Appendix 7: Random Ambient Monitoring System Information

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Random Ambient Monitoring System

The Random Ambient Monitoring System (RAMS), started in January 2007, is a component of DWR's Ambient Monitoring System (AMS). RAMS is a probabilistic monitoring initiative where sampling locations are randomly located on freshwater streams (non-tidal, non-lake/reservoir, non-saltwater) throughout the state. RAMS has its origins in EPA's Probabilistic Monitoring Initiative. The EPA has recommended to the states that probabilistic monitoring be incorporated into the 305(b) water quality reporting process. For this reason and several others DWR has chosen to implement RAMS.

This appendix is to highlight where the AMS and RAMS have differences. Most of the differences are due to AMS being a long-term, judgmentally based program and RAMS being a probabilistic approach on a much smaller scale. However, much of the day-to-day operation of the two programs is the same since the staff involved for management, field sampling, laboratory analysis, and reporting are the same for AMS and RAMS. There are differences in the reasons for sample collection, how stations are selected, which indicators are measured and frequency, quality control processes, and data reporting.

DWR's ambient monitoring network has historically focused on large rivers and areas with known water quality problems. As a result, the ambient program does not have much data on smaller streams. Because most streams in North Carolina are small, the majority of RAMS sites are also on small streams. In addition, RAMS allows DWR to answer broad questions about the water quality of North Carolina streams without the bias inherent in fixed station sampling. RAMS also allows DWR to cost-effectively collect data on water quality parameters that are rarely examined by existing monitoring programs. Finally, it will also aid in the development of alternative methods of measuring metals, such as dissolved concentrations and toxicity via biotic ligand models.

Objectives

The Primary objectives of RAMS are:

- To obtain unbiased evaluation of all freshwater surface waters in North Carolina without bias introduced through fixed station monitoring.
- To determine, at a state-wide perspective, whether water quality standards are being met for all the pollutants listed in "Standards for Toxic Substances and Temperature" (15A NCAC 02B .0208) and "Fresh Surface Water Quality Standards for Class C Waters" (15A NCAC 02B .0211).
- To identify the presence and magnitude of analytes not collected in the ambient and coalition monitoring programs i.e. volatile organics, semi-volatiles, pesticides, dissolved metals, and low-level mercury.

Bias

RAMS has a probabilistic monitoring design which helps to reduce bias in the sampling locations. However, some bias may be introduced during the station location process due to accessibility concerns. Sites that are not reasonably accessible on a monthly basis are not used for sampling.

The use of consistent sampling methods, SOPs and analytical methods minimizes bias from other sources.

Completeness

It is expected that monthly sampling will occur at each RAMS site for physical and chemical measurements, provided there is water present at the time of sampling. Since RAMS sites are commonly located on smaller headwater streams (Strahler order 1 & 2), seasonal variations or drought conditions may result in low flow conditions or dry streams. These conditions should be noted and sampling resumed once water returns to the stream. Other problems such as inclement weather, road construction, or equipment problems may result in a site not being sampled one month, but sampling should be conducted twice in the following month, if possible.

Biological assessments are completed are all sites unless: 1) the sampling protocols for the benthic macroinvertebrate and/or fish assessments are not met (e.g. streams are not wadable, an Index of Biological Integrity (IBI) for fish has not been developed for some watersheds) or 2) flowing water is not present.

Station Selection

RAMS station selection began with USEPA's National Health and Environmental Effects Research Laboratory Freshwater Ecology Branch in Corvallis, Oregon providing a list of 330 randomly selected sites to DWR. These sites are based upon the 100K hydrography digital map dataset. Each potential monitoring site is reviewed: 1) to determine if each site is located on freshwater streams (sites that were tidal, saltwater or lake/reservoirs are excluded from the list), and 2) determine if the site could be accessed easily over a two year monthly monitoring period.

Each freshwater site is examined using MapTech's Terrain Navigator software and Google Maps to determine if a bridge is within ¼ mile or road access is within a 1/8 mile and located with the same stream segment. The proximity of the site to a bridge crossing or road criteria are necessary to minimize site access difficulties, since monitoring locations are accessed 24 times. If both of these criteria are not met then the site is excluded from the list. Once a site meets these criteria, a site visit is completed to verify the stream location, evaluate physically accessibility, and identify if private property permission would be needed for access. The first thirty potential sites that met all the criteria become sampling locations for the two year sampling cycle. This station selection occurs every two years during the spring/summer before sampling is to begin the following January. Stations selected for each two year cycle are available on the RAMS webpage at <u>https://deq.nc.gov/about/divisions/water-resources/water-resources-data/water-sciences-home-page/ecosystems-branch/random-ambient-monitoring-system</u>. Figure 1 below is a map of the 2015-2016 stations.



Figure 1- Map of RAMS stations for 2015-2016

Sampling schedule

The RAMS is a continuous project of indeterminate duration with no planned end date of data collection. Thirty stations are visited monthly for two years for the collection of field measurements and analytical samples. Every two years a new set of thirty stations is selected and sampled. Biological assessments for benthic macroinvertebrate and fish community are conducted once at each site that have wadeable, flowing water and developed metrics for rating.

Sampling methods

Samples and measurements are to be taken in accordance with the ISB Standard Operating Procedures (SOP) and Laboratory Section Quality Assurance Manual (QAM). Biological assessments for benthic macroinvertebrates and fish community are taken in accordance with each program's appropriate SOPs and QAPPs which are available on the Biological Assessment Branch's website (<u>https://deq.nc.gov/about/divisions/water-resources/water-resources-data/water-sciences-home-page/biological-assessment-branch</u>).

All field measurements and samples are taken just below the surface (depth=0.1m). All total samples are grab samples with sample bottles directly filled either by submersing them by hand in the waterbody or by using a bridge sampler. If it is necessary that an intermediary collection device be used to collect the grab sample, for organics the intermediary device should be a new, certified clean glass jar and for other parameters the intermediary device should be made of a non-reactive material (e.g. Teflon or Nalgene bottle). All dissolved samples (DOC and NC AMS QAPP Approved: July 2017 Version 2.0

dissolved metals) are to be collected as grab samples and then field filtered through a 0.45 μ m pore filter within 15 minutes of collection.

Low-level mercury samples follow the same guidelines as other samples but have additional sampling protocols in order to reduce the potential for contamination. EPA method 1669, which documents the sampling method for trace metals, is followed for the collection of the low-level mercury field blank and environmental sample.

Indicators measured and sampling frequency

The selection of RAMS indicators is primarily focused on those with NC water quality standards or those which will aid in the development of alternative methods for measuring metals, such as dissolved concentrations and toxicity via biotic ligand models. The following indicators are collected once per month for a total of 24 times in two years: dissolved oxygen, specific conductance, temperature and pH; alkalinity, chloride, fluoride, sulfate, dissolved organic carbon, turbidity, total metals, dissolved metals, mercury, and volatile organics. The following indicators are collected once every other month for a total of 12 times in two years: cyanide, sulfide, semi-volatile organics, pesticides, and PCBs. Table 1 details the indicators measured, sampling frequency, sampling/analytical methods, and practical quantification limit (PQL) for laboratory analysis.

Indicator (unit)	Sampling Frequency	Sampling/ Analytical Method	POL
Field Measurements			
Water Temperature (°C)	Monthly	EPA 170.1	
Specific Conductance (µS/cm at 25°C)	Monthly	EPA 120.1	
Dissolved Oxygen (DO) (mg/L)	Monthly	EPA 360.1	
pH (SU)	Monthly	EPA 150.1	
Samples			
Alkalinity (mg/L as CaCO ₃)	Monthly	APHA 2320B (20 th ed.)	1 mg/L as CaCO ₃
Chloride (mg/L)	Monthly	EPA 300.0	1 mg/L
Cyanide (mg/L)	Bi-monthly	APHA 4500CN-C&E	0.02 mg/L
Dissolved Organic Carbon (DOC) (mg/l)	Monthly	APHA 5310B	2 mg/L
Fluoride (mg/L)	Monthly	EPA 300.0	0.4 mg/L
Sulfate (mg/L)	Monthly	EPA 300.0	2 mg/L
Sulfide (mg/L)	Bi-monthly	APHA 4500-S2-D	0.1 mg/L
Turbidity (NTU)	Monthly	APHA 2130B (20 th ed.)	1 NTU
Arsenic, total & dissolved (µg/L)	Monthly	EPA 200.8/200.9	2 µg/L
Beryllium, total & dissolved (µg/L)	Monthly	EPA 200.7	5 μg/L
Cadmium, total & dissolved (µg/L)	Monthly	EPA 200.8/200.9	0.5 μg/L
Calcium, total & dissolved (mg/L)	Monthly	EPA 200.7	0.10 mg/L
Chromium, total & dissolved (μ g/L)	Monthly	EPA 200.8/200.7	10 µg/L
Copper, total & dissolved (μ g/L)	Monthly	EPA 200.8/200.9	2 µg/L
Iron, total & dissolved (μ g/L)	Monthly	EPA 200.7	50 µg/L
Lead, total & dissolved (μ g/L)	Monthly	EPA 200.8/200.9	$2 \mu g/L$
Magnesium, total & dissolved (mg/L)	Monthly	EPA 200.7	0.1 mg/L

Table 1- RAMS Indicators: Field and Analytical Samples

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	Sampling	Sampling/	
Indicator (unit)	Frequency	Analytical Method	PQL
Manganese, total & dissolved (µg/L)	Monthly	EPA 200.8/200.7	10 µg/L
Mercury, total (ng/L)	Monthly	EPA 1631 E	1.00 ng/L
Nickel, total & dissolved ($\mu g/L$)	Monthly	EPA 200.8/200.9	$2 \mu g/L$
Potassium, total & dissolved (mg/L)	Monthly	EPA 200.7	0.10 mg/L
Selenium, total & dissolved (µg/L)	Monthly	EPA 200.8/200.9	5 μg/L
Sodium, total & dissolved (mg/L)	Monthly	EPA 200.7	0.10 mg/L
Zinc, total & dissolved (µg/L)	Monthly	EPA 200.8/200.7	10 µg/L
Volatile Organics (µg/L)	Monthly	EPA 624	Varies ¹
Semi-Volatile Organics (µg/L)	Bi-monthly	EPA 625	Varies ¹
OrganoChlorine Pesticides (µg/L)	Bi-monthly	EPA 608	Varies ¹
OrganoNitrogen Pesticides (µg/L)	Bi-monthly	EPA 619	Varies ¹
OrganoPhosphorous Pesticides (µg/L)	Bi-monthly	EPA 614	Varies ¹

¹Visit the DWR's Laboratory Section website for a current list of analytes and their PQL's <u>https://deq.nc.gov/about/divisions/water-resources/water-resources-data/water-sciences-home-page/microbiology-inorganics-branch/methods-pqls-qa.</u>

Quality Control

Field meters are calibrated at the beginning of each sampling day and checked at the end of each sampling day to ensure no calibration drift. These procedures are the same as those followed for the AMS program.

In order to ensure a high level of quality data, quality control (QC) samples are completed in the form of trip blanks for volatile organics, equipment blanks for filtered samples (DOC and dissolved metals), and field blanks for low level mercury samples. The results from the QC samples are reviewed for completeness and evaluated to identify results above detection. If an analyte from a QC sample is above detection or no required QC sample was collected, then the analyte result in the corresponding stream sample is flagged in the dataset.

Duplicate samples are also completed at each station once a year. The relative percent difference (RPD) is calculated for stream sample and duplicate sample. Sample results which are greater than five times the PQL and have a RPD greater than 25%, are flagged in the dataset.

Reporting

Reporting of RAMS data occurs once the first two cycles of sampling have been completed and then every two years following. Data are reviewed and all results with quality control concerns (e.g. data qualifiers or QC flags) are not used in any summaries. The data are analyzed as a whole in order to determine the percentage of waters meeting NC's water quality standards for C class waters.

The data for each station are also summarized in the same manner as AMS station summaries. For each station, if >10% of the results for any particular indicator exceed the applicable water quality standard, that particular stream segment may be subject to listing on the 303(d) list. More information about the listing process can be found on the Water Planning Section's

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website at <u>https://deq.nc.gov/about/divisions/water-resources/planning/modeling-assessment/water-quality-data-assessment</u>.