling effort is required. Laboratory costs must be budgeted. At the conclusion of this process, a final report must be prepared, presented and

submitted. Costs of developing site-specific criteria must be carefully weighed against potential benefits achieved.

Is the Segment Average Representative of the Area of Concern?

Most USGS gauges are located on main stems within a segment. If an area of concern encompasses a main stem, it is likely that data collected in the 70's and 80's are representative of historical averages. However, water quality on main stems may be influenced by conditions that occur far upstream from the segment (e.g. upstream salt springs). Therefore, mineral concentration in a main stem stream may differ significantly from those of tributaries contained within the segment. Areas containing tributaries may be viable candidates for site-specific mineral criteria. Preliminary screening may be accomplished to see if site-specific criteria will differ by more than 20% from segment averages. If not, site-specific criteria may be inappropriate.

2. Data Availability?

Existing Data

The Oklahoma Water Resources Board, Oklahoma Conservation Commission, Oklahoma Corporation Commission and other entities have collected mineral concentrations since 1983. This data was not available for use in criteria development in Appendix F. This data may be used in site-specific criteria development if the site may be defined to include the sampling location, saving valuable resources. All data acquired for establishing site-specific criteria must have a rigorous quality review. Data used should have been collected with a corresponding quality assurance plan and documented measures to assure accuracy and precision. The data should be free from seasonal or flow bias. The laboratory should be certified and its methods should be documented in the corresponding quality assurance plan. A justification document will be required to determine that the data are "*more appropriate*". For example, "*more appropriate*" may mean that the new data are from a smaller, more geologically similar watershed than the segment shown in Appendix F or from a nearby reference stream of similar drainage area and hydrology.

Combining Data

Existing data may be combined with data collected for the purpose of criteria development to satisfy minimum requirements, as long as the data are compatible. All appropriate data must be used. Existing data collected within a site cannot be ignored.

3. What is the General Process For Developing Site-specific Criteria?

Developing a Work Plan

A detailed work plan should be developed for each site at which mineral criteria are being developed. Work plans should contain quality assurance plans. The work plan must be approved by OWRB before sampling begins.

Defining the Site.

In the general context of site-specific criteria, a "site" may be a watershed, a water body, a portion of a water body, or a specific point in receiving water. Site-specific toxicant criteria apply at a specific point in a waterbody. The goal for site-specific mineral criteria is to reflect mineral concentrations for a given stream reach or tributary at historic levels that are significantly different than the segment values, yet not adversely impact existing downstream agricultural practices.

Irrevocability of Site-specific Criteria.

Site-specific toxicant criteria must be revised when conditions that affect toxicity change. This is not the case for site-specific mineral criteria. Once site-specific criteria that represent historical mineral concentrations are established, they can never be changed.

Determining Yearly Mean Standards and Sample Standards.

Yearly mean standards are defined as an arithmetic mean of available TDS, chloride or sulfate concentrations plus one standard deviation. Therefore the mean and standard deviation must be computed. A yearly mean standard is a long-term average concentration. Sample standards are the mean plus two standard deviations. They are considered shorter-term averages. Both yearly mean standards and sample standards may be used for different purposes in water quality management. For example, a yearly mean standard may drive a permit, but the sample standard may be used to determine Agricultural use impairment. Therefore, site-specific criteria for both sample standards and yearly mean standards must always be computed.

4. How Should the Field Sampling Plan Be Designed?

Importance of Field Sampling Design.

The field sampling design provides strategic information that helps in work plan preparation. It will ultimately affect the success of site-specific criteria development. The field sampling design should be incorporated in the work plan.

Background Concentration.

Unlike site-specific toxicant criteria development, no special sampling is required to determine background concentration for minerals. The arithmetic mean of the concentrations, without anthropogenic inputs, used to compute mineral site-specific criteria is representative of background concentration.

Sampling Dates

Sampling events should be spread out over at least a year to capture seasonal variability. Ideally samples should reflect the variety of mineral concentrations experienced at the sampling location. This may be assured by collecting flow data at the same time as the samples for criteria development. Sample dates may either be randomly distributed across the month or assigned to fixed dates. This will eliminate some of the bias that can arise from sampling only in good weather. If enough samples are collected, all flow regimes may be reflected in the data set.

Sample Locations.

Water samples will be collected at a location which is representative of the site for which criteria are being developed. "Representative" means that the sampling location has the same morphology, land use, soil type, etc. as the rest of the segment. It also means that mineral concentrations at the sampling locations are representative of historical conditions. Therefore, the sampling location must be relatively un-impacted by anthropogenic activities. The sampling location should not be on an effluent dominated stream. Neither should it be in an area where chloride control projects have been implemented. The sampling location(s) should remain consistent for all sampling events and should be accessible and safe for field personnel.

Mineral constituents in a water body have some inherent variability. Sampling should attempt to capture this variability on a large water body by collecting samples at various depths and

locations across the water body. Care must be taken to avoid backwaters and areas unduly influenced by man.

Sampling Protocol for Streams.

Discrete grab samples, collected at intervals across the width and throughout the depth of a big stream, should be composited. Field quality-control samples should be incorporated into the sampling protocol at predetermined frequencies to verify that field techniques are providing high quality samples. Water samples must be of sufficient volume and collected, transported, handled and stored in a manner acceptable to OWRB. Proper record keeping and chain of custody procedures should be used throughout each sampling event.

Sampling protocols may need to be revised due to circumstances found in the field. These changes must be documented and included in the final report submitted to the OWRB.

Verification of Representative Conditions.

Temperature, pH, dissolved oxygen and conductivity should be measured at the sampling locations to verify that the samples collected are representative. Anomalies must be noted. Conditions may be such that mineral concentrations are not representative.

Site-specific Criteria for Lakes.

Mineral conditions are likely to be changed by reservoir construction. Some reservoirs (e.g. Foss) tend to concentrate minerals due to evaporation. Because Oklahoma has virtually no natural lakes (a few ox-bows), reservoir mineral conditions cannot be considered historical. Therefore, **site-specific reservoir mineral criteria are not allowed**, even though lake mineral concentrations may differ significantly from segment averages.

Number of data points.

For the determination of site-specific criteria for minerals in streams, **at least 24 data points collected across at least twelve months will be required**. Not all of these will need to be collected in the course of the criteria-development project. These may be consolidated from existing data and may include data from municipal monitoring "upstream" USGS gauging stations, state agency collections, etc. (See section on existing data.)

Mineral Concentration Sampling Using Field Instruments

In some cases, mineral concentration is adequately measured with field instruments. Concentrations adequately measured in the field may be used to determine site-specific criteria. Field measurements must be compared with sufficient laboratory analyses to show a correlation greater than 90% if the field methodology is not EPA approved. Careful quality assurance/quality control (QA/QC) records, including calibration, must be included in the final report if field measurements are used.

5. How Should Laboratory Tests Be Conducted?

General.

Properly conducted laboratory tests will result in defensible data that can support the development of site-specific criteria. Chemical analyses must be conducted by an Oklahoma-certified laboratory that follows appropriate control procedures. A list of acceptable laboratories may be obtained from Oklahoma's Department of Environmental Quality lab certification section. It may be acceptable to use another lab if they have an approved Quality Assurance Plan on file with Region VI EPA in Dallas. Determination of laboratory qualifications and

acceptability should be part of the workplan submitted to OWRB prior to beginning work. A description of laboratory methods should be included in the work plan.

Chemical Analyses.

Containers and holding times should comply with table 1060:1 of Standard Methods of Water and Wastewater Analysis (19th edition) or CFR 40 part 136.

Sample analysis for total dissolved solids (TDS) should follow method 2540 C of Standard Methods of Water and Wastewater Analysis (19th edition). Sample analysis for chloride should follow methods 450 B, C, or E and sample analysis for sulfates should follow methods 4500 so 4-2 C or D or those approved in CFR 40 part 136.

Alternative analytical methods may be allowed with appropriate quality control measures and prior approval by OWRB.

Interpreting Test Results.

All data used for calculating site-specific criteria should be validated according to the approved workplan and corresponding quality assurance plan contained within it. This includes evaluating the final results against data quality objectives (e.g. accuracy, completeness, representativeness, compatibility) established in the work plan. All data must be provided to OWRB staff with the final report. All laboratory QA/QC backup materials will be required with the final report. If you have any questions about data usability, include it in the final report.

6. How are Site-Specific Criteria Developed?

General.

The appropriate results can be calculated if the data is adequate. This section includes a description of the relevant calculations.

Computation of the Mean.

Since OAC 785:45 requires the use of an arithmetic mean,

$$\bar{x} \equiv \frac{1}{N} \sum_{i=1}^N x_i$$

where \bar{x} = is the arithmetic mean, N is the number of concentration observations available for site-specific criterion development (≥ 24) and x_i is the i th concentration analyzed.

Computation of the Standard Deviation.

The standard deviation is required for the determination of yearly mean standards and sample standards. The standard deviation is defined by

$$s \equiv \sqrt{\sum \frac{(x_i - \bar{x})^2}{N - 1}}$$

Many spreadsheet programs have this function built into the existing abilities so this will be an easy determination.

Yearly Mean Standard.

The yearly mean standard is defined in OWQS as the mean plus one standard deviation (s).

$$YMS = \bar{x} + s.$$

Sample Standard.

The sample standard is defined in OWQS as the mean plus two standard deviations (2s).

$$SS = \bar{x} + 2s.$$

Site-specific Criteria.

YMS and SS are the proposed site-specific criteria. In order to be used in water quality management, proposed site-specific mineral criteria must be submitted to Oklahoma's Water Quality Standards revision process as a final report and successfully promulgated into the Water Quality Standards. An oral presentation to introduce site-specific criteria must be made at an informal meeting during the Water Quality Standards revision process. Following the Administrative Procedures Act, OWRB will place approved site-specific criteria in OAC 785:45 Appendix F.

7. The Final Report

The final report should be submitted in a timely fashion so that OWRB staff have time for review before presentation at the informal public meeting. Some changes will be inevitable even if the guidance is meticulously followed. OWRB staff concurrence will be necessary before going through the informal Water Quality Standards review process and Administrative Procedures Act. Below are some of the things that need to be included.

- Site for which site-specific criteria apply (map)
- Locations at which sampling occurred (map)
- Dates of sampling events
- Sources of existing data and sampling sites for each source (table)
- Mean annual average flow at site
- Flows at which sampling occurred (table)
- List of sample ID's (table)
- Sampling QA/QC including procedures used to obtain, transport and store samples
- Physical conditions at sampling location for each sampling event (including pH, temperature, DO and conductivity).
- Name and location of analytical laboratory and laboratory certifications
- Results of analytical measurements (concentrations, etc.)
- All data generated in the laboratory
- Results of data validation (e.g. blanks, duplicates, spikes, etc used in QC process)
- Summary of relevant calculations (mean, standard deviation, yearly mean standards, sample standards, etc.)
- Proposed site-specific criteria
- Conclusions

It should be noted, however, submitting the final report and presenting the evidence is not a guarantee of a site-specific criterion being incorporated into OWQS. The public will have opportunity to comment and refute findings at both informal meetings and the formal

hearing. EPA may still deny the criterion for various reasons usually based upon the data provided.

CONCLUSIONS

This guidance covers most situations that will be encountered in site-specific mineral criteria development. It is designed to produce a reasonable estimate of historical mineral concentrations without requiring excessive resources.

This guidance will not be finalized as “rule”, because it cannot be made general enough to cover all situations. Deviation from the guidance will be allowed with adequate justification. Every deviation must be explained to the satisfaction of OWRB staff.