

Factsheet on Approaches to Pollution Prevention for Cyanide

Introduction

Many Bay area POTWs have identified cyanide as a pollutant of concern due to the determination that there is reasonable potential for cyanide levels in effluent to cause or contribute to a water quality criteria exceedance. Cyanide levels in effluent may exceed final effluent limits resulting in the discharger requesting an interim effluent limit. This factsheet has been prepared to answer frequently asked questions about pollution prevention approaches for cyanide.

In addition, the Regional and State Water Boards have approved a site specific objective (SSO) for cyanide for San Francisco Bay. The effluent limits based on the SSO became effective on July 22, 2008, upon EPA approval. With the SSO in effect, more Bay Area POTWs will be able to comply with final effluent limits for cyanide. Even so, under the SSO implementation plan, Pollution Prevention (P2) requirements are required to address cyanide pollution prevention.

When is Cyanide considered a Pollutant of Concern for my P2 Program?

Cyanide should be included as a pollutant of concern if your NDPES permit has an interim effluent limit for cyanide, if you have exceeded your effluent limit for cyanide or if there are specific requirements in your NPDES permit requiring cyanide source control or source identification. In addition, POTWs will need to meet the requirements of the Cyanide SSO. Specific permit language regarding the SSO requirements is included in most permits adopted since mid-2006. The remaining permits will include these requirements the next time they are reissued. These requirements are discussed below.

What are the steps to identifying cyanide sources?

If cyanide is identified as a pollutant of concern for your program, the possible sources or causes include:

- Byproduct of a chlorine-based disinfection process.
- Artifact of analytical method/ preservation techniques
- Regular discharges from industrial or commercial facilities
- Intermittent or illegal slug discharges from industrial or commercial facilities

A systematic approach to determining the degree to which these potential sources warrant investigation is as follows:

- 1. Compare influent and effluent data. If influent data is not available, a monitoring program for influent should be initiated. As discussed below, influent monitoring will be required under the Cyanide Action Plan in the Cyanide SSO. If cyanide is rarely detected in the influent, this is an indication of the absence of regular discharges from upstream industrial or commercial sources. If cyanide concentrations are higher in the effluent than in the influent, this is an indication of in-plant production of cyanide as a result of the chlorination process.
- 2. Investigate analytical methods. Cyanide detection may be an artifact of the analytical method, especially the use of sodium hydroxide for preservation. Reporting levels for cyanide should be less than 3 µg/l and as low as possible.

- 3. If cyanide is detected sporadically in influent or at concentrations below effluent concentrations, it is likely that cyanide levels may be an artifact of the analytical method or generated in the treatment process.
- 4. If cyanide is detected in greater concentrations in influent than in effluent, source identification in the service area and implementation of control strategies targeting identified sources should be pursued.
- 5. Cyanide may also be the result of intermittent or illegal slug discharges that could result in an occasional 'spike' in influent and effluent cyanide levels. To reduce the potential for this type of occurrence, periodic assessment of the cyanide use by industrial or commercial dischargers should be conducted. In addition, an emergency monitoring and response plan should be developed in case such an event occurs. The Cyanide Action Plan in the staff report¹ for the Cyanide SSO includes a requirement to develop an emergency response and monitoring plan if it is determined that potential cyanide contributors exist within a discharger's service area (see 'What are the P2 requirements of the Cyanide SSO?' below).

What should I investigate in analytical methods?

Past and ongoing investigations of cyanide levels in treated effluent produced at the City of Vacaville Easterly Wastewater Treatment Plant and in other POTWs² (have shown that effluent cyanide levels determined using USEPA's standard method 335 series are prone to false positive results. Analytical results may vary based on where in the treatment process the sample is taken, on the disinfection method at the POTW, and on the presence of other compounds in the effluent that cause analytical interferences with the cyanide sample using this standard method. Sample preservation techniques appear to contribute to 'false positive' results for cyanide. POTWs, including the County Sanitation Districts of Los Angeles County and the City of Vacaville, have conducted cyanide analyses within 15 minutes of sample collection to avoid the need for sample preservation and have seen consistent reductions in cyanide levels as a result.

What if the treatment process generates cyanide?

Cyanide is a byproduct of chlorination. However, the chemistry is highly complex, involving both chemical and environmental factors in ways that are still poorly understood despite considerable research. In addition, it is not known whether the form(s) of cyanide that are measured in POTW effluents exhibit toxicity in these environments. A 3-year \$1.5 million cyanide investigation sponsored by the Water Environment Research Foundation (WERF) was completed in late 2002. Several Bay Area POTWs participated in this study which described a number of possible mechanisms for cyanide formations. While the study shed new light on analytical issues, it found no process or operational measures that could be implemented by dischargers to reduce observed cyanide levels in their effluent.

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¹ California Regional Water Quality Control Board, San Francisco Bay Region. Staff Report on Proposed Site-Specific Water Quality Objectives for Cyanide For San Francisco Bay. December 4, 2006.

² Weinberg et al. 2005; City of San Jose 2004; WERF 2003; Zheng et al. 2003; Carr et al. 1997; Wilmot et al. 1996

Focusing on cyanide creation through chlorination, some dischargers have considered switching from chlorine disinfection to alternative processes such as UV disinfection. However, the cyanide SSO concludes that:

"Available information on cyanide formation by UV disinfection is very limited at this time. The information hints that switching from chlorination to UV could reduce cyanide effluent levels, but much more investigation and full scale evaluation using very low detection limits would be needed to verify this preliminary hypothesis. (p5-35)"

If significant cyanide is detected in influent, what are some of the potential sources I should investigate?

If cyanide is detected in influent, dischargers should investigate potential sources (Table 1). The primary focus of such an investigation should be sources that use cyanide in their operations including metal finishers, jewelry manufacturing, and organic chemical, plastic and pesticide manufacturing. These facilities should also be evaluated for their potential to illicitly or accidentally discharge cyanide. Isolated instances of elevated effluent cyanide levels may be due to slug loadings from these sources.

A secondary focus would be facilities using chlorination for disinfection. Because cyanide is a byproduct of the chlorination process, it follows that chlorinated spas and pools as well as hospitals using chlorinated bleach could contribute to cyanide loading. Source identification studies by Sonoma County Water Agency found wineries, spas, and hospitals had elevated cyanide concentrations in their discharge. As a poison, cyanide is in some pest control products, so exterminators are a commercial source and residential users may use these products themselves.

Commercial and Institutional Residential Industrial Laboratories Pools Mining Steel Wineries Pesticides Metal finishing and electroplating Tree protection products Spas Petroleum Athletic clubs with pools Used motor oil Pharmaceuticals **Hospitals** Pesticide manufacture Exterminators Jewelry manufacture Vehicle service facilities **Plastics** Synthetic fibers Chemical

Table 1. Possible Sources of Cyanide in the Service Area

What are the P2 requirements in the Cyanide SSO?

The basin plan amendment for the cyanide SSO states that if cyanide effluent limits are included in an NPDES permit, the discharger shall be required to implement a monitoring and surveillance program that includes influent, effluent and receiving water monitoring. It also requires dischargers to review sources of cyanide to its influent at least once every five years and, if potential cyanide contributors are identified, a program to prevent illicit discharges to the sewer system must be developed.

Potential contributors are primarily industrial facilities that use or generate cyanide thus having the potential to accidentally discharge cyanide. Most of these facilities will be regulated by a

POTW's Pretreatment Program and inspection and monitoring requirements under the Pretreatment Program will also fill certain requirements of the Cyanide Action Plan. In addition to Pretreatment Program requirements, POTWs will be required to report inspections and other activities as they pertain to cyanide in their Annual Pollution Prevention Report and develop an Emergency Monitoring and Response Plan.

The purpose of the Emergency Monitoring and Response Plan is to prevent and/or address the impacts of illicit discharges. A key element to this plan will be WWTP influent monitoring to identify illicit discharges. There is flexibility as to the other elements of the plan.

The Cyanide Action Plan described in Section 8.4 of the staff report³ provides more detailed information on the implementation of these requirements and specific language describing the cyanide action plan will be included in all permits.

References

Carr, S., Baird, R., Lin, B. 1997. Wastewater derived interferences in cyanide analysis. Water Research. 31:7, 1543-1548.

City of San Jose. 2004 (September). Cyanide attenuation study – investigations into the fate and transport of cyanide in the wastewater treatment process at the San Jose/Santa Clara Water Pollution Control Plant and the determination of a receiving water attenuation factor for cyanide in lower South San Francisco Bay. San Jose.

Water Education Research Foundation (WERF). 2003. Cyanide formation and fate in complex effluents and its relation to water quality criteria. WERF No. 98-HHE-5. Alexandria, VA.

Weinberg, H., Cook, S., Singer, P. 2005 *Insights to false positive total cyanide measurements in wastewater plant effluents*. Water Environment Research 77:5, 491-499.

Wilmot, J., Solujic, L., Milosavljevic, E., Hendrix, J., Rader, W. 1996. Formation of thiocyanate during removal of sulfide as lead sulfide prior to cyanide determination. Analyst 121, 799-801.

Zheng A., Dzombak, D., Luthy, R., Sawyer, B., Lazouskas, W., Tata, P., Delaney, M., Zilitinkevitch, L., Sebroski, J., Swartling, R., Drop, S., Plaherty, J. 2003. *Evaluation and testing of analytical methods for cyanide species in municipal and industrial contaminated waters*. Environmental Science & Technology 37:1, 107-115.

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³ California Regional Water Quality Control Board, San Francisco Bay Region. Staff Report on Proposed Site-Specific Water Quality Objectives for Cyanide For San Francisco Bay. December 4, 2006.