Memorandum

VIRGINIA DEPARTMENT OF ENVIRONMENTAL QUALITY

Division of Water Program Coordination 9th Floor, 629 East Main Street, Richmond, VA

SUBJECT: GUIDANCE MEMORANDUM 01 –2011
Monitoring Toxic Trace Metals in Surfacewaters

TO: Regional Directors

FROM: Larry G. Lawson, P.E.

DATE: April 16, 2001

COPIES: Regional Permit Managers, Regional Water Permit Managers, Regional Compliance and Enforcement Managers, Jean Gregory, Martin Ferguson, Dale Phillips, Ron Gregory, Alan Pollock, Durwood Willis, Don Smith, Gary Du, Charlie Morgan, Roger Stewart

Attached is guidance for monitoring toxic trace metals in surface waters. The purpose of this guidance is to provide direction to the Regional Offices on selecting ambient monitoring sites for monitoring toxic metals in the water column. This guidance should be considered when the Regional Offices prepare their annual monitoring plans.

Please contact Roger Stewart, at 804/698-4449 or Roger E. Stewart@WQA@DEQ with any questions about the application of this guidance.

DISCLAIMER

This document provides procedural guidance to the permit staff. This document is guidance only. It does not establish or affect legal rights or obligations. It does not establish a binding norm and is not finally determinative of the issues addressed. Agency decisions in any particular case will be made by applying the State Water Control Law and the implementation regulations on the basis of the site specific facts when permits are issued.

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Attachment

Ambient Toxics Studies

Monitoring Toxic Trace Metals in Surfacewaters

In September of 1991 the US Geological Survey in a technical memorandum[1] repudiated all previous dissolved toxic trace metal data collected by their agency from measurements made in the nations surfacewaters[2]. The data were suspect because contamination of samples had occurred in the field and laboratory. In January of 1992 the US Environmental Protection Agency came to a similar conclusion after careful review of historic data and current operating procedures[3].

In May of 1992 the Department adopted new Water Quality Standards for specific toxic metals at concentrations several orders of magnitude below the historic reporting levels. The standards were expressed as dissolved metals whereas historic data represented the total concentration. Between 1994 and 1996 the Department, with assistance from the Virginia Division of Consolidated Laboratory Services, USGS and EPA, developed field and analytical procedures that would reliably produce data at background concentrations for freshwaters. Recently procedures have been developed for use in brackish and saltwater matrices.

Beginning in May of 1997 trace metal sampling in freshwaters was added to the ambient water quality monitoring program. From this time to the end of 1998, 113 samples were collected at 102 separate sites in all major basins except for the most western basin, Tennessee Big Sandy. The result of this effort indicates that the average dissolved concentrations of trace metals in Virginia rivers are consistent with the global distributions observed by other researchers. The attached table DISSOLVED TRACE METAL CONCENTRATIONS IN FRESHWATER, ug/L contains a summary of the reliable clean metals data collected by various research groups compared to data collected by the Department. Other than situations where direct input of pollutants are occurring or where there are unusually low pH values, the concentrations of dissolved metals in the freshwaters of Virginia are in a well defined range. Furthermore this range is below the chronic effect level.

Two sites were identified as having concentrations well above the expected range. The first site 8-CON005.38 is located at 38:03:54W 077:52:50N on Contrary Creek in Louisa County. This site is downstream of an abandoned mining operation which continues to contribute acidic leachate to the stream despite many years of remedial efforts. The pH at the site during the time of sample collection was 3.8. The second site 7-SBB000.17 is located at 37:54:46W 075:35:30N on Sandy Bottom Branch in Accomack County. This site is identified as the HOLLY FARMS, INC. - IMPACT STATION, and is located immediately downstream of a significant point source discharge, VA0004049.

Beginning in the later half 1998 the Virginia Division of Consolidated Laboratory Services developed the analytical technique for analyzing metals in seawater. Seawater presents a very difficult matrix for the analysis of extremely low level dissolved metals because of interference caused by high concentrations of the major cations. Consequently saltwater procedures for toxic

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[1] Contamination of Dissolved Trace Element Data: Present Understanding, Ramifications, and Issues that Require Resolution.

[2] Inadequacy of NASQAN Data for Assessing Metals Trends in the Nation's Rivers, Windom Herbert L., et.al, Environ. Sci. Technol., Vol 25,No.6 1991.

[3] Evaluation of Trace-Metal Levels in ambient Waters and Tributaries to New York / New Jersey Harbor for Waste Load Allocation, EPA Contract No. 68-C8-0105, January 9, 1992.

metals were developed after the freshwater procedures. The attached table DISSOLVED TRACE ELEMENT AND MAJOR CATION CONCENTRATIONS IN SEAWATER, ug/L contains a summary of the reliable saltwater dissolved clean metals data collected by various research groups compared to data collected by the Department.

Samples collected by the Department from the Atlantic Ocean and the Gulf of Thailand in 1998 and 1999 were used to establish background concentrations and for comparison purposes to previous studies of trace element concentrations. The results obtained by DCLS when compared to these studies indicate that the distribution of trace elements in naturally occurring areas is consistent on a global scale. Furthermore as seen from the table the DCLS and DEQ study represents the most comprehensive compound list to date.

In 1999, 64 measurements at 14 sites in the Elizabeth River were completed. The Elizabeth River is a mixture of approximately 55% freshwater and 45% saltwater, which makes direct comparison to background saltwater or freshwater concentrations impractical. Compared to the Virginia Water Quality Standards two copper values exceeded the chronic limit at two stations located on the Southern Branch during sampling events two months apart. More significantly the toxic metal concentrations of copper, zinc, and cadmium on the Southern Branch increase from the station that is located 8.40 miles from the mouth to the station that is 1.53 miles from the mouth. This increase is the opposite of what is expected as freshwater mixes with saltwater under natural conditions. From the data presented for freshwater, except for Arsenic, normal freshwater background concentrations are higher than normal saltwater background concentrations, therefore as fresh is diluted with salt the toxic trace elements precipitate from solution and are deposited in the sediment. As predicted for natural environments Aluminum, Manganese, and Nickel exhibit decreasing concentrations towards the sea. In the case of the Southern Branch of the Elizabeth River direct input from anthropogenic sources is suspected as the cause of the elevated copper, zinc, and cadmium.

As a result of the previous freshwater and saltwater work, the strategy for monitoring toxic trace elements in the water column should now shift from ambient waters and focus on major point source discharges and other known or suspected problem areas. Monitoring at all major point source discharges and other target SICs based on the permit cycle, 303(d)[4] listed waters, acid mine drainage (AMD) sites, and the Elizabeth River are prime areas where metals monitoring is necessary. Some pristine background stations will be necessary for monitoring long term trends. In the following sections specific recommendations on station and or segment locations for each of these targeted monitoring groups will be presented.

VPDES Monitoring

Monitoring above and below major industrial, municipal, and other targeted SIC discharges will serve two purposes. First it will provide the necessary data for determining background levels for the calculation of permit limits, if needed, and the data are useful in comparison to expected values. This will serve to better protect the ecosystem from harmful effects, as the current practice is to assume zero concentration in the receiving water when calculating loading from the effluent. Secondly the data will indicate if discharges are contributing toxic levels of metals to the receiving stream. In those cases where elevated concentrations are detected continued monthly sampling for metals and biological assessments are necessary.

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[4] 303(d) Total Maximum Daily Load Priority List and Report, Virginia Department of Environmental Quality and Department of Conservation and Recreation, October 1998.

Monitoring at VPDES outfalls should be prioritized according to the permit schedule for reissuance. In reverse chronological order the process for determining the monitoring schedule is:

1. Data should be available for use in permit development 8 months prior to the DATE PERMIT EXPIRES: from the events screen in the Comprehensive Environmental Data System Permit Tracking and Compliance module, CEDS. The corresponding code is FLED

2. To be included in the yearly planning schedule site reconnaissance should occur in January and February prior to the beginning of the monitoring season, which begins on 1 July.

For example, to develop the schedule of sites for the July 2001 to June 2002 monitoring year, permits that expire on 02/28/2003 would be the earliest ones for consideration. Furthermore it is the responsibility of the individual permit writers to provide the facilities list to the monitoring staff by the 31 December of each year. This will allow the field staff to do site reconnaissance in January and February prior to the start of the monitoring year in June.

In some instances multiple outfalls may be located in a very small geographic area making sampling between each difficult and impractical. Best professional judgment should be used to determine the most appropriate sample locations. Factors such as mixing zones, tidal influences, combined sewer overflows and stormwater discharges are important for consideration when selecting the above and below outfall site locations.

303(D) Targeted Segments

Watersheds listed in the 303(d) report are also prime candidates for exploratory sampling. Three sections of the report include sites which will trigger clean metals sampling: PART 1 – IMPAIRED WATERS, PART 2 – WATER QUALITY BASED EFFLUENT LIMITS, and PART 4 – FULLY SUPPORTING BUT THREATENED WATERS. Sampling in a subset of these watersheds, as described below, should become part of the annual routine monitoring program. The amount and frequency of sampling should be driven by the available resources. To begin with, the frequency of sampling the 303(d) segments can be only one sample per year. After evaluation of the data more frequent sampling may be initiated. The next consideration is the number of sites that can be done in one year without significant expenditures of resources. The option remains to sample only a subset of these segments each year with the goal of completing monitoring in all these segments within a five year time span.

As other waters are identified for possible impairment additional monitoring resources may be required.

Part 1 – Impaired Waters

Several streams are listed as impaired for mercury due to contaminated sediments and fish tissue levels that exceed a healthy level for human consumption. The mercury contaminated segments have not been targeted for remediation as the technology involved would be more of a disturbance to the ecosystem than the gradual loss of mercury due to the natural process of covering by sediment deposition. However monitoring in these areas is the only measure that can determine if the concentrations are decreasing.

The Virginia Department of Health has identified a 103.40 mile segment of the South River and South Fork Shenandoah Rivers and a 80.40 mile segment of the North Fork Holston River for fish

consumption advisories due to high levels of mercury in edible tissues. Monitoring for dissolved mercury in the water column over the entire length of each segment on a bimonthly frequency will provide the necessary long term data to monitor the expected downward trend in concentration. Stations should be located to be representative of the segment with a minimum of 1 site located every 20 to 25 miles along each segment.

All other Part 1 waters impaired for pH should be monitored at least once annually to determine if sediment bound metals are becoming solublized. Depressed pH levels will account for the increase in the dissolved concentrations of trace elements. Continued monitoring over the next five years will provide the necessary data to determine the potential risk of these low pH waters.

Part 2 – Water Quality Based Effluent Limits

Water Quality Based Effluent Limited segments are those sections of water that receive advanced wastewater treatment. The purpose of advanced wastewater treatment is to maintain or attain water quality or to achieve the requirements of antidegradation[5]. Monitoring for trace metals has not been a routine procedure for ambient monitoring until recently so very little data exists, which would show if these effluent limited segments are meeting water quality standards or are maintaining antidegradation.

Part 4 – Fully Supporting But Threatened Waters

Waters listed in Part 4 of the 303(d) list include those that are fully supporting their intended use but are threatened. Generally these are listed because contaminated sediments were found and no sediment quality standard exists. Monitoring within all these threatened segments should be a goal of the regional program.

Acid Mine Drainage Sites

Acid mine sites exhibit the potential for transfer of metals from the sediment to the dissolved phase due to depressed pH levels. At least on one occasion data from a known AMD site on Contrary Creek above Lake Anna contains some of the highest levels of dissolved toxic elements ever measured and is well above the water quality criteria.

The Department of Mines Minerals and Energy has conducted a survey of approximately 1300 potential sites that may contribute significant pH influences to receiving streams. Of the sites identified in the study 68 had pH values of 5 or less. These sites are candidates for our ambient monitoring program.

Elizabeth River Watershed

The Elizabeth River watershed should continue to be a study area because of the already detected contamination in the Southern Branch. Long term trends of the system must be determined to better understand the dynamics and potential for increasing impairment. Bimonthly monitoring for both dissolved and total recoverable metals should continue indefinitely.

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[5] Ibid., page II-1, revised October 1998.

Background Monitoring

An important aspect to determining the anthropogenic contributions of trace elements to the ecosystem is their measurement under conditions that are most likely to exhibit pristine conditions. Statewide approximately 10 surfacewater stations (free flowing springs) and several groundwater stations will be selected by identifying ancient waters using USGS age dating data. Ideally, groundwaters that are in excess of 9000 years old should be selected.

Routine yearly monitoring of these sites will provide over time a historical record of background conditions and will be used for comparison to other trace metals monitoring sites. To stay current with the Standard Operating Procedure the Office of Water Quality Monitoring and Assessment will conduct the background monitoring.