Cooling Tower Monitoring and Environmental Compliance

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1. Introduction

Most of the water employed for industrial purposes is used for cooling a product or process. The availability of water in most industrialized areas and its high heat capacity have made water the favored heat transfer medium in industrial and utility type applications. Direct air cooling is finding increasing use, particularly in water deficient areas but is still far behind water in total numbers of applications and total heat transfer loading.

During recent years, the use of water for cooling has come under increasing scrutiny from both environmental and conservational points of view and as a result, cooling water use patterns are changing and will continue to do so.

From the conservational point of view, many systems pass cooling water through the plant system only once and return it to the watershed. This creates a high water withdrawal rate and adds heat to the receiving stream. On the other hand, cooling towers permit reusing water to such a large extent that most modern evaporative cooling systems reduce stream withdrawal rates by over 90% compared to once through cooling. This substantially reduces the heat input to the water streams but not to the environment, since the heat is transferred to the air.

From the environmental point of view, the particulates from the drift loss, blowdown from the cooling towers and the Volatile Organic Compounds (VOC) and Hazardous Air Pollutants (HAPs) that would leak from the heat exchangers into the cooling water systems and then be emitted to the adjacent areas need to be controlled. Especially in environmentally sensitive areas, the leakage of VOC and HAPs into cooling water systems has caused a great concern and may require hydrocarbon leakage monitoring by the regulatory agencies.

2. Inherent Cooling Water Environmental problems

Most of the evaporative types of cooling water systems consist of cooling towers of different types and heat exchangers. The common environmental problem is hydrocarbon leakage into the cooling water from the aging heat exchangers, which subsequently causes high Biological Oxygen Demand (BOD) and Chemical Oxygen Demand (COD) levels at the blowdown. Other problems are possible leaching of lumber treatment chemicals, particulate from the Total Dissolved Solids (TDS) as carryover in the drift loss; uncontrolled pH, high discharge temperature, TDS and residual chlorine in the cooling tower blowdown.

Hydrocarbon leakage could be due to the failure of tube sheets, and the rupture of exchanger tubes caused by corrosion or poor materials of construction. Depending on the size of the leaks, the leakage is normally unnoticed by operations and maintenance personnel and the plant is kept in production until the next planned turnaround. Should there be leakage in the cooling water system, the light hydrocarbons usually find their way out the cooling tower exhausts by means of air stripping which may cause air pollution problems in terms of VOC or HAPs emissions. Heavier hydrocarbons can find their way out via the cooling tower blowdown and if discharged into the public water streams can cause water pollution problems in term of high BOD, COD and priority pollutants levels at the outfall.

In most of the refinery plants that usually handle heavier hydrocarbon chemicals and involve multiple plant units, the cooling tower blowdown is usually collected and treated with other wastewater streams before discharged to the outfall. Volatile hydrocarbons considered as fugitive VOC emissions sometimes are unavoidable due to an unexpected heat exchanger leakage and may find their way out via the cooling tower exhausts. Chemical plants handling lighter chemicals are usually considered cleaner plants and usually discharge their cooling tower blowdown directly into the outfall without treatment.

Particulates resulting from the TDS in the drift loss containing salts and minerals, once being dried in the ambient air will become very fine particulates, which are usually smaller than 10 micron in size. They could have some impact on sensitive areas in terms of PM_{10} and $PM_{2.5}$ regulations concerning their impact on the local vegetation, soil contamination, and hazards to personnel, automobiles, and plant equipment. Visible steam plumes from the cooling tower exhaust stacks if not controlled may also impact on the visibility of the nearby air and ground transportation vehicles.

Other cooling tower problems are the free oil and grease (O&G) leaked from the exchangers handling the hydrocarbons and need to be skimmed off in the cooling tower basin. Sludge build up from the suspended solids containing in the makeup raw water, ambient air scrubbing, algae, and piping corrosion products could be contaminated by leaking hydrocarbons and free O&G and accumulated in the bottom of the cooling tower basin and pump sump. Such contaminated oily sludge may become hazardous and must be collected and disposed of in a sound environmental manner. Changes in environmental rules, such as Resource Conservation Recovery Act (RCRA) and the 1990 Clean Air Act Amendment, NESHAPS and HON rules have forced the plant management and the Design Engineers to change the old way of using

treatment chemicals, engineering concepts, disposal methods, and testing and monitoring programs.

During cooling tower operation, pH of the cooling water overtime will increase due to the addition of water treatment chemicals, increase of alkalinity while operating at higher cycles, and adding CO₂ from scrubbing ambient air. Therefore, in most of the cases, acid is added to the tower basin to reduce the pH to an acceptable discharge limit range at the blowdown to between 6 and 9. Residual halogens can be a problem due to the use of the non-oxidizing and oxidizing biocides for microbial controls. Most permits have a residual halogen limit.

Temperature of the cooling tower blowdown is also an environmental concern for its effects on the aquatic life in the body of water. The discharge temperature limit at the mixing zone is usually set by the Government Agency in the wastewater permit and can not be exceeded. Therefore most of the cooling water systems discharge their blowdown from the cold supply side of the cooling water system. Water plume dispersion may need to be performed to evaluate the mixing zone temperature at the cooling tower blowdown discharge.

In some countries, the total dissolved solid (TDS) concentration is also limited at the wastewater discharge and thus restrict the number of cooling tower operating cycles depending on the TDS concentration in the makeup water.

3. History of Treatment Programs

Over time, some cooling water treatment chemicals have been identified to have an adverse impact on the environment. Since then the treatment chemicals have been continuously under technological improvement to have less impact on the environment. The earliest chemical for treating recirculating cooling waters were inorganic polyphosphates and natural organic materials. This concept was to add a small amount of acid to control the stability index to a slightly scale forming value. Organic corrosion inhibitors include organic phosphorus compounds; specific synthetic polymers, organic nitrogen compounds, and long chain carboxylic acids.

The next cooling water treatment was chromate, an exceptionally reliable corrosion inhibitor. Acid was added to the system to lower the pH preventing solids from precipitating. Although chromate has done an outstanding job for years, increasing environmental concerns have brought pressure on research into new corrosion inhibitors with potentially less environmental impact.

By the Mid 1960s it was apparent that even the low chromate residuals employed in most chromate programs could be harmful to fish and other aquatic life. Federal, state and local regulations brought increasing pressure against the use of heavy metals like chromium and zinc. In 1971 Congress approved the National Pollution Discharge Elimination System (NPDES) which called for plants discharging into interstate water ways to file for permits with the U S Environmental Protection Agency (EPA).

The physical and chemical characteristics of the discharge were submitted; and based upon these factors and the parameters of the receiving stream, the EPA determined how much, if any, heavy metals could be contained in the discharge. Since the Act was passed into law, most states have adopted similar procedures for discharge into interstate waterways. More recently, the Federal EPA imposed a complete ban on the use of hexavalent chromium in comfort cooling towers (40 CFR Part 749 1/2/90). (3)

Subsequently, the introduction of organophosphorus compounds arrived. Organoposphours compounds do not breakdown like inorganic polyphosphates except under severe microbiological attack.

In the past, cooling water chemistry and operating parameters were analyzed by using grab samples to optimize cooling water system operation by adding inhibitors to inhibit piping and exchanger corrosion, by adding dispersants to minimize solid precipitation, and to control microbial growth by adding oxidants. The cooling system is monitored based on manual sampling and laboratory results. Most of the NPDES and wastewater permits required only infrequent grab samples for reporting purpose for pH, temperature, TSS, O&G, and COD at the blowdown or outfall. Continuous monitoring systems were seldomly used. However, online testing and sampling approaches are quickly becoming recommended, as they become more technologically available.

4. History of Regulations and Monitoring

Air emissions from cooling towers are regulated under a number of different federal laws. These laws have resulted in regulations that can require certain monitoring, air pollution controls, work practice standards, and permitting requirements for cooling towers.

During an air permitting review, the cooling tower VOC emission is required to use EPA-AP-42 emission factor for Refinery industries of 0.7 lb/MMgal of recirculating cooling water to calculate the total VOC emission if the plant does not have any acceptable specific actual plant test data. For a large cooling tower, the VOC estimate could be a very significant contributor of the total plant wide VOC emission and may be required to be verified and make corrections after a test program identifies the true baseline level of emission during plant operation. Some of these laws and the resulting regulatory requirements are identified below:

<u>Prevention of Significant Deterioration (PSD) Permits:</u> The PSD permit program originated from the 1977 Clean Air Act Amendments. The PSD program is a permitting program for large new, modified, or reconstructed sources in clean air areas (areas that are in compliance with National Ambient Air Quality Standards [NAAQS]). The PSD program was intended to protect the air quality in these areas, while allowing some industrial growth and expansion.

For large new, modified, or reconstructed sources, the emissions from all sources must be evaluated, including cooling towers. Cooling towers emit PM10 and VOC's (or HAPS) and if included in a PSD review, these emission sources would be required to: (1) Install Best

Available Control Technology (BACT), and (2) Assess the impact (with air dispersion modeling) on the appropriate NAAQS. Generally, monitoring, record keeping, and reporting requirements are established in the PSD permit.

<u>Non-Attainment New Source Review (NSR) Permits:</u> The NSR permit program originated from the 1977 Clean Air Act Amendments. The NSR program is a permitting program for large new, modified, or reconstructed sources in "dirty" air areas (areas that are not in compliance with National Ambient Air Quality Standards [NAAQS]). The NSR program was intended to regulate stationary sources in non-attainment areas and to improve the air quality in these areas.

For large new, modified, or reconstructed sources, the emissions from all sources must be evaluated, including cooling towers. Cooling towers emit PM10 and VOCs (or HAPS) and if included in a NSR permit review, these emission sources would be required to: (1) Install Lowest Achievable Emission Rates (LAER), and (2) Obtain offsets for the emissions increases associated with the project. Generally, monitoring, record keeping, and reporting requirements are established in the NSR permit.

<u>Title V Operating Permits</u>: The Title V Operating Permit program originated from the 1990 Clean Air Act Amendments. The Title V Operating Permit is required for all "major" sources of air pollution, and identifies emissions limits, regulatory requirements, monitoring and record keeping provisions, and reporting requirements. For a major source that includes a cooling tower, the emissions associated with the cooling tower must be assessed and included in the Title V Operating Permit. Generally, monitoring, record keeping, and reporting requirements are established in the Title V Operating Permit.

National Emission Standards for Hazardous Air Pollutants (NESHAPS) Regulations: The NESHAPS Program originated from the 1970 Clean Air Act Amendments, and was radically changed in the 1990 Clean Air Act Amendments. The Clean Air Amendments require the Environmental Protection Agency to develop the NESHAPS regulations. One of these NESHAPS is the Hazardous Organic NESHAPS (HON), which requires the installation of Maximum Achievable Control Technology (MACT) at all affected organic chemical manufacturing facilities. The HON contains specific requirements for cooling towers, including monitoring, record keeping, and reporting provisions.

<u>Toxic Chemical Release Inventory (TRI) Reports:</u> Reporting TRI Releases on an annual basis is required by Section 313 of the Emergency Planning and Community Right-to-Know Act (EPCRA, or Title III of the Superfund Amendments and Reauthorization Act [SARA] of 1986). Reporting of annual TRI releases was intended to provide the public with information regarding releases of the identified compounds in their communities, and to assist the EPA in determining the need for additional regulations. The TRI rules include a list of chemicals and classes of chemicals that must be reported, many of which may be present in cooling water systems. For affected facilities, monitoring and assessing cooling tower emissions is required to maintain compliance with the TRI rules.

Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) Release Reports: CERCLA was passed in 1980 and requires the person in charge of a facility to immediately report any release of a hazardous substance greater than its reportable quantity (RQ) to the National Response Center (NRC). Reporting of CERCLA releases was intended to provide the public with information regarding releases of the identified compounds in their communities, and to assist the EPA in determining the need for additional regulations. The CERCLA rules include a list of chemicals and classes of chemicals that must be reported, many of which may be present in cooling water systems. For affected facilities, monitoring and assessing cooling tower emissions is required to maintain compliance with the CERCLA rules.

<u>Enforcement Provisions:</u> The Clean Air Act Amendments of 1990 included new, enhanced enforcement provisions for implementing the Clean Air Act. This includes civil penalties of up to \$25,000 per day per violation and Criminal Penalties of up to 5 years in jail, for knowingly violating a provision of the Act.

5. Present Monitoring

Due to increasing of environmental concerns and impacts of the inherent cooling tower problems, air and water discharge permits have become more stringent, and more online and in situ continuous monitoring and sampling systems to reduce potential hydrocarbon leakage, pH upset, excessive residual chlorine, temperature and organic discharge may be required.

A review of a recent air permit granted for a new petrochemical plant located in a nonattainment area, the State of Texas (TNRCC) required that the plant's cooling water system must be monitored for benzene and total organic carbon concentrations in the return cooling water. The Operator has committed in the permit application that all exchangers containing cooling water/hydrocarbons will use welded tube sheet construction to minimize possible leakage as compared to potential leakage from the bolted flanges. This additional heat exchanger design requirement thus became one of the special conditions and requirements in the approved permit.

Additionally the Operator is required to perform sampling of the cooling tower using an air stripping device and other testing as necessary to establish the pounds per hour (lb/hr) of VOC being emitted into the atmosphere from the cooling tower. The sample must be collected in a sample bag (Tedlar bag) and analyzed by gas chromatography within 24 hours of sample collection. The Permit has set a minimum detection level of the testing system, which is equivalent to 0.015 ppmw concentration in water.

The VOC concentration (ppmv) in the exhaust from the air stripping testing system or equivalent testing system and the corresponding pounds of strippable VOC per gallon of cooling water should be reported. These will be used to determine the level (either ppmv or lb/VOC/gal) at which a leak into cooling water will be assumed in the ongoing monitoring program. The appropriate equipment must be maintained so as to minimize fugitive VOC emissions from the cooling tower. The results of the monitoring and maintenance efforts must be recorded, and such records must be maintained for a period of two years. The leak shall be repaired as soon as practical but not later than 45 calendar days after the owner or operator receives results of monitoring a leak.

In addition to the above VOC sampling requirements, the operator also has to conduct daily liquid samples (analyzed by gas chromatography) on each cooling water return for benzene at a 0.013 ppmw detection limit. This sampling for benzene using a mass spectrophotometer must be conducted every month. If the analyzed cooling water detects a benzene concentration greater than 0.013 ppmw, the analyzer must be used to help determine the area of the plant site from which the leak into the cooling water system has occurred. A sampled benzene concentration of greater than 0.013 ppmw on five consecutive days shall be considered a leak.

The above special hydrocarbon leakage sampling and detection requirements will not be found in a written Federal or State regulations, but yet can be imposed by the State authority on case by case basis during the permit evaluation and approval stages, especially in an Ozone non-attainment area.

As a good engineering practice and to ensure that the hydrocarbon leakage can be detected early in a cooling water system, an on-line TOC analyzer may be installed in the common cooling water return header, and provided sample connections at different cooling water return subheaders for easy leak identification. The TOC analyzer detection limit must be set based on the TOC concentration in the raw make up water to the cooling tower. For example, if the TOC at the makeup water is 10 ppm, with 7 tower cycles operation, the maximum background TOC in the re-circulating cooling water should be about 70 ppm or less for a new non leaking cooling water system, and must be verified during system startup. Any substantial increase in TOC concentration could be due to hydrocarbon leakage from process equipment.

In addition to a TOC analyzer, an on-line pH analyzer and a conductivity meter may be installed at the cooling water return header to monitoring the tower operating cycles. The pH meter is used to control acid injection into the tower that is not only for the operation, but also ensures that the blowdown can be discharged within a permit allowable pH range of 6 to 9. Also, temperature, flow rate and residual chlorine are normally monitored at the cooling tower blowdown line before discharged to the outfall for permitting reporting purpose.

The on-line residual chlorine analyzer can be used to control the addition of de-chlorination chemicals so that the residual chlorine at the blowdown will not exceed the permitted limit at the outfall.

An Ontario Canadian refinery has installed an on-line process gas chromatograph to continuously monitor the cooling water discharge for benzene, toluene, xylene and ethyl benzene. The ability to rapidly identify even trace amounts of hydrocarbons means that corrective actions can be taken immediately. The current state-of- the art gas chromatograph can easily detect hydrocarbons in ppb range.

Westlake is a light hydrocarbon plant and it currently discharges its cooling tower blowdown to the outfall. At all of the Westlake plants the cooling tower blowdown is sampled four times a day for pH, chlorine residual, temperature and conductivity. In addition at WPT2, the newest plant, the cooling tower blowdown is continuously monitored for TOC, pH, and temperature.

Each individual plant's discharge and the combined outfall is sampled weekly for BOD, TSS, VOCs, and residual chlorine.

Typical Weekly Analytical Data

	BOD	TSS	TOC	VOC	Residual Cl	pН
Typical Total	6.72 mg/l	5.47 mg	54.21 mg/l	Non	0.138 mg/l	7.35
Outfall Data				Detectable		

Typical Daily Analytical Data

	TOC	VOC	Residual Cl	pН
Typical Cooling	70 – 80 mg/l	Non Detectable	0.2 – 0.4 ppm	7.2 - 7.8
Tower Blow				
Down Data				

6. Current Regulations

Conventional testing of cooling tower performance to assess air emissions impacts following standard EPA protocols is not feasible. The standard EPA test methods analyze the emissions across a traverse in a stack or duct, at a minimum distance from any disturbance such as a fan. This is not possible with a cooling tower, where the air discharge to the atmosphere is generally immediately after the fan.

Monitoring cooling tower performance to assess air emissions impacts can still be accomplished in several different ways. Some monitoring may be specifically required by a source's air operating permit, an air pollution regulation, or the source's NPDES water discharge permit. Some additional monitoring may be needed to ensure compliance with other laws or regulations. Site-specific issues and the propensity for cooling tower emissions or releases would determine this source specific monitoring. Some of the monitoring which may be required for a cooling tower are identified below:

<u>Total Dissolved Solids (TDS)</u>: The TDS of the cooling tower water is a surrogate monitoring parameter for PM10 emissions from cooling towers. The Environmental Protection Agency's AP-42 Emission Factor Manual identifies emission factors for most industrial sources. For PM10 emissions from cooling towers, the emission factor is a function of the circulation rate and the TDS of the cooling water. PM10 emissions or significant deviations in PM10 emissions from cooling towers on the TDS of the cooling water.

The TNRCC of Texas has developed an "Air Quality Permit Technical Guidance for Chemical Sources: Cooling Towers" and the BACT Guidelines for cooling towers monitoring of VOC and design of the tower to reduce drift. To reduce the PM10 emissions, the operators and design

engineers of the cooling towers sometime have to install a high performance mist eliminator to reduce the drift loss as low as 0.0005%. This increases the cost and operating horsepower of the cooling tower to reduce the potential future environmental impacts.

<u>Organic Loading of the Cooling Water:</u> Organic loading of the cooling water can be determined by a number of tests of the cooling water, including total HAP, total VOC, speciated HAP, total organic compound (TOC), or chemical oxygen demand (COD). These tests will identify the total organic loading or the specific chemical loading of the cooling water. As a result of the operation of the cooling tower, many of these organic compounds will be volatilized and emitted to the atmosphere.

Lower Explosive Limit (LEL) Monitoring: LEL monitors can be placed in the vicinity of the cooling tower, to monitor the cooling tower for episodic releases of combustible organic compounds. The LEL monitors would provide near real-time indication of a release from the cooling tower.

<u>Material Balance</u>: A material balance of a facility's operation can also be utilized as an indicator of large on-going releases, or large episodic releases. The material balance could indicate a significant loss in the facility, which may be a result of cooling tower emissions. The material balance method could only be utilized for large losses, due to the inefficiency of the balance.

7. Future Possible Regulations

The evolution of environmental regulation indicates that monitoring cooling tower performance will be enhanced in the future. This will be facilitated by the development of new technology. Three of these technologies are identified below, and are currently being implemented at sites in the United States. Although not specific cooling tower monitoring schemes, these technologies may assist in the monitoring of cooling tower performance in the future.

<u>Open Path FTIR Monitoring:</u> Open Path Monitoring utilizing a Fourier Transform Infrared (FTIR) technology can provide real time ambient air monitoring along an open-air path (or fence line). The open path FTIR transmits infrared (IR) light along the monitoring path to a retro-reflector mirror, which returns the IR beam back to the FTIR. Gaseous compounds present in the beam absorb IR energy at characteristic wavelengths. The amount of energy absorbed is directly proportional to the concentration of the gas. The use of this system would establish a path or fence line monitoring system, which would provide an indicator of the cooling towers performance to monitor and detect releases and emissions to the atmosphere.

<u>Open Path UV Monitoring:</u> Open Path Monitoring utilizing a ultraviolet (UV) technology can provide real time ambient air monitoring along an open-air path (or fence line). The open path UV transmits ultraviolet light along the monitoring path to a retro-reflector mirror, which returns the UV beam back to the monitor. Gaseous compounds present in the beam absorb UV energy at characteristic wavelengths. The amount of energy absorbed is directly proportional to the concentration of the gas. The use of this system would establish a path or fence line monitoring system, which would provide an indicator of the cooling towers performance to monitor and detect releases and emissions to the atmosphere.

<u>Multi-Point Species Specific Monitoring of VOCs</u>: The continuous multi point species specific monitoring of ambient air VOCs can monitor simultaneously at a large number of discrete sampling points (up to 64) for a complete mixture of identified VOCs. These on-line analyzers are based on mass spectrometry and can monitor a multi component VOC mixture in seconds, thus enabling an almost immediate detection of a leak or release to the atmosphere. The use of this system would establish a complex wide monitoring system, which would include areas around the cooling towers to monitor and detect releases and emissions to the atmosphere.

8. Summary

The objectives of sampling and monitoring requirements are to demonstrate regulation compliance, to verify effluent limitations, and to aid in implementation and correction of operational problems. With increasing awareness of the environmental concerns due to hydrocarbons in the cooling water systems, regardless of the frequency, sampling and monitoring accuracy will need to be enhanced.

The regulatory permits require a record keeping and reporting program to document compliance. Plant Operators require an easy monitoring and reporting program with decreased maintenance. The Design Engineers will have to search for state-of- the art instruments and to provide accurate on-line monitoring and sampling systems to notify operators when hydrocarbons are present in the cooling tower so that the hydrocarbons in the cooling water can be minimized. Manual sampling seems simple and inexpensive, but requires extensive labor and around the clock preparation and recording to produce reasonably accurate and representative samples. While online monitoring systems seem expensive at first, in the long run they could cost less. They generally eliminate guesswork, reduce safety hazards, lower labor costs, and produce accurate results.

The history of cooling tower monitoring and environmental compliance has progressed from minimal monitoring and environmental concern to an atmosphere of increased concern. This has resulted in a positive benefit, reduced cooling tower impact to our environment.

References

- 1. Frank N. Kemmer, The Nalco Water Handbook, 2nd Edition, McGraw-Hill Co, 1988
- 2. Betz Handbook of Industrial Water Conditioning, 9th Edition, 1991
- 3. Drew Principles of Industrial Water Treatment, 11th Edition, 1994, Drew Industrial Division,
- 4. Perry, R.H., Perry's Chemical Engineering Handbook, 6th Edition, McGraw-Hill Co, 1984