Analytical Issues Surrounding Trace Elements: Cyanide, Mercury, & Cadmium

B. Bolt

Growing concerns about unexplained cadmium, mercury, and cyanide violations at municipal wastewater treatment plants have been directing attention to the possible causes. Not only have the precision and accuracy of EPA methods used to measure these substances come under scrutiny, but quality control in sampling and laboratory procedures have also been investigated. Cyanide in particular has come to the forefront as a national issue. Research has suggested that not only might cyanide violations result from lack of quality control in analytical procedures, but also from the analytical methods themselves and/or possibly even from particular treatment steps.

Combining information from the **1997 Pretreatment Workshop and a seminar given by Dr. Howard Weinberg of UNC-Ch on 12/1/97**, the following information summarizes some of the issues and on-going research surrounding these substances.

Cyanide Issues

The three main issues surrounding cyanide (CN) level determination are:
- inconsistencies in laboratory results
- influent measurements less than effluent measurements (i.e. an apparent "production" when there should be none), and
- poor recoveries of CN in spiked influent and effluent samples.

The current *EPA standard method* (SM) is somewhat archaic; it is basically an acid distillation into a basic solution, converting collected HCN into $CNCl^-$, followed by complexation with pyridine-barbituric acid and analysis. This method can only process one sample at a time, at a rate of about 3 hours per sample!

At the Pretreatment Workshop, William Kreutzberger (CH2M Hill) discussed a study that used the *Method of Standard Additions* to investigate presence of CN in both the influent and effluent of POTWs, evaluate the efficacy of the method, evaluate variability, and determine a "quantitation" level for compliance purposes.
Highlights from Kreutzberger's presentation:
- Water Quality Standard is 5.0 µg/l (based on chronic criterion) and 22 µg/l, a daily max. based on acute criterion.
- Spikes < 15 µg/l were not measurable in *influent*; apparent interference from 5 to 50 µg/l.
- Highly variable *effluent* results in 5 to 15 µg/l range
- Apparent quantitation level is 15 to 25 µg/l. Study indicates inability to trace sources with this method and shows significant masking of CN in 5 to 50 µg/l range.

Dr. Weinberg's seminar ("Assessment of Trace Element Concentrations in Municipal Wastewater Treatment Plant Discharges in North Carolina") discussed a study which investigated a group of municipalities experiencing periodic violations of CN, Mercury (Hg), and Cadmium (Cd). (The cities of High Point, Winston-Salem, Burlington, Durham, and Charlotte were among the participants.)

The concentrations of these pollutants appeared to increase inside the plant, which was unusual, given that it seemed unlikely the substances would be formed during treatment. (As a side note, though, Weinberg admitted the researchers are no longer "as arrogant about that.") Major peaks happened once or twice a year and did not seem to be correlated with anything.

These erratic analytical results led investigators to:
- Review each facility's history of compliance

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- Ascertain current procedures used for sample collection, handling, and analysis of Cd, CN, and Hg.
- Develop workable protocol
- Test protocol on participating utilities
- Liase with EMSL and DEM for approval of protocol

Sources of CN include: water treatment sludge, cyanogenic bacteria, and metal plating industries. *Simple* cyanides are generated in the following types of reactions:

$$A(CN)_x \overset{H_2O}{\longleftrightarrow} A^{x+} + xCN^-$$

$$CN^- + H_3O^+ \longleftrightarrow HCN + H_2O$$

Complex cyanides take the form:

$A_yM(CN)_x$ e.g. $K_3Fe(CN)_6$

$[Zn(CN)_4]^{2-}$

> *where A represents an element with a positive valence number, and x and y are stoichiometric factors.*

Analytical errors:

- Sample not always dechlorinated.
- Uncertainty about preservation of samples
- Not all interference accounted for
- QA inadequate
- Extreme variability at < 10 µg/l
- Calibration curve does not take into account added preservatives or the complex make-up of the wastestream (*the calibration is based on deionized water.*)
- Known inadequacies of the distillation technique (EPA SM)

The investigators tested out a technique called Flow Injection Analysis (FIA), which can measure down to 3 µg/l. Ultimately, this technique uses a UV light to detect CN. A flow diagram below shows the design of the FIA:

an acid, base, and carrier gas are fed into a "black box," where the diffused gas goes through the process of UV digestion, and a detector senses the presence of CN. The drawback to this technique is that the FIA also measures sulfides, and sodium sulfite, sodium thiosulfite, and sodium metabisulfite are among compounds normally used to dechlorinate a waste stream. Since the detector only senses gases, however, the only sulfide compound would have to be hydrogen sulfide, which can be precipitated out at low pHs.

Role of Chlorine:

What about this mysterious "production" of CN at these plants—is it only due to the analytical methods or is there something else involved? When pre- and post-chlorination samples were compared, post-chlorination levels of CN were higher when measured with several different methods. Researchers also noticed that CN problems at facilities that changed from chlorination to UV disinfection disappeared "overnight." This observation led to a more careful look at chlorine chemistry:

$$NaCN + Cl_2 \longrightarrow CNCl + NaCl$$

$$CNCl \xrightarrow{NaOH} CNO$$

$$CNO \xrightarrow{Cl_2} CO_2 + N_2 \quad \text{or} \quad CNO \xrightarrow{H^+} NH_4$$

Hypothetical reactions that may be responsible for CN production are many. Ascorbic acid (commonly known as vitamin C), for instance, can react with NO_2 to form CN. Waters that have not been sufficiently denitrified could allow this reaction to take place.

During chlorination:

Chlorine + nitrogenous organics $\longrightarrow$ $NO_2 + NO_3$

NO_2 + ascorbic acid
sugars
starch $\longrightarrow$ CN
cellulose
alcohols

Chlorine + amino acids
polypeptides $\longrightarrow$ N-chloroamines $\longrightarrow$ HCN

During Digestion:

$NO_2 + H^+$ + ketones $\longrightarrow$ oximes $\longrightarrow$ cyanohydrin

Possible Interferences:

Thiocyanates:

$$2NO_3^- + SCN^- \longrightarrow CN^- + SO_4^{2-} + 2NO$$

Cyanohydrins [e.g. $R_2C(OH)CN$]: can decompose during distillation.

Cyanide removal:

$$SO_2 + CN^- + H_2O \longrightarrow CNO^- + H_2SO_4$$

$$CNO^- + H^+ \longrightarrow (NH_4)_2CO_3$$

Conclusions so far from the team's research are:

- EPA SM and FIA methods comparable
- Recoveries can range between 0-500%
- Chlorination produces the highest apparent levels. Not present in pre-chlorinated water.
- Interferences: Both FIA and SM respond to CNCl and sulfide.

Mercury Issues

Highlights from Jeff Poupart's (Division of Pollution Prevention and Environmental Assistance) presentation at the Pretreatment Workshop:

- Most contamination comes from air pollution, not water discharges
- Dental/Medical office discharges suspected as major mercury (Hg) source
- Water Quality Standard is 0.012 µg/l, which is 17 times lower than detection
- Toxic characteristic level 0.2 mg/l (It is actually the *methyl mercury* which is bioaccumulated and is extremely toxic to organisms)
- Safe drinking water level 2 µg/l
- North Carolina is forming a workgroup of DENR Divisions to coordinate efforts and determine action options
- A recent study from Massachusetts, which concentrated on medical facilities, showed that mercury can be absorbed in biomass inside of pipes and bioaccumulate and then sloughs off, causing Hg spikes. Numerous cities in NC have intermittent Hg slugs.

Figures 1 & 2

- Strategies for reduction included: Pressure Washing; Trap Cleaning/Replacement (Costly if collected waste is hazardous); Finding out which Industrial Users (IU) discharge Hg (though treatment difficult on IU level); Test Slime.

Dr. Weinberg did not spend a whole lot of time on mercury when presenting the results of the study in which he was involved. He did mention that the lower the amount spiked into samples by the researchers (which were split and sent off to commercial, on-site, and the state's laboratories), the worse the reported % recoveries of Hg.

Cadmium Issues

Info. presented by **Dr. Weinberg** was brief:

Methods (in order of decreasing sensitivity):
- Graphite furnace AA (atomic absorption) with Zeeman background
- "   " with Deuterium background
- Flame AA with aqueous concentration

Sources of Error:
- Poor acid purity
- Variable lab grade water
- Shipped samples not preserved
- Inadequate calibration curves
- Recoveries not determined in matrix (i.e. distilled water vs. wastewater)
- Recoveries in lab grade water at ppm levels.

QA Failures:
The lower the spikes done by researchers, the worse the recoveries (same as CN).

*Overall Conclusions from **Weinberg's Presentation**:*
- QA/QC procedures now in place at Durham, Raleigh, Charlotte
- Cd, Hg: 90-110% recovery in above labs. State and other utility labs 0-200%...on same sample!
- Commercial labs: few responses to questionnaires, some incomplete

NCDENR/DIVISION OF WATER QUALITY
Water Quality Section/Point Source Branch

December 21, 1998

MEMORANDUM

To: **NPDES Unit**

Through: **Dave Goodrich**

From: **Bethany Bolt**

Subject: **Cyanide Limits and Metals Monitoring**

Various approaches to toxicant monitoring and limits have prevailed in NPDES permits in the past, resulting in inconsistencies statewide. In addition, controversies surrounding analytical methods for parameters like cyanide (CN) and mercury have complicated implementation of limits for some facilities. This memo describes our current approach to implementing toxicant monitoring and limits, including specifically CN.

Upon renewal, a permit writer determines whether or not a limit is necessary based on reasonable potential analysis. Monitoring should then be given in accordance with the table below[1]:

Toxicant Limits?	**Class I & II**	**Class III & IV**
No—Monitoring only	Monthly	2/Month
Yes—Limit	2/Month	Weekly

Monitoring should also be specified to occur in conjunction with any Whole Effluent Toxicity (WET) monitoring at the facility, so that data may be compared with future WET test results.

In light of information available regarding cyanide measurement techniques, the Division feels it is reasonable to specify the **total cyanide quantitation limit** as 10 μg/l (10 ppb). This information should be footnoted on the effluent page(s).

A daily maximum limit for CN, based on the water quality standard of 5.0 μg/l, should be given if reasonable potential exists to exceed this level. Because North Carolina has adopted standards based on *chronic* criteria, DWQ imposes a daily maximum limit to protect against *both chronic and acute* effects (a daily maximum reflects acute criteria, and a weekly average reflects chronic). Some municipalities experience periodic violations of the daily maximum limit, however, and request that their limit be moved to a weekly average—a value more reflective of the chronic basis. DWQ has agreed to modify CN limits for these facilities upon request by including a new daily maximum limit of 22 μg/l with the appropriate weekly average (the "old" daily maximum, based on the standard). 22 μg/l is one half the final acute value (½ FAV) established by EPA[2].

The process is the same (upon request) with other metals limits—except for mercury (Hg). Because this element readily converts to the extremely bioaccumulative methyl-mercury form, the ½ FAV for Hg of 2.4 μg/l has not been deemed an acceptable daily maximum limit by DWQ at this time.

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[1] Some exceptions are made (e.g., if a municipality is monitoring for a toxicant at the discharge as part of its Long Term Monitoring Plan (LTMP) just as frequently)

[2] From December 5, 1993 Memo to Instream Assessment Unit from Dave Goodrich

Some older permits may not be consistent with this practice. Previously, the ½ FAV was compared to four times the weekly average, and the more stringent of the two was chosen as the daily maximum. This method was developed to prevent a facility from violating both limits with one measurement, but DWQ is no longer utilizing this method (the rationale being that a violation of both limits is no more reprehensible than a violation of one limit with just one data point.) The ½ FAV is given directly, without taking into account dilution, because the undiluted material (appropriately) must meet acute criteria.

NCDENR/DIVISION OF WATER QUALITY
Water Quality Section/Point Source Branch

April 28, 1999

MEMORANDUM

To: **NPDES Unit, Pretreatment Unit, Point Source Compliance and Enforcement Unit, Regional Offices**

Through: **Dave Goodrich**

From: **Bethany Bolt**

Subject: **Limits and Monitoring for Cyanide and Metals**

Various approaches to toxicant monitoring and limits have prevailed in NPDES permits in the past, resulting in inconsistencies statewide. In addition, controversies surrounding analytical methods for parameters like cyanide (CN) and mercury (Hg) have complicated compliance determinations for some facilities. This memo describes and clarifies our current approach to implementing chemical specific toxicant monitoring and limits, including CN.

Determining Need for Limits and Monitoring Frequencies

Upon renewal, a permit writer determines whether or not a limit is necessary based on reasonable potential analysis (see Attachment A). The 7Q10 (summer) flow is used for calculating allowable concentrations of toxicants with aquatic life standards and human health standards that are non-carcinogenic (e.g., CN); the average flow (Q) is used for carcinogens (e.g., benzene); and 30Q2 flow is used when applying aesthetic standards (e.g., phenolic compounds). Monitoring should then be given in accordance with the table below:

Does Reasonable Potential Exist?	WWTP Classes I & II	WWTP Classes III & IV
No—Monitoring only	Monthly	2/Month
Yes—Limit	2/Month	Weekly

Monitoring should also be specified to occur in conjunction with any Whole Effluent Toxicity (WET) monitoring at the facility, so that future data may be compared with WET test results.

Exceptions to Monitoring Frequencies:

- Unless a limit applies, a municipality that already monitors for a particular toxicant as part of its Long Term Monitoring Plan (LTMP) does not need to monitor the parameter as part of the permit.
- If the past twelve (12) months of data indicate levels are below quantitation or detection limits (especially for industries), monitoring may be reduced to quarterly.

Quantitation Levels

The lowest quantifiable level of a chemical in a sample is the "quantitation level." Depending upon the sensitivity of the analytical instrument and techniques used, various quantitation levels apply for different parameters. In light of information available regarding cyanide measurement techniques, the Division feels it is reasonable to specify the **total CN quantitation level (QL)** as 10 µg/l (10 ppb). This information should be footnoted on the effluent page(s). Cyanide values reported as <10 µg/l should be considered compliant with the permit limit.

Exceptions to Quantitation Levels:

Towns such as Winston-Salem have conducted studies to demonstrate to the Division that a quantitation level other than 10 µg/l should apply. Winston-Salem invested significant effort into conducting a **thorough, site-specific study** in order to determine a QL suitable for its own wastewater.

The Division is also now specifying the **total mercury QL** as 0.2 µg/l (also footnoted on the effluent page). It is worthy to note that EPA has proposed a new method for analyzing mercury (Method 1631), which has a quantitation level (referred to by EPA as Minimum Level, or ML) of 0.0005 µg/l (0.5 ng/l). However, the Division's laboratory feels this method poses quantitation problems in complex wastewaters and has not yet accepted Method 1631 as appropriate for effluent monitoring in North Carolina (only accepted for drinking water analysis).

For reference, the following ranges of quantitation levels (referred to by our lab as "Practical Quantitation Levels," or PQLs) are achievable for these commonly monitored metals: *Cadmium* (Cd)—1-10 µg/l, *Chromium* (Cr)—5-100 µg/l, *Copper* (Cu)—2-20 µg/l, *Nickel* (Ni)—5-100 µg/l, *Lead* (Pb)—5-100 µg/l, and *Zinc* (Zn)—10-2000 µg/l. The NPDES permit only requires that the test procedure produce data below the permitted limit, if possible; therefore, laboratory QLs may vary with the facility's calculated limit.

Compliance Periods: Daily Maximum and Weekly Average Limits

In the past, a daily maximum limit for a toxicant was the only limit placed in the permit. This limit was based on the water quality standard. Because North Carolina adopted standards based on *chronic* criteria, the Division imposed a daily maximum limit to protect against *both chronic and acute* effects (a daily maximum reflects acute criteria, and a weekly average reflects chronic). Some treatment plants experience periodic violations of this daily maximum limit, however, and have requested that their limit be moved to a weekly average—a value more reflective of the chronic basis. The Division has agreed to modify toxicant limits for these facilities by including a new daily maximum limit equal to one half of the Final Acute Value (½ FAV) established by EPA[1]. The ½ FAV is given directly, without taking into account dilution, because the undiluted pollutant must meet acute criteria (i.e., the daily maximum limit must protect for an acute exposure of aquatic life to the effluent as it initially enters surface waters).

The process is different for mercury, however. Because this element readily converts to the extremely bioaccumulative methyl-mercury form, the Division has not deemed the ½ FAV for Hg (2.4 µg/l) an acceptable daily maximum limit at this time. To solidify its policy on applying limits for metals, **the Division will now consistently apply daily maximum and weekly average limits for CN and metals (except Hg) for all facilities with reasonable potential to exceed allowable concentrations.** Daily maximum limits shall be the ½ FAV, and weekly average limits shall be based on the water quality standard and dilution at the appropriate flow conditions (see mass balance in Attachment A).

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[1] From December 5, 1993 Memo to Instream Assessment Unit from Dave Goodrich (Attachment C).

Some older permits may not be consistent with this practice. Previously, the *diluted* ½ FAV was compared to four times the weekly average, and the permit writer chose the more stringent of the two as the daily maximum. The method was developed to prevent a facility from violating both limits with one measurement, but the Division no longer applies this policy (the rationale being that a violation of both limits is no more reprehensible than a violation of one limit with just one data point.)

Exceptions to Limits:

If the ½ FAV is more stringent than the weekly average limit, then only the daily maximum limit is needed. For example, the ½ FAV for lead is 33.8 μg/l. If the weekly average limit based on the water quality standard (25 μg/l) were 40 μg/l, only the daily maximum limit would be necessary for lead.

Also, when dilution modeling is performed (such as with FORTRON or Takeda), the daily maximum and/or weekly average limit may be replaced by a value determined by the model.

Hopefully this clarifies the Division's current policy for applying metals and CN limits, as well as explains most circumstances in which exceptions are made. It is our aim to more accurately represent the criteria of the standards and to specify reasonable quantitation levels for some parameters.

Cc: Coleen Sullins, DWQ
Caroline Ejimifor, U.S. EPA