Association of
Metropolitan
Sewerage Agencies

June 7, 2004

Attn: Docket ID No. OW-2003-0070
Water Docket
U.S. Environmental Protection Agency
1200 Pennsylvania Ave, NW (4101T)
Washington, DC 20460
OW-Docket@epamail.epa.gov

VIA ELECTRONIC MAIL

Re: *Guidelines Establishing Test Procedures for the Analysis of Pollutants Under the Clean Water Act; National Primary Drinking Water Regulations; and National Secondary Drinking Water Regulations; Analysis and Sampling Procedures; Proposed Rule, 69 Fed. Reg. 18166 (April 6, 2004)*

Dear Sir or Madam:

The Association of Metropolitan Sewerage Agencies (AMSA)[1] is pleased to provide comments on the U.S. Environmental Protection Agency's (EPA or Agency) *Guidelines Establishing Test Procedures for the Analysis of Pollutants Under the Clean Water Act; National Primary Drinking Water Regulations; and National Secondary Drinking Water Regulations; Analysis and Sampling Procedures; Proposed Rule, (69 Fed. Reg. 18166; April 6, 2004).*

The Association petitioned the Agency in 2000 to conduct a formal rulemaking process to validate and approve Method 245.7 *Mercury in Water by Cold Vapor Atomic Fluorescence Spectrometry* as an alternative to EPA Method 1631 for the analysis of low-level mercury. AMSA commends the Agency for proposing to approve Method 245.7. As stated in the Association's original petition, EPA's water program continues to put a high priority on the control of mercury and has placed particular emphasis on pollution prevention initiatives as a means to achieve some

[1] AMSA represents the interests of nearly 300 of the nation's publicly owned wastewater treatment utilities (POTWs). AMSA members serve the majority of the sewered population in the United States and collectively treat and reclaim over 18 billion gallons of wastewater every day.

of these reductions. Method 1631 was developed to support ambient water quality monitoring for low level mercury and it is extremely sensitive, costly, cumbersome and ill-suited for measuring mercury in POTW influent and for pretreatment industrial effluent monitoring. Approval of Method 245.7 will provide POTWs and other stakeholders with a less expensive and less resource intensive alternative to Method 1631, while still providing quantifiable levels of mercury.

GENERAL COMMENTS

AMSA offers the following general comments that are further detailed in the attached table.

Method Detection Limits for WET Methods

Statements are made in the docket that method detection limits (MDLs) and minimum levels of quantitation (MLs) cannot be calculated for the whole effluent toxicity (WET) methods included in this rule. However, EPA has been provided procedures by the WET Coalition outlining how MDLs for WET could be calculated. By reference, AMSA resubmits the WET Coalition's comments submitted on the WET methods proposed in 2001 (66 *Fed. Reg*. 49794; September 28, 2001) as comments on the inclusion of WET methods in this proposed rule.

MDL/ML Development Process

The proposed rule includes a procedure for calculating MDLs and MLs for promulgated methods. AMSA does not support this procedure for numerous reasons submitted as part of the docket EPA developed in 2003 (68 *Fed. Reg*. 11,770; March 12, 2003) on the MDL/ML development process. AMSA resubmits, by reference, the coalition letter it signed on August 15, 2003 outlining a number of consensus principles on MDL and ML development.

Microtox 1010

AMSA opposes the use of Microtox 1010 as a "definitive" test under any circumstances, as outlined in the attached detailed comments, and questions whether it should even be included in Part 136 for purposes of screening.

Part 136.7 Reporting Requirements

The proposed changes to Part 136.7 are unclear and appear to impose additional reporting requirements contrary to what EPA states in the preamble. AMSA strongly suggests that section 136.7(b) be clarified and section 136.7(c) be deleted as outlined in the attachment.

In addition to strongly supporting the proposed approval of Method 245.7, AMSA also supports the following proposed actions:

- Extending the temperature for sample preservation from 4^0C to 6^0C is extremely beneficial for transporting/shipping samples that must be preserved by refrigeration.

Additionally, 6^0C is more readily maintained by refrigerators that may be opened/closed frequently and/or may have large numbers of samples placed in them at one time;

- Allowing shipment of unpreserved samples for metals analyses will minimize the risk of contamination due to field preservation and eliminate potential violations of DOT shipping regulations;

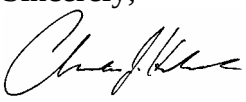
- Adopting the use of methods found in "Methods for the Determination of Metals in Environmental Samples, Supplement I" and "Methods for the Determination of Inorganic Substances in Environmental Samples" for analysis of inorganic parameters. Employing the use of more up-to-date technologies and methods with greater sensitivities is beneficial to both the permitted and laboratory communities;

- Adopting QuickChem Method 10-204-00-1-X "Digestion and Distillation of Total Cyanide in Drinking and Wastewaters using MICRO DIST and Determination of Cyanide by Flow Injection Analysis" for determination of total cyanide. The time required for distillation and the amount of hazardous waste generated will be reduced, ultimately lowering the cost per test;

- Using Standard Methods On-Line to allow immediate access to the most up-to-date methods from any PC.

If you have any questions about our comments, please contact me at 202/833-9106 or *chornback@amsa-cleanwater.org*.

Sincerely,



Chris Hornback
Director, Regulatory Affairs

ATTACHMENTS

Attachment 1 – AMSA Detailed Comments
Docket ID No. OW-2003-0070

Section	Comment
General	Statements are made in the docket that method detection limits (MDLs) and minimum levels of quantitation (MLs) cannot be calculated for the whole effluent toxicity (WET) methods included in this rule. However, EPA has been provided procedures by the WET Coalition outlining how MDLs for WET could be calculated. Statements like this do not provide the public with an accurate characterization of the uncertainty associated with the current WET methods and mislead them to think that accuracy is not an issue for stakeholders. By reference, AMSA submits all of the WET Coalition's comments submitted on the WET methods proposed in 2001 (66 Fed. Reg. 49794; September 28, 2001) as comments on the inclusion of WET methods in this rule. The WET Coalition comments can be retrieved from the referenced docket. It should be added that the new Microtox procedure includes QC criteria for reference toxicity tests (section 9.2.7.2) that are not available in any other WET procedure currently promulgated. Such a QC element is important in determining comparability of data within and between labs, which is a data quality attribute identified by EPA guidance. The proposed Microtox method also provides a procedure to eliminate intra-test outliers; the currently promulgated WET methods do not have such a procedure. We support the use of reference toxicant test limits and intra-test outlier procedures in WET test methods and requests that EPA develop these tools for all promulgated WET methods.
General	The proposed rule includes a procedure for calculating MDLs and MLs for promulgated methods. We do not support this procedure for numerous reasons submitted as part of the docket EPA developed in 2003 (68 Fed. Reg. 11,770; March 12, 2003) on the MDL/ML development process. AMSA resubmits, by reference, the coalition letter it signed on August 15, 2003 outlining a number of consensus principles on MDL and ML development.
General	EPA does not provide definitive and quantitative criteria to judge the acceptability of new/changed methods for use in the NPDES program. Therefore, stakeholders are left without benchmarks against which new/changed methods can be compared to determine their acceptability for this use. EPA's own data quality objectives (DQO) process dictates that methods be selected based on the objectives of the study. Since EPA has not defined DQOs for the National Pollutant Discharge Elimination System (NPDES) program it is not possible to determine if the methods meet the needs of the program. EPA must develop defensible and quantitative criteria for judging the acceptability of methods for use in the NPDES program before methods can be added or changed. Further, the current methods in 40 CFR Part 136 must be compared to these criteria to determine their appropriateness for this program.
III.A.1.b.	*Cyanide Microdistillation* Lachat Instrument's method of cyanide analysis by MICRO DIST and flow injection analysis has been used by an AMSA member for over a year. They have found that the method provides results comparable to current EPA methods. The low volume of sample required and the multi-sample digestion block allows for more throughput at reduced cost. Attached is some lab data comparing, the MIDI distillation method to the MICRO DIST method for total cyanide. The MICRO DIST method produced better results. See Appendix 1. *Interferences* Some AMSA members have found that when nitrites and organics are present as interferences, that higher cyanide values may be detected in wastewater samples. It is reported that during the

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	distillation, nitrites and organics may produce cyanides, giving a false positive. This interference(s) can be eliminated by the use of sulfamic acid. For wastewater samples where nitrites are suspected it is recommended that sulfamic acid be added as a regular part of the analysis. An AMSA member agency has participated in a study comparing samples with nitrites/nitrates, with and without sulfamic acid. The results of this short study are shown in Appendix 2. The sulfamic acid reduced the cyanide results, which was attributed to the distillation process. The level or combination of organic and/or nitrites that will cause the problem and the actual minimal level of sulfamic acid needed to reduce the interference were not clear from the study.
III.A.1.c.	AMSA supports the proposed *Kelada Automated Test Methods for Total Cyanide, Acid Dissociable Cyanide, and Thiocyanate'* (Kelada-01) for measuring total cyanide and acid dissociable cyanide in drinking water and wastewater. An AMSA member agency has employed this method for many years, and has found it to be a reliable procedure with better recoveries and overall results than other methods for measuring acid dissociable cyanide in wastewaters where interferences are suspected to be present.
III.A.2	EPA requests comment on whether to approve, under 40 CFR Part 136, the Microtox 1010 method for determining acute toxicity of wastewater, receiving waters, and other aqueous samples. Responses to this question are categorized below: <u>Test reliability</u> The method states that it is a surrogate for broader aquatic communities, yet the preamble states that the method is intended to only protect bacteria. It is unclear as to which use this test is intended to fulfill; therefore the comment period will not fully provide opportunity for meaningful comment. The relationship of Microtox with response of other organisms is not predictable, so it is not an adequate surrogate for other phyla. Slopes of LC50/EC50 regressions between Microtox and WET tests using conventionally tested organisms vary widely (Ribo and Kaiser, 1983; Jung and Bitton, 1997) and can be quite different from a value of one (a slope of one suggests a direct 1:1 relationship). If the Microtox test is a surrogate, a permittee or regulator cannot determine which test is correct in predicting toxicity. Although there are papers suggesting a strong relationship between Microtox and conventional toxicity tests there are many papers that show a poor relationship (Chang et al., 1981; Jung and Bitton, 1997). Differences between conventional species and Microtox can be as high as 200x or higher (Bulich et al., 1981). This raises questions as to which test is reliable, and since EPA has not documented the accuracy of this test, neither permittees or regulators will know which test is reliable and which is not reliable. The Microtox interlab study tested the method using only the EC50 endpoint; the study cannot be used to characterize performance of the method using any other EC value or NOAEC endpoints or other similar hypothesis test endpoints. Additionally, no other endpoint can be used to characterize the quality of a sample. The interlab study examined the Microtox method under very specific and limited conditions. Therefore, information regarding performance of this method is only available when these conditions exist and information regarding performance under different conditions (test duration, for example) is unknown. This demands that any changes made to Microtox 1010 relative to the interlab study conditions must be validated in another interlab study as well as a field-lab validation study. The endpoint of this test is a “biomarker” intended to be a surrogate for other physiological

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	indicators. This endpoint has not been recognized as reliable in either the water quality criteria or NPDES program. It is premature to ask the public to comment on the use of this method in the NPDES program without much more dialogue on the reliability of such endpoints to predict instream conditions as well as determining reasonable potential and permit limits. A review of the literature does not provide evidence of adequate study to show the reliability of the Microtox tests to predict instream effects. This is a fundamental requirement of all WET methods since EPA avoids defining accuracy for these tests. This method cannot be considered for use in the NPDES program until sufficient information is made available documenting the reliability of this method to predict instream effects, particularly for marginal toxicity scenarios. Some papers suggest that the Microtox method does not accurately predict toxicity, or the lack thereof, instream (Hartwell et al., 1995; Cancilla et al., 2003). The method does not require a concentration-response relationship as one of the test acceptance criteria for determining the validity of a test. The WET Coalition submitted comments to this effect on the last proposed rule regarding the current WET methods. This relationship is critical, as acknowledged by EPA, in defining point estimate endpoints (LC50, EC50, IC25) and is an important tool in determining whether the response measured in a toxicity test is sufficiently reliable for permit-related decisions. The method cannot be used in the NPDES program without a requirement for a concentration-response relationship. The interlab study performed by AZUR environmental did not test blank or control water. Therefore, only toxic samples were tested. In fact, the report provides biased conclusions because some of the labs did not measure toxicity when the sample was supposedly toxic and these test results were not considered part of the study's results. The interlab study did not address false positive rates and no information was provided to address false positive rates. In its interlab study of WET methods to gauge false positive rates EPA tested blank waters, but this approach was not taken in this interlab study. The method cannot be adopted in 40 CFR Part 136 regulations without documenting false positive rates and providing a mechanism to quantitatively account for false positive indications of toxicity, particularly when toxicity is marginal. The interlab study is biased in testing only samples that are very toxic in contrast to those that are marginally toxic. The average EC50 for the entire study was 37.8 percent, which is by most toxicologists' standards a very significant degree of toxicity. It is a commonly known fact that variability in organism response to stress is lowest when stress significantly exceeds the organism's tolerance threshold. It would be fair to say that the vast majority of tests used in the interlab study exceeded the test organism's tolerance threshold, and therefore measures of variability in response both within and between labs are biased in representing variability for only a part of the entire scale of stress. For example, response due to exposure to the effluent E2 sample suggested lack of toxicity when the mean EC50 was 75.73%. One would expect that more of these tests would have shown no toxicity at EC50s > 80%. It is in this range that it is difficult, if not impossible, to differentiate whether responses across labs are false positives or false negatives depending on whether toxicity was measured or not, respectively. This range is where the test has difficulty differentiating real measures of response to stress from those due solely to natural response, which is the basis of the detection level concept. One could argue that EC50s somewhere between 80% and 100% have intolerable levels of uncertainty, and that one cannot be sure whether the sample is truly toxic in this range. Therefore, somewhere in this range lies the MDL for the method. This phenomenon was observed in EPA's interlab study of the C. dubia chronic toxicity test with a reference toxicant. The Microtox interlab study's use of only very toxic samples provides a biased perspective of the

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	reliability of the method; this level of reliability does not translate to lower degrees of toxicity. Therefore the reliability of the method assumed by EPA does not apply to marginally toxic samples and EPA has provided no procedure in the method to address the lack of reliability of tests suggesting marginal toxicity. The method does not adequately address the data quality attributes defined by EPA's Quality Staff, including comparability, completeness, representativeness, bias, precision and sensitivity. There must be DQIs and MQOs defined for each attribute in the method before the method can be considered for use in the NPDES program. The interlab study states "effluent sample selection, evaluation, distribution, and testing were planned to minimize data variability caused by sample toxicity variability". This statement clearly shows that the interlab study results are not representative of the results one would expect if these variables were not controlled, not unlike in the NPDES program. Permittees do not have the option of controlling all of these variables and therefore must accept the results as they are generated. Therefore the variability of the method reported in the interlab study will not represent the variability one would expect in the NPDES program. For example, the study uses only one piece of software to calculate the EC50s. However, different labs could use different statistical packages to calculate EC50s. Different statistical approaches often generate different results; this is observed consistently in the current WET NPDES program. Therefore the variability observed if this test were used in the NPDES program would likely be higher than that observed in the interlab study. The interlab study also required each participating lab to only use a pipette provided by AZUR for preparing dilutions. This is another way of minimizing variability in an unrealistic fashion when compared to conditions available to permittees. Permittees do not have the ability to control which software or pipettes are used to conduct these methods, therefore the reliability and certainty of data available to permittees will be less than that inferred by the interlab study. The interlab study report on percent completion is biased because it states that 162 tests out of 162 tests were completed and met all requirements. However the report did not acknowledge that 27 results were omitted from this statistic, making the completion rate 86% rather than 100%. Additionally, the report states that two more tests failed the acceptability criteria; therefore they were not completed according to QC of the method. This brings the completion rate down to 85%. Further the method requires that reference toxicant tests be conducted with each test and that the test response fall between limits specified in the method (section 9.2.7.2 of the method). However, the interlab study does not list this as a requirement for tests to be considered complete. This could mean that some of the tests in the interlab study did not meet a method requirement but were still considered complete. This is a significant deficiency in the interlab study and must be addressed adequately before the method can be considered for use in the NPDES program. This observation requires that all tests in the interlab study be reviewed for compliance with section 9.2.7.2 of the method and the completion rate adjusted accordingly. EPA is expected to assert that analytical precision for this test method is within the range of variability commonly observed for chemical analyses. The Agency fails to note that the adverse regulatory implications of analytical variability are significantly reduced by using detection and quantification levels to define the limits of the test's valid dynamic range. No such safety factor is applied to bioassay testing or the Microtox method and, therefore, decisions based on Microtox method results are inherently more vulnerable to error than those based on chemical-specific methods.

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	Implementation The preamble states that this test could be used in permitting if found to be the most sensitive of a suite of tests. Sensitivity is not as important in NPDES testing as reliability in predicting impact instream. EPA uses the MDL as example of a DQI for the sensitivity attribute. The MDL is defined not only by a concentration that can be measured but the uncertainty of that measurement. Information has not been provided to document the uncertainty and predictive reliability of the Microtox method in relation to surface water condition, particularly for moderate or marginal (detectable) instream toxicity scenarios. A very sensitive test may detect differences that have little or no ecological ramifications. A test may be very precise at low levels of toxicity, but if the test is inaccurate it is useless. The Technical Support Document for Water Quality-based Toxics Control (EPA, 1991) states that regulatory agencies are only bound to protect fish, invertebrates, and plants. Protection of bacterial populations is not required or even mentioned in the TSD. A decision to protect these populations is a major change in EPA policy and cannot take place without sufficient public discussion and without documentation to support it. This decision must not be made simply by adding a test to 40 CFR Part 136. EPA must first provide opportunity for open dialogue on the topic before adding bacteria to the groups of organisms to be protected by the NPDES program. The method states that accuracy cannot be determined for WET methods or the Microtox 1010 method. This is not true and unfairly biases public review of the method. Accuracy can be tested with both a properly designed field-lab validation study and comparisons of response among controls. In the latter case there must be an immeasurable negative response in the controls for the test to be accurate at low levels of toxicity. If controls provide a negative response they are not accurate within the bounds of that response in control water. The same concept applies to chemical-specific measurements; accuracy is unknown where response in controls (background) occurs. This range of concentration is typically referred to as the MDL. If Microtox were to be used in the NPDES program EPA would presumably advocate conversion of Microtox EC50s into toxic units (TUs) and then use the TSD reasonable potential approach to determine if limits are necessary and the magnitude of limits if needed. As with other WET tests this is problematic because not all TUs are equal. For example, TUs for a 15-minute test cannot be equated with a 48-hour fish test TU. The Microtox test cannot be used in the NPDES program as long as EPA continues to treat WET test data in this fashion. Further, we cannot support use of the TSD approach to permitting for any WET test, including Microtox, because of numerous issues previously presented to EPA by the WET Coalition. The method states that MDLs cannot be calculated for Microtox or other toxicity tests. This is not true and falsely biases public review. EPA has been provided methods for calculating MDLs for WET that recognize the variability within the methods and their statistical limitations (see WET Coalition comments on WET methods proposed in 2001). The Microtox 1010 test is run for 15 minutes at 15^{o}C, but both of these conditions could be unrepresentative of instream conditions and exposures. If bioluminescence changes with temperature, and temperature is > or < than 15^{o}C, one would expect the results to not be representative of instream effects. The test must be more flexible in its protocol or the use of the method must be restricted before it can be considered for use in the NPDES program.

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	If effluent must be salinity-adjusted to test, and EPA believes this is justified in marine and estuarine tests because of instream mixing of effluent and saline waters, EPA must also state in the method that one cannot test 100% effluent when that effluent is not naturally saline. In this case effluent does not exist at the tested salinity without dilution. EPA must state in the method that such a test cannot be conducted on effluent at effluent dilutions below a reasonable level, such as 70% effluent. The method must include a requirement that test results reported include 95% confidence intervals for each result before it can be considered for use in the NPDES program. Given that the accuracy of the method for each test is not determined there is much more uncertainty associated with reported toxicity test results. This uncertainty must be addressed when data is reported and the method must require it to ensure that all parties using the data understand its uncertainty. <u>Method-specific</u> The method lists possible interferences in section 4.0, but only states that specific steps to address interferences "should" or "can" be taken. If EPA uses this test in 40 CFR Part 136 for any purpose these steps must be a requirement rather than an option. This change must also occur in sections 8.5 and 8.6. The method states in section 7.2 that reference toxicants "should" be dissolved in non-toxic reconstitution solution and all WET tests with this method "should" be followed by a reference toxicant test. For use in a regulatory context these recommendations must be converted to requirements and "must" exchanged for "should". The reference toxicants suggested in the method are not recommended for use in labs when other chemicals are available and pose less risk to humans. In particular, EPA must address unnecessary exposure of pregnant women to the reference toxicants recommended for this method. This method should provide safer but comparably reliable alternatives for reference toxicants. In sections 8.1.1, 8.2 and 8.3 of the method change "should" to "must". Section 8.2 requires sample storage at 4^{o}C, yet the new regulation proposed allows sample storage up to 6^{o}C. This discrepancy must be addressed. The method requires a pH of 6.0-8.0, yet salinity-adjusted effluent pH can rise well above 8.0, sometimes as high as 9.0. The method requires a parallel test with adjusted pH if this occurs. Buffers are suggested for adjusting pH, however the current WET methods allow adjustment with CO2. The method must include this option to be consistent with the other methods and to provide an option minimizing contamination and manipulation of the sample. Section 12.2.3.2 only requires five valid data points covering two concentrations to calculate an EC50, yet the current acute WET methods require 10 data points covering five concentrations. A reliable point estimate cannot be attained with only five data points covering two concentrations. The test requirements must be consistent or exceed that of other acute WET methods and require a minimum of 10 valid data points; two valid data points for each of five dilutions. There must be criteria for reagent performance much like the TAC of other acute WET tests, otherwise users will not know if the response measured in a test is reliable between tests. EPA found such a requirement necessary for acute WET tests; it should be required with this test.

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III.A.2	EPA requests comment on the appropriateness of including a bacteriological test to measure toxicity for regulation in permits. The preamble to the rule states that bacteria are "ecologically relevant links in nutrient and energy recycling and, consequently, are generally important to assessing the health of the environment." The ecological importance of bacteria is not disputed, however EPA has provided no data or evidence that the Microtox test can predict impacts on environment health through nutrient or energy recycling. Atkinson and Switzenbaum (1986), according to Blum and Speece (1990), compared responses of Microtox bacteria to anaerobic bacteria using lab and literature data and found little correlation between the two species of bacteria. They then concluded that Microtox would not be an acceptable surrogate for anaerobic bacteria in such tests. EPA's statement and assumption require far more work before Microtox can be used in a regulatory context. The preamble also suggests that POTW pretreatment programs could use this test for rapid analysis of industrial discharges to the POTW, but EPA provides no evidence in the record that these tests are reliable predictors of impacts on plant treatment processes and can be used in this manner.
III.A.2 *Limitations*	EPA invites comment on the uses of the Microtox 1010 test to measure samples and protect water quality. The Microtox 1010 test cannot be used to represent sample quality in the NPDES program for numerous reasons presented in these comments (no MDL, no lab-field validation study, requirement to adjust salinity, etc.). Data have not been provided to show that the results of these tests can be used successfully to protect water quality. The Microtox 1010 test may be used to measure samples, but the measures themselves are unreliable as indicators of sample quality and therefore meaningless without addressing the issues raised in these comments.
III.A.2 *Use in Discharges to Marine and Estuarine Water*	EPA invites comment on whether adjusting the salinity of discharges to marine and estuarine waters inappropriately introduces a variable to the measurement of acute toxicity. Salinity adjustment of wastewater samples may change the toxic potential of a sample measured by the Microtox method. ASTM D5660-96 states that "osmotic adjustment may make some components of a wastewater less soluble, reducing concentrations in solution and altering exhibited toxic inhibition". Additionally salinity adjustment of samples will drive pH up, increasing the concentration of unionized ammonia and some dissolved metals in the sample. Since unionized ammonia and the dissolved form of metals are more toxic than other forms of ammonia or particulate metals, respectively, salinity adjustment impacts the toxicity of the sample. There is published evidence that the addition of salt alone to samples can impose toxicity independent of pH changes, perhaps due to the instability of the newly adjusted sample. Even EPA states in the preamble "the modified sample may not represent the characteristics of the actual effluent." It is clear that the salinity adjustment required of the Microtox method will inappropriately influence the toxicity measured by the method, which precludes its use in the NPDES program.
III.A.2 *Use in Discharges to Marine and Estuarine Water*	Within the context of the proposed rule (analytical methods supporting NPDES permitting activities) there is no use of the Microtox 1010 test with marine and estuarine waters that is appropriate. The method has significant shortcomings and has not been field validated.
III.A.2 *Use in Discharges to Marine and Estuarine Water*	EPA asks if the use of Microtox 1010 should be precluded where toxicity in discharges is known to be due primarily to metals and/or ammonia. This premise does not coincide with the intent of this rule and the issues with metals and ammonia completely preclude the use of the method in NPDES permitting. The methods in this rule are used, in part, to monitor the quality of wastewaters discharged to surface waters. Information regarding the quality of the discharged wastewater is then used to determine the need for permit limits. One must have representative data to adequately but fairly make this assessment. Comments submitted above clearly show that this will not be the case for metals and ammonia. Further the interlab study showed that variability associated with toxicity due to zinc was much higher than for other toxicants. This suggests that the reliability of the method with metals like zinc is compromised; making it unfit for use in any NPDES permit scenario.

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	Finally, one will not know that toxicity is due to metals and/or ammonia until a TIE is conducted. Therefore one cannot qualify the results of the Microtox tests used in reasonable potential determinations and limit derivation until after the TIE. From a permittee's perspective this information will come too late and the permittee will get a limit for Microtox before finding out that the test is inappropriate for that discharge.
III.A.2 *Use in Discharges to Marine and Estuarine Water*	EPA has asked if they should approve this proprietary test procedure and how should the Agency reflect the essential attributes of the test that are not proprietary if it promulgates a final regulation approving the procedure. EPA must not approve proprietary test procedures because the cost to permittees will no longer be determined by a competitive market but by a single entity. Publication of this method for use in the NPDES program will essentially allow the manufacturer of Microtox equipment and supplies to price these items at any level they wish independent of the actual cost to the manufacturer. This puts permittees and any regulatory agency wishing to use the method at a significant financial disadvantage.
III.A.2 *Use in Discharges to Marine and Estuarine Water*	EPA has asked if the regulated community will require additional guidance from EPA regarding the implementation of Microtox 1010 in the WET monitoring scheme. AMSA does not believe that additional guidance is needed as Microtox 1010 is not appropriate for use in any WET monitoring scheme.
III.A.2 *Use in Discharges to Marine and Estuarine Water*	EPA has asked if testing with Microtox 1010 and three other species in the currently approved WET test procedures (e.g., fish, invertebrates, and plants) should be conducted quarterly for one year to address concerns of sensitivity to metals, ammonia, and/or unidentified toxicants. We do not concur that the Microtox 1010 method be used in any fashion in the NPDES program; therefore the frequency of testing is not an issue. Again, EPA must first adequately address issues associated with implementing the current methods before it raises additional issues with a new method.
III.A.2 *Use in Discharges to Marine and Estuarine Water*	EPA has asked if there are additional bacteria-based methods that EPA should consider. We are unaware of any other such methods that meet all of the requirements of a method to be used in the NPDES program, as commented above. If other commenters suggest additional methods the issues raised herein must be addressed with those methods before they can be considered for use in the NPDES program.
III.A.3.a & Table 1B *Footnote 4*	Total Recoverable metals are addressed in Sections III.A.3.a, b and c. EPA Methods 200.7, 200.8, 200.9 and 200.2 also specify total recoverable metals. However Footnote 4 of Table 1B states that "….results of the analysis…are reported as "total" metals." Use of the term "total" metals for the digestion described in Footnote 4 is inappropriate. The term "total metal" digestion refers to the complete dissolution of all components in the sample matrix. This type of complete digestion is typically used for digestion of geological samples. The total recoverable digestion procedure found in these methods may not achieve complete dissolution, making the term "total" an incorrect usage. Additionally, NPDES permits with metals monitoring either require total recoverable and/or dissolved metals NPDES Form 2A Application specifies total recoverable metals. Use of the term "total" metals would conflict with existing permit verbiage.
III.A.3.a.	Total Recoverable Elements Digestion The described method specifies the use of HCL/HNO_3, rather than HNO_3 alone as do EPA methods 3015 (aqueous samples) and 3051 (sediments, sludges, soils, and oils) for microwave-assisted digestion. In consideration of the proposed rulemaking, it should be clarified whether the latter two methods continue to be approved digestion procedures for the analysis of wastewaters and sludges using ICP-AES technologies. Further, although the proposed method is less labor intensive, there is some concern that the use of HCL in the proposed digestion procedure will precipitate silver ions and result in lower recoveries.

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III.A.3.b.	Method 200.8 AMSA supports approval of this method. Please clarify if strontium is an approved metal for analysis at the ICP-MS level. It is missing from Table IB. Please clarify if this is an omission or if strontium is not approved.
III.A.3.d.	Method 218.6 AMSA supports approval of Method 218.6. The method has been successfully used in AMSA member laboratories; the presence of color in the samples does not appear to affect the analysis as is often the case when using colorimetric methods. However, the daily sample load that can be processed will be reduced.
III.A.3.e.	Method 300 AMSA supports the approval of Method 300.
III A. 3. h.	The 1993 and 1994 revisions of the methods listed in Table I contain specific acceptance ranges for QC. For some of the QC elements these ranges are too restrictive when these methods are used to analyze wastewater samples. The 90-110% range for LFM for method 335.4 (CN^-) and 420.4 (Phenols) does not take into account the negative bias associated with these methods in the wastewater matrix. The language for the LFM should be changed to show acceptance limits more in line with the limits in EPA 200.7 (metals by ICP). This method states: "…Compare the values to the designated LFM recovery range of 70-130% or a 3 sigma recovery range calculated…" It may be necessary to gather LFM recoveries for method 335.4 and 420.4 from laboratories to determine an applicable acceptance range, but the current 90-110% requirement is not reasonable for these two methods.
III.A.4.a	This Federal Register notice incorrectly states the MDL for EPA Method 245.7 for Mercury as 5.0ng/L. Method 245.7, published in December 2003, states the MDL as 1.8ng/L and the ML as 5.0ng/L. The currently listed MDL must be consistent with the one determined in the method validation study.
III.A.4.a	EPA is requesting comments on whether Footnote 17 of Table II should apply to EPA Method 245.7. Including this footnote with Method 245.7 is appropriate because of the similarity between Methods 245.7 and 1631, Rev. E. Both methods are used to determine mercury at low and sub-part-per-trillion levels. Both methods reference Method 1669 for clean sampling protocols. Additionally, both Methods 245.7 and 1631, Rev. E have the same contamination issues and concerns. Therefore, these methods should be treated alike for filtration and preservation requirements.
III.A.7.a.	AMSA supports EPA's goal of replacing hazardous chemicals with chemicals that are less hazardous in its approved methods. Our support for this general goal of reducing toxic hazards notwithstanding, we urge EPA to carefully consider any evidence it may receive regarding the technical acceptability of substituting copper sulfate for mercuric sulfate as a catalyst in Total Kjeldahl Nitrogen (TKN) methods. We believe that there may be circumstances under which this substitution might lead to inferior performance of the analytical test. We would prefer an approach that would allow users of these methods to retain the use of the mercuric sulfate catalyst under these circumstances. In view of the lower disposal costs of the copper sulfate alternative, we believe that those who employ TKN methods would have sufficient incentive to utilize this less toxic alternative, using the mercuric sulfate catalyst only in cases where it is necessary to achieve the desired level of performance.
III.A.7.b.	At least one AMSA member currently utilizes Hach StablCal as an alternative to formazin as the turbidity standard (using Standards Methods 2130 B). Excellent results have been obtained.
III.A.7.c.	Capillary Columns Retention times generated as part of the calibration tables should be acceptable. The retention times are updated, as required, to reflect changes in column parameters.

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III.A.7.d.	AMSA agrees with this proposed change in analytical requirements for multi-analyte methods (Target Analytes)
III.A.8.b.	AMSA agrees with EPA's proposal to delete EPA Method 625 as an approved liquid-liquid extraction procedure for dichlorobenzenes and the substitution of EPA Method 624 for this purpose for the reasons stated.
III B.2 *Changes to General Requirements* & Table II	This section proposes changing temperature requirements to make them more consistent with NELAC, which specifies 4±2 ^{0}C. The proposed change requires samples to be cooled to ≤6.00^{o}C. The expression of temperature to three significant figures is excessive, and to require laboratories to procure temperature-measuring devices that can measure to this sensitivity will be burdensome. EPA also did not provide data to support the need for confirming temperature at three significant digits, or the problems encountered if temperature exceeds 6^{o}C by 0.01 degrees, 0.02 degrees, etc. The text and Table II should be changed to show temperature requirements to be to ≤6 ^{o}C. This is consistent with the sensitivity level of the 4^{o}C t currently in effect and achievable by commonly used measurement devices. All references to ≤6.00^{o}C in Table II and it's footnotes should be changed to ≤6 ^{o}C.
III. B.2 *Requirements for Inorganic* Parameters & Table II	This section states "…fluoride will explicitly limit sample collection to polyethylene containers." However, Table II, Footnote 1 states that ' "P" is polyethylene or polytetratfluoroethylene…' EPA needs to clarify whether the polyethylene or polytetratfluoroethylene as described in "P" of Footnote 1 is appropriate or if this parameter is restricted to polyethylene containers only. If fluoride is restricted to polyethylene only, another descriptor is needed in Footnote 1.
III.B.2 *Requirements for Inorganic Parameters* & Table 1B *Footnote 21*	Clarification is needed for the preservation and holding time of hexavalent chromium when using EPA Method 218.6 and Standard Methods 3500-Cr D. Holding time can be extended to 28 days if the sodium hydroxide and ammonium sulfate buffer solution in Method 218.6 are used to preserve the sample. It does not appear that addition of these chemicals to the sample when Standard Methods 3500-Cr D is to be used for analysis would be appropriate. Specific use of these chemicals for extending the holding times and clarification of their use with Standard Methods 3500-Cr D is needed.
III.B.2 Requirements for Organics in Table 1C and Footnotes in Table II	Some AMSA members have experienced similar problems as described by other labs when using ascorbic acid as the anti-chlorinating agent in the acidified samples to extend the holding time of purgeable aromatic hydrocarbons from 7 days to 14 days. A black precipitate was formed and interfered with the analysis. Hopefully, the new anti-chlorinating agent (sodium borohydride) recommended by the EPA (in footnote #5, page 18216) will not cause any problems with acidification of the samples. EPA should present data to support the use of $NaBH_4$ as an acceptable alternative for ascorbic acid.
III.B.2 *Footnotes in Table II*	EPA has requested comment on preservation procedures that may improve total cyanide recoveries. One proposal by EPA is to reduce the sample pH and remove hydrogen sulfide by air stripping. We are concerned that significantly reducing (i.e., pH<2) sample pH may cause liberation of cyanide, yielding falsely low results. Specifications regarding the type of acid used and the minimum sample pH must be included in any protocol using air stripping as a means to remove hydrogen sulfide interferences.
Table 1A	The following methods are provided for use in the NPDES program: acute D. pulex and D. magna, acute C. leedsi, acute O. mykiss and S. fontinalis, acute M. menidia and M. peninsulae, chronic P. promelas embryo-larval survival and teratogenicity, chronic C. variegatus embryo-larval survival and teratogenicity, chronic A. bahia fecundity, chronic C. parvula, and chronic A. punctulata. None of these tests have been properly validated in the field or lab and therefore cannot be considered for use in the NPDES program. This comment also applies to any of the chronic fish growth tests and the chronic mysid growth test based on the fact that any field validation conducted was based on a

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	growth endpoint calculated differently than the procedure in the current methods. Additionally these tests do not include DQIs or MQOs for the data quality attributes identified by EPA; precluding their use in the NPDES program. Like the other WET methods in this table these tests do not require a concentration-response curve as a TAC; this is a significant shortcoming that cannot be overlooked. These tests should be removed from this regulation until these issues, as well as those provided by the WET Coalition on the WET testing rule of 2001, have been thoroughly addressed.
Table 1A	This regulation uses the IC25 approach for calculating chronic test endpoints despite the fact that the Agency has been provided with information to indicate that this approach is flawed. Specifically, the IC approach does not use all of the data in each test but only data for the two concentrations bracketing 25% effect, it does not require a concentration-response relationship, it biases IC calculation when effluent exposures out-perform control exposures, it does not always provide confidence intervals, and it tends to reduce IC values when the upper confidence interval exceeds 100% effluent. These issues must be corrected or the endpoint should be deleted from the regulation.
Table IB Parameter 48	Phenols is spelled "phenois." Correct spelling to "phenols."
Table 1B *Parameter 62*	EPA Method 272.1 is no longer available for use in the analysis of silver using FLAA. Although other methods can be used for the analysis of silver using FLAA, Method 272.1 is the only method in 40 CFR Part 136 that contains the cyanogen iodide procedure for the analysis of silver in photographic waste streams containing high concentrations of silver. Traditional hotplate digestions cause a loss of silver in these types of matrices. It is imperative that this procedure remains promulgated for use with CWA regulatory programs such as the Industrial Pretreatment Program. EPA must either keep Method 272.1 in Table 1B or include the cyanogen iodide procedure for silver analysis as a footnote to Table 1B.
Table II *Footnote 2*	The term "aliquot" is used improperly in this footnote. It appears that EPA is equating an aliquot with a grab sample during preservation. A grab sample is analyzed and a discrete value is reported. An aliquot is part of a composite sample. Aliquots are collected flow proportionally so that the composite sample will represent the effluent characteristics over a period of time. A grab sample is taken without regard to the flow rate. Therefore, a grab sample and a composite sample should be preserved within 15 minutes. An aliquot should be preserved when the compositing process is completed. This parallels EPA's clarification of holding time beginning when the composite sample is completed.
Table II Footnote 4	Please clarify what the "date of sample" collection would be under these changes for composite samples. Is the sample date the day of the first grab sample or the day of the last grab sample? EPA guidance originally specified the date of sample collection as the day the composite was started. Does this revision change that practice?
Table II *Footnote 7*	EPA proposes to modify footnote 7 to clarify that samples analyzed for dissolved metals should be filtered within 15 minutes of sample collection, as opposed to "immediately" as currently stated. This requirement would necessitate onsite (field) filtration when the samples are collected. Field filtration is more expensive and is performed under less desirable and controlled conditions. The EPA should present data to support the need for this adjustment. A statement needs to be added to this footnote regarding collection of dissolved metals using an automatic sampler. The sample should be filtered at the completion of the composite period and prior to preservation. Furthermore, there is a conflict between Footnotes 2 and 17. Footnote 17 regarding trace dissolved mercury states that "… filtering should be conducted in the laboratory if possible. If circumstances prevent overnight shipment, then the filtering should be conducted in a designated clean area in the field." Footnote 2 states to "…preserve the sample or aliquots within

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	15 minutes of collection." We have included data (Appendix 3 and Attachment 2) providing evidence that there is no statistical difference between a composite sample collected manually with each aliquot filtered and preserved, and a composite sample collected automatically with filtering and preservation performed at the end of the composite period. Clean metals sampling has many of the same associated contamination issues as EPA Methods 1631 and 245.7. Yet, these contamination issues associated with filtration and preservation are being treated in totally different manners. Requiring a permittee to filter and preserve each aliquot under the clean metals sampling process imposes a significant resource burden with no added value. This requirement is also not performance-based because quality of data is independent of the requirement in this case.
§136.7(b)	This section needs to specify that any data associated with a QC failure that is reported must be flagged to ensure the results are not used for permit compliance decisions. A clarification of the QC failure should accompany the flagged data. As noted in Paragraph (a), this data cannot be used to determine permit compliance. This section may present situations where permittees or dischargers are determined to be out of compliance with their permit due to random QC failure. There is also a possibility a permittee could be considered out of compliance if the stream being sampled shows unexpected matrix interference for a particular parameter. If MS/MSD or other sample specific QC fails, it may be necessary to dilute the sample to eliminate the interference. If this dilution results in the report limit being higher than the permit limit or if the interference cannot be removed, the data must be flagged and the permittee would be considered out of compliance even though they have made their best effort to generate valid results. There are also QC failures associated with QC acceptance limits. Though some methods specify QC limits, others do not. For these methods QC ranges are developed based on 90 to 95% percent confidence limits. Based on these limits, QC failures are expected 5 to 10 % of the time. If limits are set wide enough for a 100% pass rate, the limits are too wide and QC results cannot be used to evaluate the quality of an analytical system. Due to short holding times, or high sampling frequency (daily or weekly) required by permit it may be impossible to reanalyze or resample to meet the sampling frequency requirements if there are QC failures. If a permittees meet sampling frequency requirements, cannot resample or reanalyze but must flag data due to QC failures they should be considered in compliance with permit monitoring and frequency requirements because they have collected the samples, and have made their best effort to produce valid analytical results. Otherwise, the permittee will not be in compliance with permit sampling frequencies and the regulatory agency can conclude they are in non-compliance with permit limits per Paragraph (a).
§136.7 (c)	Paragraph (c) should be deleted as it imposes additional reporting requirements. EPA states in the preamble that they do not intend in create any new reporting requirements by adding 40 CFR 136.7. However, Paragraph (c) imposes reporting limits on the permittee. Paragraph (a) of this section clearly states the purpose of analytical testing is to demonstrate permit compliance. Permit limits are based on environmental concerns, water quality and technology based standards, not analytical capabilities. Therefore, based on Paragraph (a), the permittee should be required to report to a level that demonstrates permit compliance only.

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Appendix 1

Comparison of Cyanide Results obtained using the MIDI Distillation Unit and the MICRO DIST unit

An APG Performance sample was analyzed using the same Lachat QuikChem Flow Injection Analyzer (FIA) after being distilled using the MIDI Distillation unit and the MICRO DIST unit.

The true value of the APG Standard was 0.760 mg/L.

APG PE sample	MIDI Results (mg/L)	MICRO DIST results (mg/L)
Replicate1	0.2068	0.7387
Replicate 2	0.2416	0.6931
Replicate 3	0.3761	0.7281

Appendix 2

The Effect of Sulfamic acid on Cyanide recovery when nitrates and nitrites are present in a sample.

	Cyanide w/sulfamic	Cyanide w/o sulfamic	NO3/NO2	NO2	Ammonia
2/23/2004WW Flume 0725	0.0016	0.6439	118.98	19.78	9
2/23/2004WW Flume 1630	0.0022	0.2035	376.29	2.08	0.18
2/23/2004Flume 1015	0.0027	0.131	344.37	4.09	2.08
2/24/2004Flume 0730	0.00323	0.1605	315.89	2.15	0.25
2/24/2004Flume 1030	0.0004	0.879	347.75	11.05	0.67
2/24/2004Flume 1530	0.0042	0.7294	372.13	10.89	0.16
2/25/2004Flume 0130	0.0021	0.4648	343.97	12.68	0.12
2/25/2004Flume 1530	ND	2.3812	220.01	14.5	2.16
2/25/2004Flume 1830	ND	1.9091	352.83	19	2.21
2/26/2004Flume 0430	ND	0.9266	322.85	15.26	3.62
2/26/2004Flume 0830	0.0011	0.8898	248.6	9.49	1.2
2/26/2004Flume 1630	ND	0.0241	119.17	5.95	13.05
2/27/2004Flume 1130	ND	0.5078	387.65	13.97	0.19
2/27/2004Flume 1630	ND	1.8477	171.99	13.4	2.53
2/27/2004Flumne 0630	ND	0.4319	358.28	12.37	0.2

MDL: CN (0.005) Nitrates/Nitrites (0.5) NH3 (0.5)

The above samples were distilled with the Lachat MICRO DIST unit and analyzed using Lachat FIA instrument following Lachat's QuikChem Method 10-204-00-1-X for determining cyanide in wastewater.

Appendix 3

Application of Automated Systems for Clean Composite Sampling

Introduction

The quality of data used for regulatory purposes such as establishing wastewater permit discharge limitations and in determining the compliance status of dischargers must meet very high standards due to the legal liability of this data. The quality of trace metal data may be compromised due to contamination of samples during collection, preparation, storage and analysis. The use of clean techniques for sampling and analysis is critical to obtaining representative and accurate data.

To address these issues, an automated sampling system involving the collection of an "intermediate" composite sample was developed. The sample is split into total recoverable and dissolved fractions upon sample completion. Filtering after composite completion reduces sample labor costs, decreases the risk of sample contamination from increased sample handling, and increases the probability of obtaining a representative sample.

Though earlier studies demonstrated that dissolved metal concentrations do not change over the 24-hour time period prior to sample filtration, concerns about the accuracy of dissolved data collected in this manner continue to arise. To further address these issues, a prior study comparing dissolved metals concentrations in grab and composite samples was expanded to provide a more robust data set. Results demonstrate that automated composite sample concentrations are not significantly different than those obtained by manual grab sampling and that delays of up to 48 hours in filtration/preservation do not significantly affect the sample values.

Study Plan

Treatment 1: Grabs collected manually in which each dissolved aliquot is filtered and preserved immediately upon collection.

Treatment 2: Composite collected via automated sampler in which the dissolved sample is not filtered and preserved until after the 24 hour composite period is complete (intermediate sample is kept on ice during composite period).

Treatment 3: Composite collected via automated sampler in which the dissolved sample is not filtered and preserved until 24 hours after the 24-hour composite period is complete (for a total of 48 hours from the start of the composite period)(intermediate sample is kept on ice during composite period).

At the designated CTW sampling point for each of 3 plants, we will set-up a flow-through chamber, which will act as a reservoir for collecting automated composite samples and manual grab samples. 15 minutes prior to aliquot collection, the influent and effluent valves of the reservoir will be closed and the water will be allowed to recirculate. The automated composite system will mimic the existing clean sampling system using HDPE intermediate bottles and Teflon tubing. The grab equipment will also mimic the existing grab clean metals sampling system.

One concern is that we have quantifiable concentrations of metals in the CTW (Cd, Cr, Cu, Ni, Pb, Zn, Hg). To avoid this problem, we propose conducting sampling at 3 facilities, which should have quantifiable levels of the 7 metals.

The aliquots for both the grabs and the automated composite will be collected once every 1-hour for 4 hours. The automated composite aliquot (2 L aliquot) will be collected first immediately followed by the grab (1L aliquot) for total recoverable and dissolved metals. Samples will be collected following the established SOP's for clean metals composite and grab sampling.

The intermediate composite sample from the automated composite will be kept on ice until the sample is filtered and preserved. A subsample of the intermediate sample will be split into total recoverable and dissolved fractions and preserved immediately after the composite period has ended (24 hours after the start of the composite). An additional 24 hours later (48 hours after the start of the composite) another subsample will be split into total recoverable and dissolved fractions and preserved.

Samples will be analyzed for the above listed metals. The mean of the grab aliquots for each plant will be compared to the value obtained from the composite filtered and split 24 hours after the start of the composite period and will also be compared to the value obtained from the composite filtered 48 hours after the start of the composite period. The results will be analyzed by ANOVA.

n = 3, dependent variable = metals concentrations: immediate filtration and preservation vs. filtration and preservation 24 hours later; and immediate filtration and preservation vs. filtration and preservation 48 hours later.

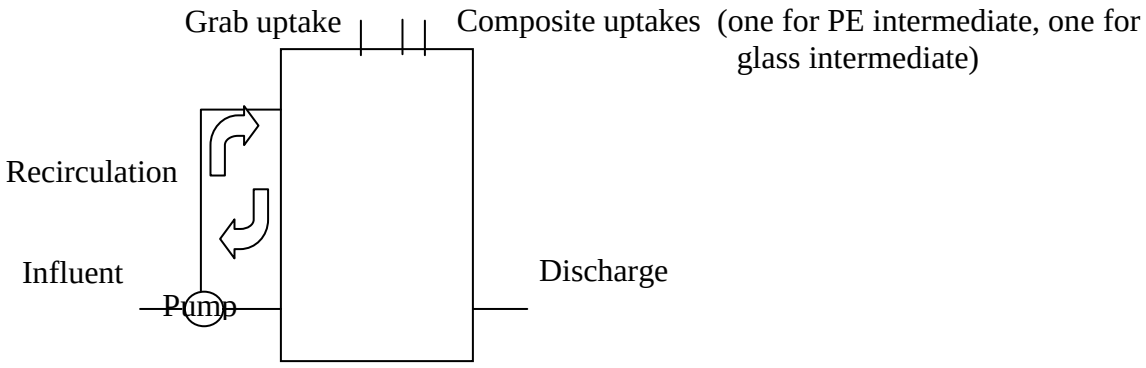
A field blank will also be subjected to the above sample handling and analyzed.

Number of samples to be analyzed for n = 3 (includes field blank) – TR and DS
Hg 1631 – 80 (includes glass intermediate plus glass intermediate FB)
Metals – 64

Conclusions

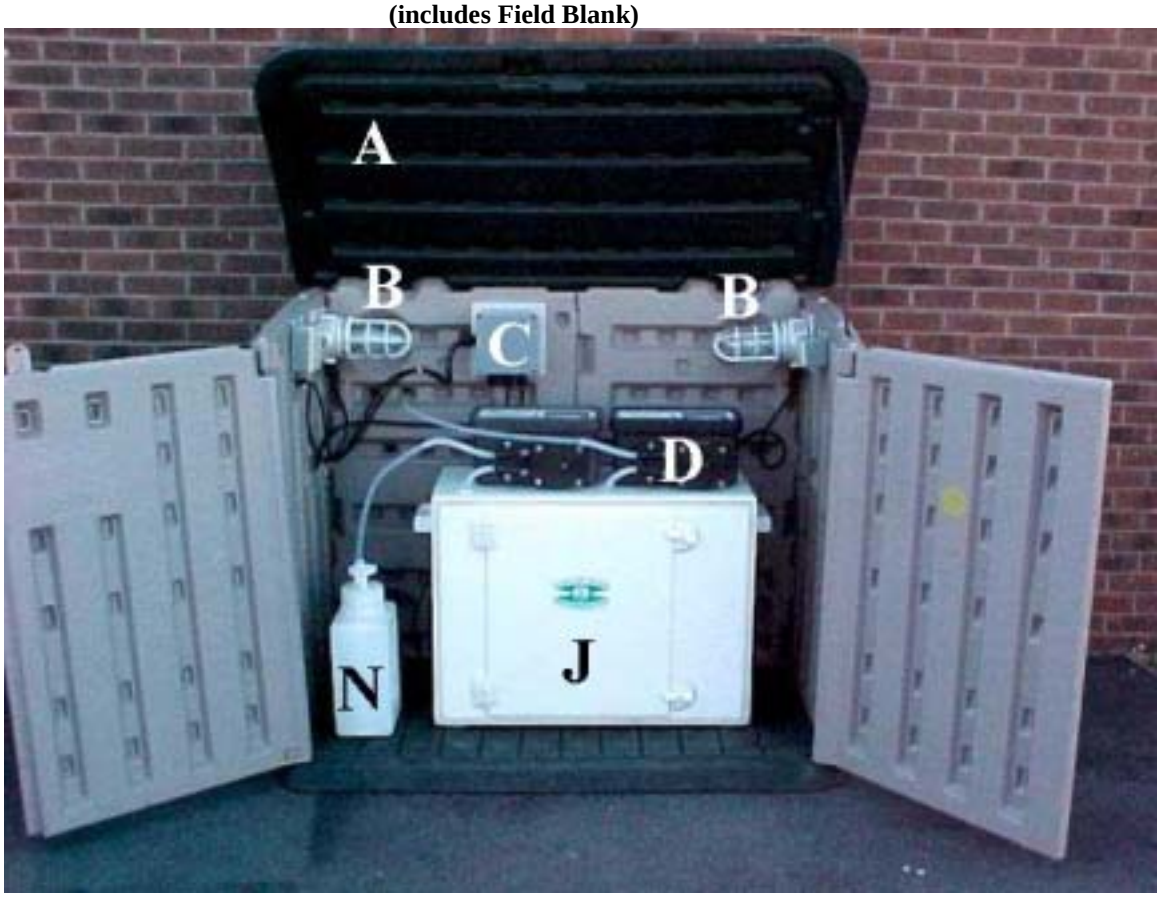
Though the power of the test comparing the 3 plants was low, the individual plant results indicate that there is no difference in dissolved metals concentrations in samples collected via automated and manual aliquots with filtration and preservation delays of up to 48 hours. Differences in concentrations seemed to relate more to sampling and analytical variability and there were no evident trends.

DIAGRAM OF RESERVOIR AT CTW (SCE)



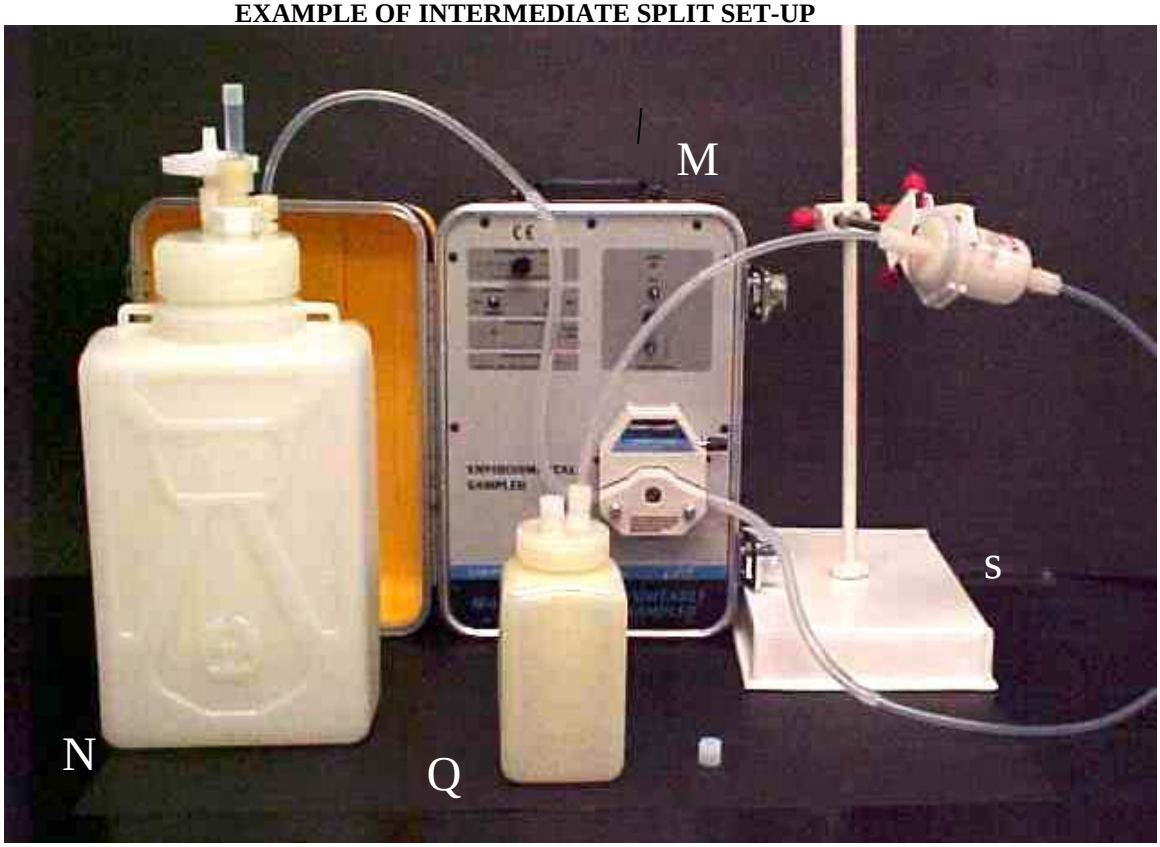
Recirculation will occur when the 3-way valve at the pump is closed to the influent.

EXAMPLE OF CLEAN COMPOSITE SET-UP
(includes Field Blank)



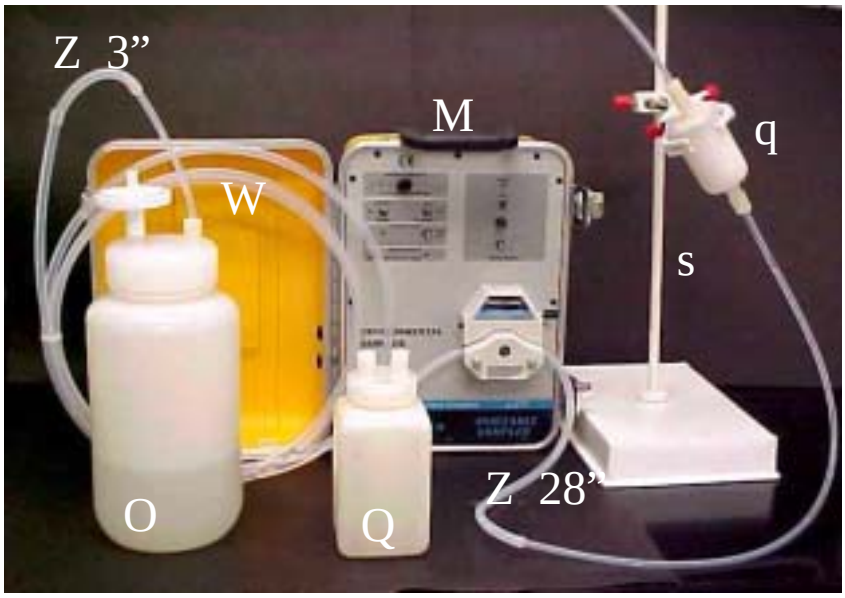
A) Rubbermaid® Hut
B) Rig-A-Lite® Assembly
C) Junction Box
D) ISCO® 3710 Controller
J) Double-wide Sampling Box
N) 2 gal HDPE bottle (Field Blank Source)

EXAMPLE OF INTERMEDIATE SPLIT SET-UP

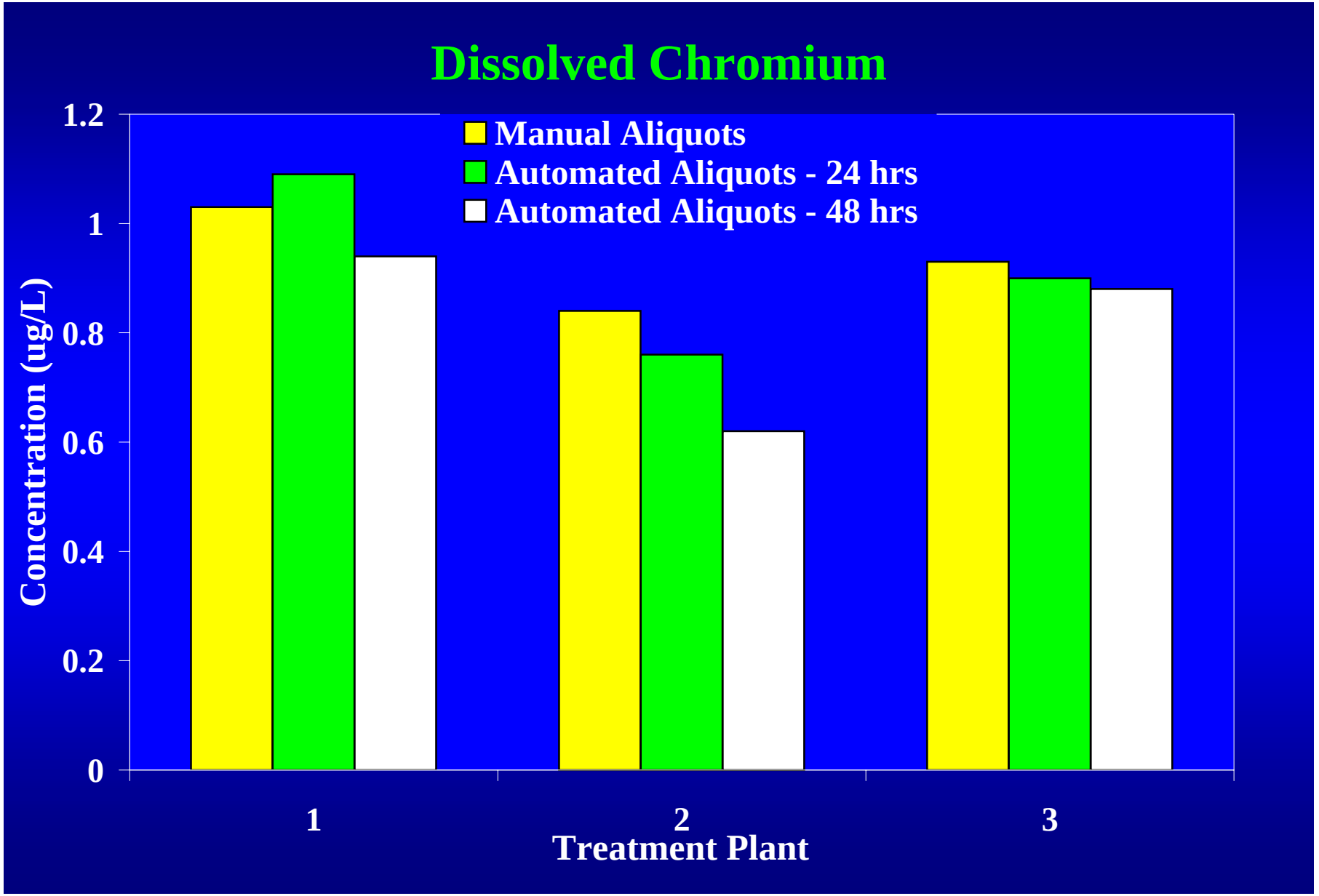


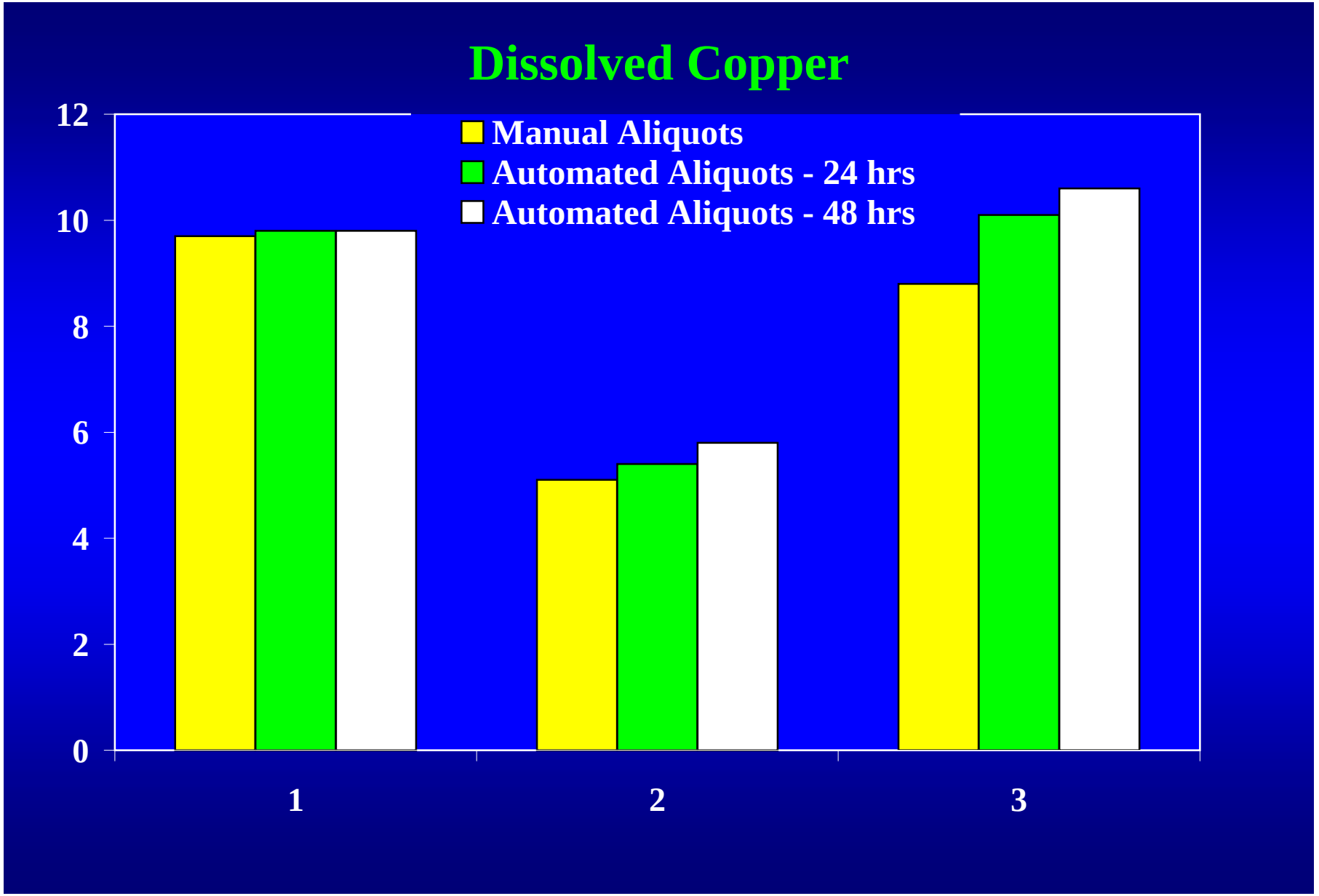
M) Masterflex® Pump
N) Intermediate 2 gal HDPE Bottle
Q)1 Liter HDPE Bottle
s) Dissolved Filter Stand Assembly

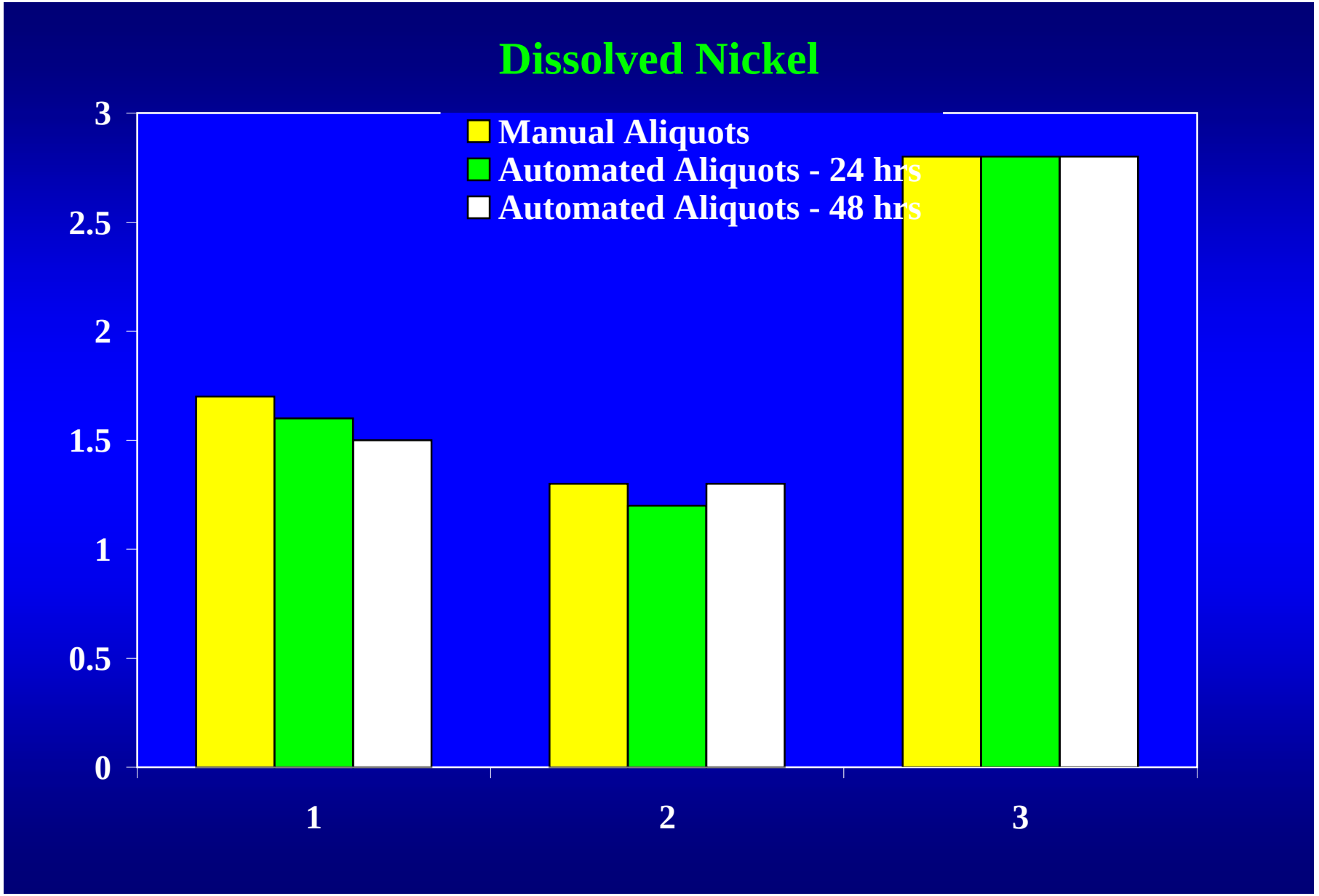
EXAMPLE OF CLEAN FIELD BLANK GRAB
(FNE set-up is similar minus the field blank source bottle)

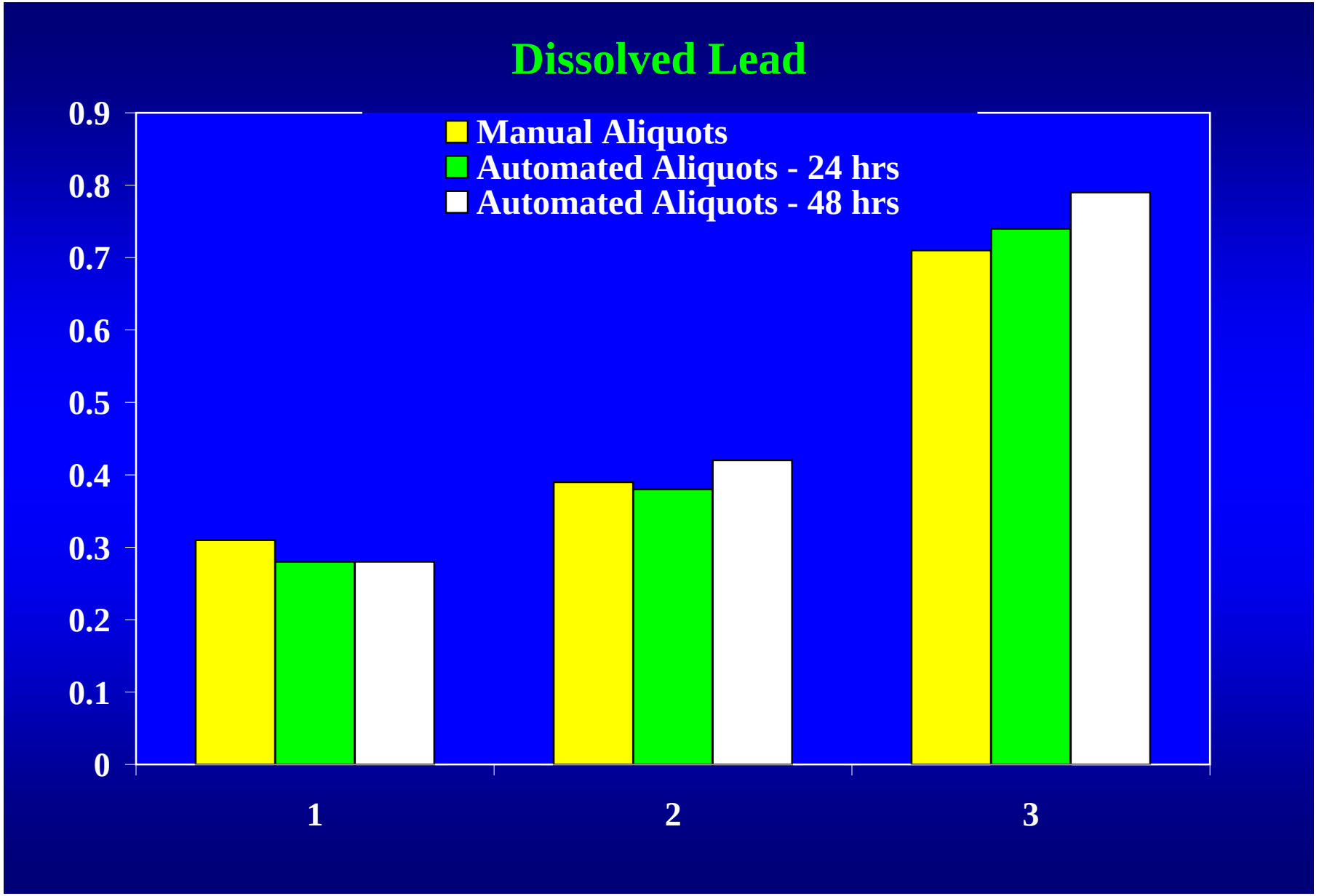


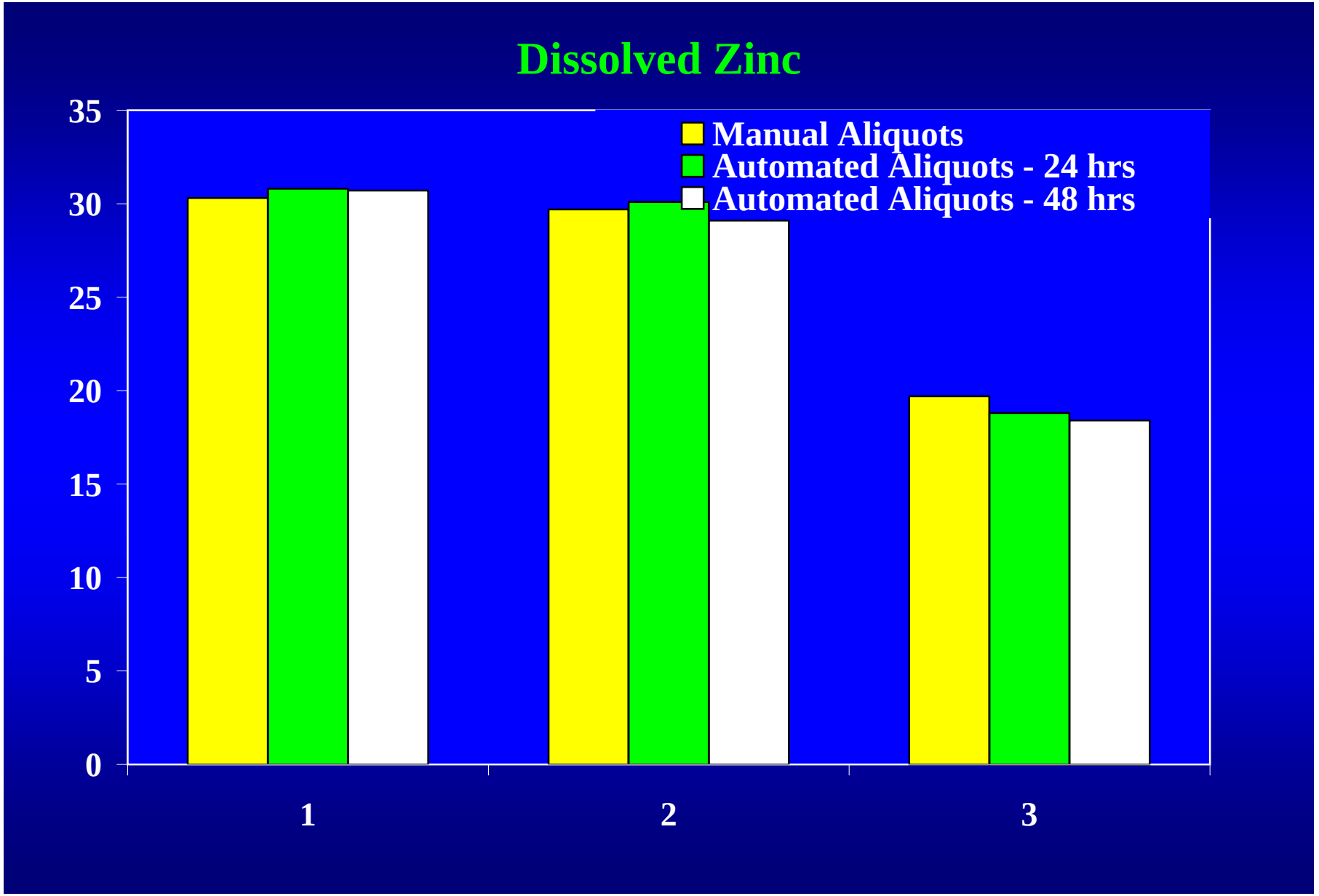
M) Masterflex® pump
O) 1 gal HDPE bottle
Q) 1 L HDPE bottle
W) 3/8” PFA tubing
Z) Masterflex® tubing
q) capsule filter (0.45µm)
s) dissolved filter support assembly


Dissolved Chromium
Manual Aliquots
Automated Aliquots - 24 hrs
Automated Aliquots - 48 hrs
Concentration (ug/L)
1.2
1
0.8
0.6
0.4
0.2
0
1
2
3
Treatment Plant


Dissolved Copper
Manual Aliquots
Automated Aliquots - 24 hrs
Automated Aliquots - 48 hrs
12
10
8
6
4
2
0
1
2
3


Dissolved Nickel
Manual Aliquots
Automated Aliquots - 24 hrs
Automated Aliquots - 48 hrs
3
2.5
2
1.5
1
0.5
0
1
2
3


Dissolved Lead
Manual Aliquots
Automated Aliquots - 24 hrs
Automated Aliquots - 48 hrs
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
1
2
3


Dissolved Zinc
35
30
25
20
15
10
5
0
1
2
3
Manual Aliquots
Automated Aliquots - 24 hrs
Automated Aliquots - 48 hrs

ANALYTICAL REPORT

Project: Special Study (Dissolved Metals Collection)
Plant: Plant 1

Parameter		DS Cd	TR Cd	DS Cr	TR Cr	DS Cu	TR Cu	DS Ni	TR Ni	DS Pb	TR Pb	DS Zn	TR Zn
Method		EPA 200.8	EPA 200.8	EPA 200.8	EPA 200.8	EPA 200.8	EPA 200.8	EPA 200.8	EPA 200.8	EPA 200.8	EPA 200.8	EPA 200.8	EPA 200.8
Units		ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L
Report Limit		0.1	0.1	0.10	0.10	0.5	0.5	0.2	0.2	0.10	0.10	1.0	1.0
Sample Code	**Date**	**Result**	**Result**	**Result**	**Result**	**Result**	**Result**	**Result**	**Result**	**Result**	**Result**	**Result**	**Result**
MANUAL GRAB 1	4/14/2004	<0.1	<0.1	1.08	0.92	10.0	8.7	1.6	1.5	0.32	0.36	29.3	27.3
MANUAL GRAB 2	4/14/2004	<0.1	<0.1	0.98	1.06	9.3	9.3	1.6	1.5	0.31	0.33	28.4	28.8
MANUAL GRAB 3	4/14/2004	<0.1	<0.1	0.98	0.97	9.7	9.8	1.7	1.6	0.30	0.34	30.5	30.7
MANUAL GRAB 4	4/14/2004	<0.1	<0.1	1.07	1.10	9.9	10.4	1.7	1.6	0.31	0.38	33.0	33.9
FIELD BLANK MANUAL GRAB 1	4/14/2004	<0.1	<0.1	0.20	0.26	<0.5	0.8	<0.2	<0.2	<0.10	<0.10	1.0	1.1
FIELD BLANK MANUAL GRAB 2	4/14/2004	<0.1	<0.1	0.24	0.26	<0.5	0.5	<0.2	<0.2	<0.10	<0.10	<1.0	1.8
FIELD BLANK MANUAL GRAB 3	4/14/2004	<0.1	<0.1	0.30	0.26	<0.5	<0.5	<0.2	<0.2	<0.10	<0.10	<1.0	1.5
FIELD BLANK MANUAL GRAB 4	4/14/2004	<0.1	<0.1	0.32	0.33	<0.5	0.6	<0.2	<0.2	<0.10	0.14	1.1	1.4
AUTOMATED COMPOSITE - 24 HOURS DELAYED FILTRATION	4/14/2004	<0.1	<0.1	1.09	1.19	9.8	12.9	1.6	1.7	0.28	0.38	30.8	32.3
AUTOMATED COMPOSITE - 48 HOURS DELAYED FILTRATION	4/14/2004	<0.1	<0.1	0.94	1.01	9.8	10.1	1.5	1.6	0.28	0.35	30.7	32.6
AUTOMATED COMPOSITE - 24 HOURS DELAYED FILTRATION	4/14/2004	<0.1	<0.1	0.34	0.31	<0.5	<0.5	<0.2	<0.2	<0.10	<0.10	1.0	1.6
AUTOMATED COMPOSITE - 48 HOURS DELAYED FILTRATION	4/14/2004	<0.1	<0.1	0.25	0.27	<0.5	<0.5	<0.2	<0.2	<0.10	<0.10	1.8	1.5

Notes

Report Limit is lowest concentration at which quantitation is demonstrated.

ANALYTICAL REPORT

Project: **Special Study (Dissolved Metals Collection)**
Plant: **Plant 2**

Parameter		DS Cd	TR Cd	DS Cr	TR Cr	DS Cu	TR Cu	DS Ni	TR Ni	DS Pb	TR Pb	DS Zn	TR Zn
Method		EPA 200.8	EPA 200.8	EPA 200.8	EPA 200.8	EPA 200.8	EPA 200.8	EPA 200.8	EPA 200.8	EPA 200.8	EPA 200.8	EPA 200.8	EPA 200.8
Units		ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L
Report Limit		0.1	0.1	0.10	0.10	0.5	0.5	0.2	0.2	0.10	0.10	1.0	1.0
Sample Code	**Date**	**Result**	**Result**	**Result**	**Result**	**Result**	**Result**	**Result**	**Result**	**Result**	**Result**	**Result**	**Result**
MANUAL GRAB 1	4/15/2004	<0.1	<0.1	0.85	0.91	5.1	7.6	1.3	1.4	0.41	0.46	31.6	35.3
MANUAL GRAB 2	4/15/2004	<0.1	<0.1	0.82	1.02	5.3	9.8	1.2	1.5	0.39	0.56	30.6	38.7
MANUAL GRAB 3	4/15/2004	<0.1	<0.1	0.93	1.06	5.0	17.5^	1.3	2.2^	0.37	1.02^	28.4	51.9^
MANUAL GRAB 4	4/15/2004	<0.1	<0.1	0.77	0.85	5.0	8.3	1.2	1.6	0.37	0.51	29.0	40.7
AUTOMATED COMPOSITE - 24 HOURS DELAYED FILTRATION	4/15/2004	<0.1	<0.1	0.76	0.77	5.4	7.9	1.2	1.2	0.38	0.40	30.1	30.5
AUTOMATED COMPOSITE - 48 HOURS DELAYED FILTRATION	4/15/2004	<0.1	<0.1	0.62	0.93	5.8	12.9#	1.3	1.4	0.42	0.82	29.1	36.0

Notes

Report Limit is lowest concentration at which quantitation is demonstrated.

Verified by analyzing an undigested sample.

^Sample redigested in replicate and spike for confirmation.

ANALYTICAL REPORT

Project: **Special Study (Dissolved Metals Collection)**
Plant: **Plant 3**

Parameter		DS Cd	TR Cd	DS Cr	TR Cr	DS Cu	TR Cu	DS Ni	TR Ni	DS Pb	TR Pb	DS Zn	TR Zn
Method		EPA 200.8	EPA 200.8	EPA 200.8	EPA 200.8	EPA 200.8	EPA 200.8	EPA 200.8	EPA 200.8	EPA 200.8	EPA 200.8	EPA 200.8	EPA 200.8
Units		ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L
Report Limit		0.1	0.1	0.10	0.10	0.5	0.5	0.2	0.2	0.10	0.10	1.0	1.0
Sample Code	**Date**	**Result**	**Result**	**Result**	**Result**	**Result**	**Result**	**Result**	**Result**	**Result**	**Result**	**Result**	**Result**
MANUAL GRAB 1	4/15/2004	<0.1	0.1	0.89	2.14*	8.3	17.6	3.0	4.5	0.68	2.08	19.2	42.9
MANUAL GRAB 2	4/15/2004	0.1	<0.1	1.02	2.14	10.4	17.8	3.1	4.6	0.79	1.95	20.6	43.9
MANUAL GRAB 3	4/15/2004	0.1	0.2	0.99	2.85	8.5	23.7^	2.8	4.9	0.73	2.39	20.4	54.3^
MANUAL GRAB 4	4/15/2004	<0.1	0.1	0.83	2.17*	7.9	18.7	2.4	3.6	0.65	1.99	18.6	43.19
AUTOMATED COMPOSITE - 24 HOURS DELAYED FILTRATION	4/15/2004	<0.1	0.1	0.90	2.19	10.1	20.7	2.8	4.4	0.74	2.07	18.8	44.7
AUTOMATED COMPOSITE - 48 HOURS DELAYED FILTRATION	4/15/2004	<0.1	0.1	0.88	2.28	10.6	20.2	2.8	4.5	0.79	2.04	18.4	47.6

Notes

Report Limit is lowest concentration at which quantitation is demonstrated.

* *Spike recoveries were out of range due to possible matrix interference.*

^Sample redigested for confirmation.

1.03	0.84	0.93		9.7	5.1	8.8		1.7	1.3	2.8		0.31	0.39	0.71	30.3	29.7	19.7
1.09	0.76	0.9		9.8	5.4	10.1		1.6	1.2	2.8		0.28	0.38	0.74	30.8	30.1	18.8
0.94	0.62	0.88		9.8	5.8	10.6		1.5	1.3	2.8		0.28	0.42	0.79	30.7	29.1	18.4