

Modeling Water Quality Impacts of Stormwater Runoff-Associated Pollutants¹

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It is a common practice in assessing water quality impacts of stormwater runoff to use hydrology-based “water quality” models to estimate total concentrations of chemical contaminants at a particular location in the runoff and/or receiving waters. Those estimates are then compared with US EPA worst-case-based water quality criteria and state water quality standards. One of the stated “Purposes” listed for the California Water Environmental Modeling Forum (discussed in Newsletter 10-8) was assessment of “water quality impacts.” However, the results of stormwater hydrology-runoff models, such as some of those discussed at the Forum workshop and in the literature, do not, in fact, properly assess water quality impacts. This is largely because they focus on total concentrations of chemicals rather than on those forms that are, or could become, available to affect water quality/beneficial uses of the receiving water.

It has been known since the 1960s that the total concentration of a potential pollutant, such as a heavy metal, pesticide, or other organic, is not a reliable indicator of the pollutant’s water quality impact or of impairment of aquatic life-related beneficial uses of a water. This is because many chemical constituents of water quality concern exist in a variety of chemical forms, only some of which are toxic or otherwise available to adversely affect beneficial uses of waterbodies/aquatic-life-related water quality. In order to reliably assess potential water quality impacts of a chemical in runoff water, it is necessary to incorporate information on the aquatic chemistry/toxicology of the potential pollutant(s) in the runoff and receiving waters. Current hydrology-based modeling efforts typically do not incorporate the availability of chemical contaminants and have limited ability to reliably relate predicted concentrations of potential pollutants in the runoff to water quality impacts of the modeled constituents.

Another problem with modeling efforts is that the predicted concentrations are compared with numeric water quality criteria/standards for assessing impacts. As part of developing the 1972 “Clean Water Act,” the US Congress dictated that the US EPA develop numeric water quality criteria that would be protective of water quality (e.g., aquatic life) in any water of the nation. That led to the development of worst-case-based water quality criteria, i.e., concentrations of available forms of contaminants to which aquatic organisms could be exposed without adverse impact.

It was recognized then, and continues to be recognized, that the use of those criteria as discharge limits applied to total concentrations of individual chemicals could lead to

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over-regulation of wastewater and stormwater discharges. It is also recognized that in many situations there is need to make site-specific adjustments of the national water quality criteria to account for the aquatic chemistry and toxicology of potential pollutants that cause them to be less toxic/available in a particular waterbody. The US EPA has developed guidance for adjusting the worst-case-based criteria for site-specific conditions. Updated information on the US EPA Water Quality Standards Handbook is provided at <http://www.epa.gov/waterscience/standards/handbook/>.

While the guidance for implementation of Clean Water Act requirements dictate that an exceedance of an aquatic life-based criterion/standard constitutes an “impairment” of water quality, in fact, since the US EPA water quality criteria are based on worst-case conditions, application of those criteria without appropriate site-specific adjustments for the water quality characteristics of the waterbody, can readily lead to significant over-regulation of the runoff. Overall, while hydrology-based modeling approaches may have capability to model concentrations/impacts of conservative (non-reactive) chemicals such as chloride and sodium, they are rarely reliable for predicting true water quality impacts of most of the potential pollutants in urban and agricultural stormwater runoff.

Chemical Composition versus Water Quality. A fundamental error made in the water quality management field is the consideration of chemical concentrations (as typically measured by US EPA or “Standard Methods” analytical procedures) as being synonymous with “water quality.” By Clean Water Act requirements, “water quality” is assessed relative to the designated beneficial uses of a waterbody. Since it is not possible to directly translate total concentration of a chemical in either a discharge or within a waterbody to an impairment of beneficial uses, it is not appropriate to characterize a set of chemical concentration data as an assessment of water quality. While such data describe certain water characteristics, it is only when those characteristics are appropriately integrated with other information, such as chemical bioavailability and behavior, duration of organism exposure, organisms of interest, habitat characteristics, desired use of the waterbody, etc., that they can provide insight into the role of those chemical contaminants in “water quality,” i.e., their impact on beneficial uses of the waterbody.

Chemical “constituent” or “contaminant” is not synonymous with chemical “pollutant.” Chemical contaminants or constituents are only “pollutants” when they adversely impact the beneficial use of a particular waterbody (e.g., cause toxicity that affects organisms of concern, cause bioaccumulation of chemicals in edible organisms to render them unsuitable for use as food, change organism assemblages, adversely affect the character of the water for domestic water supply, etc., depending on the waterbody). This nomenclature distinction recognizes the paramount role of site-specific aquatic chemistry and toxicology/biology in water quality evaluation and more properly focuses the public and private funds available on cost-effective water quality protection and management. Focusing on chemical impacts rather than on concentrations of regulated chemicals also enables better focus on assessment of the impact of unregulated constituents, those without numeric water quality criteria/standards, that may be causing water quality impairment. The current approach of finding an exceedance of a numeric water quality

criterion/standard and then developing treatment works/control programs, without properly evaluating whether or not the exceedance is, in fact, adversely affecting beneficial uses of the waterbody, can be wasteful of public and private funds and at the same time fail to address significant water quality problems in the waterbody. This is especially true in the evaluation and management of water quality problems associated with stormwater runoff from urban and rural/agricultural areas, and in “water quality modeling.”

When these types of significant technical deficiencies in the chemical information used in water quality evaluation are brought to light, it is often claimed that the necessary chemistry and toxicology/biology/impact information is too complex to understand and model, and difficult to obtain. Thus, while recognizably unreliable for water quality assessment, using total concentrations of chemicals for water quality evaluation is comparatively cheap and easy. Some distance themselves from its unreliability by arguing that it is only for “screening” purposes. Others try to dilute its unreliability with other, often appropriate, measures in multiple-aspect assessment approaches, such as “weight-of-evidence” approaches. Still others flout its unreliability in espousing “co-occurrence” evaluation approaches, which rely on the erroneous presumption that the co-occurrence of a chemical and an “impact” in one location is evidence that the chemical “caused” the impact at that, and other, locations. While toxicity and excessive bioaccumulation are readily measurable characteristics of an aquatic ecosystem, as are the numbers, types and characteristics of aquatic life in a particular system of concern, and total concentrations of chemical constituents present in the system, the total concentration measurements often have no relationship to the impact of potential pollutants on beneficial uses. The fact remains that no matter how cheap or easy or cursory it may be, use of such approaches renders unreliable determinations – an outcome that actually heightens the concern about using such information as initial screening levels supposedly undertaken to identify and rank areas of greatest water quality concern.

The use of “co-occurrence” information, or its inclusion in more expansive evaluation approaches, is especially insidious when dealing with bedded sediments. Under this approach, the total copper, zinc, lead, and sometimes cadmium concentrations above a co-occurrence-based threshold (such as the Long and Morgan, McDonald, or similarly-developed thresholds), in bedded sediments of waters receiving urban area and highway stormwater runoff is assumed to be adverse to aquatic life. This “association” or “co-occurrence”-based identification of copper, zinc, lead and cadmium as significant “pollutants” derived from urban area and highway stormwater runoff could result in the expenditure of large amounts of public and private funds for treatment of runoff waters to remove those metals so that their concentrations do not accumulate in the sediments to levels above the “threshold” values. While that action may reduce the concentrations of those constituents in the bedded sediment, it cannot be presumed to result in improvement in sediment quality or water quality. Lee and Jones-Lee (2004) discussed how chemical information should be used in evaluating sediment quality. They emphasized the importance of appropriately incorporating aquatic chemistry information in sediment and water quality evaluations.

“Aquatic Chemistry.” There is a general lack of understanding and consideration of the importance of aquatic chemistry in water quality evaluation and management. Aquatic chemistry can be complex and not easily modeled, and requires a more in-depth understanding than many in the field possess. It can also be more challenging to explain why removal of particular “chemicals” in a situation is not warranted for water quality protection than it is to cause the development of a treatment works. That notwithstanding, it has been well-known since the late 1960s that the total concentrations of potentially toxic constituents in the water column and/or sediment is an unreliable basis for estimating the water quality impacts on the Clean Water Act-designated beneficial uses of a waterbody.

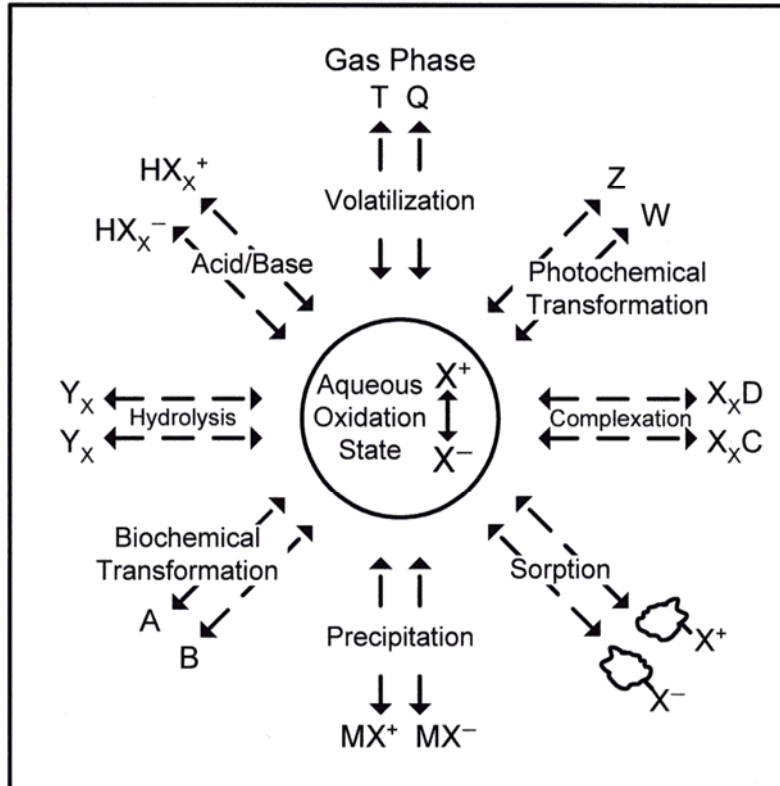
The reason that total concentrations of a selected chemical(s) are unreliable in assessing water quality/use-impairment is that many chemical constituents in aquatic systems exist in a variety of chemical forms, only some of which are toxic or otherwise available to adversely affect water quality. This is shown conceptually in the aquatic chemistry “wheel” presented in Figure 1. The forms of a chemical can have vastly different degrees of impact on the beneficial uses of a waterbody (such as aquatic life propagation or wholesomeness of aquatic life used as food). The forms in which a chemical exist in a particular aquatic system depend on the nature and levels of detoxification materials in the water and sediments. These materials, such as organic carbon, sulfides, carbonates, hydrous oxides, clay minerals, etc., react with potentially toxic forms of chemicals yielding chemical forms that are non-toxic, less toxic, or otherwise less available to aquatic life. The reactions that actually take place and the toxicity/availability of the various forms of chemicals that are created through these reactions depend on the nature of the particular contaminant as well as the characteristics of the aqueous environment being considered.

Represented at the “hub” of the wheel in Figure 1 is a chemical in its readily available state. The spokes about the hub represent reactions into which a chemical can enter in aqueous environmental settings (volatilization, photochemical transformation, complexation, adsorption and absorption, precipitation, biochemical transformation, hydrolysis, and acid/base transformation), and the resulting products formed. The bioavailability of those transformation products can be more or less than that of the available form at the hub. The extent to which a particular chemical participates in each of those reactions to generate the transformation products depends on the nature of the chemical and the characteristics of the aqueous environmental setting, and is controlled by the kinetics (rates) and thermodynamics (positions of equilibrium) of the reactions. The total concentration of a chemical includes the most available form at the hub as well as the less-available/unavailable transformation products at the spokes of the diagram. Using the total concentration of a chemical contaminant as a measure of impact presumes that all of the forms are equally and totally available.

The Stumm and Morgan (1996) graduate-level text, **Aquatic Chemistry**, provides information on the chemical issues that need to be considered in evaluating the “chemistry” of a potential pollutant in aquatic systems.

Figure 1
(Developed by G. Fred Lee, 1980)

Aquatic Chemistry of Chemical Constituents



- Distribution among Species Depends on Kinetics & Thermodynamics of Reactions in the Particular Aquatic System
- Each Chemical Species Has Its Own Toxicity Characteristics
Many Forms Are Non-Toxic

While shown simplistically in Figure 1, these reactions are often not readily modeled mathematically in a manner that accurately represents a real aquatic system. Rarely is information developed on the amounts of the active forms of detoxification components of water and/or sediments and the characteristics of the reactions that occur with the potentially toxic/available forms. Therefore, it is not possible to predict, based on typical chemical analyses, the toxic/available forms of potential pollutants such as heavy metals, selected organics, nutrients, etc., that impact the beneficial uses of a waterbody of concern to the public.

In order to try to better represent aquatic chemistry in water quality assessment, the US EPA developed the MINTEQA2 exposure assessment model. Information on that model and its use is available at, <http://www.epa.gov/ceampubl/mmedia/minteq/index.htm>.

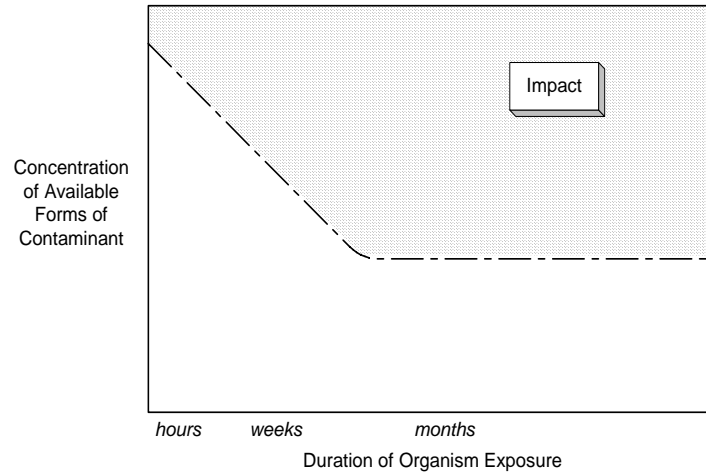
According to that US EPA website for the MINTEQ model,

“MINTEQA2 is a equilibrium speciation model that can be used to calculate the equilibrium composition of dilute aqueous solutions in the laboratory or in natural aqueous systems. The model is useful for calculating the equilibrium mass distribution among dissolved species, adsorbed species, and multiple solid phases under a variety of conditions including a gas phase with constant partial pressures. A comprehensive data base is included that is adequate for solving a broad range of problems without need for additional user-supplied equilibrium constants. The model employs a pre-defined set of components that includes free ions such as Na^+ and neutral and charged complexes (e.g., H_4SiO_4 , $\text{Cr}(\text{OH})^{2+}$). The data base of reactions is written in terms of these components as reactants. An ancillary program, PRODEFA2, serves as an interactive pre-processor to help produce the required MINTEQA2 input files.”

MINTEQA2 can be used to some extent to describe the position of equilibrium for the potential reactions that a chemical may undergo in an aqueous environmental system. However, it does not account for the kinetics of those reactions, i.e., the rates at which equilibrium is attained and hence the actual concentrations of the various forms expected in a particular system. The rates of some of the reactions that govern the distribution of the components of potential pollutants are sufficiently slow that equilibrium may not be achieved in runoff waters as they mix with receiving waters. Site-specific studies are needed to determine if this situation exists for a particular chemical and runoff situation. The MINTEQ models also do not include information on the concentration of each of the chemical species that may impact aquatic life-related beneficial uses or how the concentrations of specific chemical species change with time. Thus, while the MINTEQA2 model is useful in describing the aquatic chemistry of a constituent, it must be used in conjunction with site-specific investigations of the site to which it is being applied.

Duration of Exposure. In addition to considering the bioavailability of the chemical species present in a given aquatic system, it is necessary to consider the duration of exposure that aquatic life of concern can receive as the runoff waters mix into the receiving waters. Figure 2 illustrates the general relationship among the concentration of available chemical forms, duration of organism exposure, and laboratory toxicity measurement (“impact”). As shown, comparatively high concentrations of available forms of a toxic chemical can be tolerated by some forms of aquatic life without impact as long as the duration of exposure is sufficiently short. As the duration of exposure is increased, the concentration of available forms that can be tolerated without impact lessens until, for many chemicals, a concentration is reached to which an organism can be exposed for a lifetime or over critical life stages without adverse impact.

Figure 2
Critical Concentration/Duration of Exposure Relationship
(from Lee *et al.*, 1982a,b)



How this relationship is manifested in an aquatic environment can be influenced by the characteristics of the organisms of concern, the nature of the discharge being considered, as well as the hydrodynamics of the receiving water. Some discharges, such as stormwater runoff, are short-term and episodic in nature; organisms would be unlikely to be exposed to the discharge for a substantial duration. Mobile organisms such as fish may move in and out of an effluent/receiving water mixing area, altering the exposure it receives to contaminants in the discharge. There can be characteristics of a discharge, such as its temperature, that attract fish to it; other characteristics may repel fish. Some discharges contain some aspects that attract fish as well as others that repel them. These discharge characteristics, thus, affect the exposure a mobile organism may receive. There may also be zones of passage in a receiving water such that a mobile organism may avoid exposure altogether. To reliably model potential water quality impacts of stormwater runoff it is necessary to conduct site-specific studies of the mixing of the runoff waters with the receiving waters.

Since the concentrations of potential pollutants in runoff are typically the greatest at the point at which the runoff enters the receiving water, there is concern about whether there can be toxicity to aquatic life at or near the point of runoff entry. There is also concern about toxicity in areas outside of the mixing zone of runoff with the receiving water. The concentrations of runoff-associated contaminants in those areas are typically substantially more dilute than those in the runoff water itself. Potential impacts within the mixing zone, as well as out of the mixing zone, need to be addressed. One of the difficulties with the application of some states' regulations to stormwater runoff is that they do not allow a mixing zone for runoff-associated constituents in the receiving waters. Such a regulatory approach presumes that the concentrations in the discharge persist in the receiving water, which is rarely the case.

Overall. It is not possible to develop a simple mathematical model for water quality impacts of potential pollutants in urban stormwater runoff. The nature and availability of the actual chemical species present in the particular runoff and receiving water, as well as the site-specific, complex, and variable exposure an organism may receive in the receiving water requires that a different approach be used to evaluate the water quality impacts of urban stormwater and agricultural runoff. This is described subsequently.

Example Provided by Copper

Copper provides an example of the need to focus on water quality impacts rather than principally on concentrations, and to properly incorporate aquatic chemistry/toxicology and receiving water characteristics into the evaluation of potential impacts of stormwater runoff. Copper is a chemical in urban and highway stormwater runoff that is of concern because of its potential to adversely impact aquatic life-related beneficial uses of a waterbody. It is not unusual for the concentration of total copper, and even of dissolved copper, in urban stormwater runoff to exceed US EPA worst-case-based water quality criteria. This does not mean that that copper is causing adverse impacts.

Studies on the aquatic chemistry of copper have shown that “dissolved” copper is comprised of numerous species which, while in the same oxidation state (Cu II), have significantly different toxicities to aquatic life. As discussed in reference to Figure 1, dissolved copper also enters into several complexation reactions with hydroxyl ions, carbonate, and various organics. Dissolved copper can precipitate with hydroxide and carbonates and sorb onto inorganic and organic solids. Particulate forms of copper, such as may be found in stormwater runoff, can dissolve in the receiving waters especially in acidic waters with low alkalinity. Metallic copper can be oxidized to Cu(I) and Cu(II). If the receiving water is anoxic, Cu(II) can be reduced to Cu(I). Several of these reactions take time to come to equilibrium, with the result that the copper species distribution, and therefore its toxicity, is changing during and following a stormwater runoff event. In order to reliably model the toxicity of copper to aquatic life during a runoff event it is necessary to be able to develop differential equations for each of the reactions into which copper may enter during the runoff event. The MINTEQ model can be used predict some of the reactions governing copper species distribution at equilibrium, but as noted above, not the position of equilibrium (kinetics) to yield concentrations of the various forms that may be expected in the receiving water. Site-specific studies would be needed to try to address the kinetics of the reactions that govern the concentrations of toxic forms of copper.

Complicating the modeling further is the fact that during a runoff event, the concentration of each chemical form of copper is changing due to mixing of the runoff waters with the receiving waters. Even if it were possible to mathematically model the toxic forms in a runoff event, site-specific and event-specific studies would be needed to define the mixing of the runoff waters with the receiving waters for each runoff event since the mixing characteristics of runoff with receiving waters can be different with each runoff event.

Beginning in the 1960s G. Fred Lee and his graduate students conducted a series of studies on the aqueous environmental chemistry of several heavy metals. These studies included the PhD dissertation of I. Sanchez (1971) on the aquatic chemistry of copper in Lake Monona in Madison, WI. For many years Lake Monona was dosed with large amounts of copper sulfate to control the excessive growths of planktonic algae. The Sanchez studies found that the aquatic chemistry of copper in this lake's water and sediments was as expected based on thermodynamic considerations. The redox reactions occurred as expected based on the oxic and anoxic conditions that occur in the lake; copper precipitated as a carbonate in oxic waters and as a sulfide in anoxic waters.

In the early 1980s G. F. Lee was a member of a US EPA peer review panel that reviewed the then-proposed, updated water quality criteria for copper. It was clear that the application of the proposed worst-case-based numeric criteria to waters would be highly over-protective for some sources and in some waters.

In the mid-1980s Lee and Jones became involved in reviewing water quality in New York/New Jersey Harbors. They found the copper concentrations to be above the US EPA water quality criteria. Subsequently it was found that the copper in the harbor waters was not toxic. The US EPA (1996) adopted site-specific water quality criteria for New York/New Jersey Harbor waters, allowing adjustment of the criteria for the presence of non-toxic forms of copper in evaluating the water quality impacts of copper in the harbor.

The regulation of copper in stormwater runoff and wastewater discharges in San Francisco Bay has been an area of considerable interest to the authors. It was found in the 1990s that the copper in San Francisco Bay waters exceeded the US EPA worst-case-based water quality criteria. A portion of the elevated copper was derived from the copper used in automobile brake pads, a finding that led to environmental groups' calling for restricting the use of copper in brake pads. However, in the mid-1990s the San Francisco Estuary Institute (SFEI) reported that the Bay waters in which the copper criteria were exceeded were not toxic to *Mytilus* (clam) larvae, the same organism that was used to develop the worst-case-based criterion. This led Lee (1994) and Lee and Jones-Lee (1993, 1997) to point out that the exceedance of the copper water quality criterion was an "administrative" exceedance of the criterion, rather than an exceedance signaling adverse impact, and that that "administrative" exceedance needed to be addressed through site-specific adjustment of the criterion. Subsequently, such an adjustment was made for the lower Bay.

The San Francisco Regional Water Quality Control Board (2007) recently adopted a site-specific water quality objective for parts of San Francisco Bay. That objective adjusts the national water quality criterion for copper in marine waters to account for the detoxification of copper that occurs through reaction of copper with dissolved organic matter in the Bay waters. Adoption of that site-specific criterion could significantly change the degree of copper control required from some sources to San Francisco Bay compared to that which would have been needed if the US EPA national worst-case-

based water quality criterion were used as the basis for regulating copper inputs to San Francisco Bay, without allowing greater adverse impact to aquatic life.

In February 2007, the US EPA released its “*Aquatic Life Ambient Freshwater Quality Criteria – Copper, 2007 Revision.*” That document contains information on the biotic ligand model (BLM) and its application to criteria development, as well as a discussion of BLM uncertainties and performance. This document provides guidance for adjusting the US EPA worst-case-based copper freshwater criteria for the chemical characteristics (organics) of waterbodies that influence copper toxicity. Arnold (2005) and Arnold and Hicks (2007) reported that the toxicity of copper in San Francisco Bay is related to the dissolved organic carbon in the Bay waters. It is expected that similar relationships can be found for other waterbodies. However, as of yet, the US EPA has not developed a similar BLM approach for marine waters.

Lee and Jones-Lee (1996, 1997, 2000a, b) provide additional discussion of approaches that should be considered for appropriate regulation of heavy metals in stormwater runoff.

Recommended Approach for Incorporation of Chemical Information into a Water Quality Evaluation

The evaluation of the impact of chemical contaminants in a discharge on water quality should begin with the reliable definition of the water quality/use-impairment that is of concern. The water pollution control programs need to be shifted from comparing concentrations of chemicals to worst-case-based standards/guidelines to reliably assessing impacts on beneficial uses of a waterbody. If the beneficial uses of a water are being adversely impacted, a toxicity identification evaluation (TIE) approach needs to be followed to determine the cause/source of the problem. This is in contrast to, for example, measuring copper, lead, zinc and cadmium that typically occur in street and highway stormwater runoff, finding they exceed US EPA worst-case-based numeric water quality criteria/state water quality standards, and declaring an impact has occurred. Jones-Lee and Lee (1998) described an Evaluation Monitoring approach to focus on chemical impacts rather than chemical concentrations.

If toxicity is found in laboratory tests of an effluent or receiving water, an assessment should be made as to whether such toxicity is manifested in the water of concern and whether that toxicity significantly adversely affects the waterbody’s beneficial uses. It should not be assumed that toxicity measured in a standard laboratory toxicity test necessarily translates to toxicity that is significantly altering the numbers, types and characteristics of desirable forms of aquatic life in a waterbody. This is especially true for situations such as urban-area and highway stormwater runoff, where there can be short-term pulses of contaminants associated with a runoff event that are not of sufficient magnitude and duration to exceed the critical magnitude—duration of exposure needed to be adverse to important forms of aquatic life in a waterbody.

Examples. In the mid-1990s, Lee and Taylor initiated Evaluation Monitoring studies on the toxicity and water quality impacts of heavy metals in urban-area street and highway

stormwater runoff in the Upper Newport Bay watershed in Orange County, California. It had previously been found, as is typical in urban-area and highway runoff, that several heavy metals including copper, lead, and zinc, were present in runoff from those areas in concentrations above US EPA worst-case-based water quality criteria. That indicated that there was a *potential* for those heavy metals to cause aquatic life toxicity in the waters receiving the runoff.

The Lee and Taylor studies included collection of samples of stormwater runoff from 10 different watershed covering urban, highway, and agricultural areas. They found that the stormwater runoff from urban areas and highways frequently contained heavy metals in concentrations above US EPA water quality criteria. They also found that that runoff was toxic to the zooplankton, *Ceriodaphnia*, with as much as 10 TUa of acute aquatic life toxicity. Toxicity identification evaluations (TIEs) involving the addition of EDTA to the toxicity tests to complex (render non-toxic) copper and other heavy metals, however, revealed that the toxicity was not due to heavy metals. Rather, it was found that the toxicity was due to organophosphate-based pesticides, including diazinon and chlorpyrifos, and likely as well to pyrethroid-based pesticides used in the watersheds studied.

The Lee and Taylor studies demonstrated the appropriateness of using the Evaluation Monitoring approach to evaluate the potential water quality impacts of stormwater runoff-associated potential pollutants. [The Lee and Taylor studies were support primarily by funds from the US EPA, Santa Ana Regional Water Quality Control Board, County of Orange Public Facilities and Resources Department (stormwater runoff water quality management agency) and other sources. The overall report covering those studies (Lee et al., 2001), as well as separate reports devoted to heavy metals and aquatic life toxicity of those heavy metals (Lee and Taylor, 2001a, b) are available as downloadable files (see references).]

Overall

The reliable modeling of water quality impacts of most potential pollutants cannot be accomplished through the use of hydrological models that are primarily designed to track water movement and mixing. In order to reliably model the water quality/beneficial use impacts of a chemical constituent in stormwater runoff or wastewater discharges, detailed information on aquatic chemistry, thermodynamics and kinetics, and mixing and transport/mixing processes that occur on a site-specific basis needs to be properly incorporated into the modeling effort. It is rare that this type of information is available or can be developed without extensive, site-specific investigations. It is far more reliable to follow the Evaluation Monitoring approach to evaluate the water quality impacts of pollutants in runoff/discharges. This includes directed, site-specific investigation and evaluation of the water quality impairments such as aquatic life toxicity, excessive bioaccumulation of hazardous chemicals, etc. Where impairment are found, follow-on studies are needed to determine the cause of the impairment and the sources of constituents causing the impairment, and to develop control programs to eliminate the impairment of the water quality/beneficial uses of the waterbody of concern.

References

Arnold, W. R., "Effects of Dissolved Organic Carbon on Copper Toxicity: Implications for Saltwater Copper Criteria," *Integrated Environmental Assessment and Management, Society of Environmental Toxicology and Chemistry (SETAC)* 1(1):34–39 (2005).

Arnold, W. R. and Warren-Hicks, W. J. "Assessment of Aquatic Ecological Risk and Site-Specific Criteria of Copper in San Francisco Bay, California, USA" *Integrated Environmental Assessment and Management, Society of Environmental Toxicology and Chemistry (SETAC)* 3, (1):32–48 (2007).

Jones-Lee, A. and Lee, G. F., "Evaluation Monitoring as an Alternative to Conventional Water Quality Monitoring for Water Quality Characterization/Management," *Proc. of the NWQMC National Conference "Monitoring: Critical Foundations to Protect Our Waters,"* US Environmental Protection Agency, Washington, D.C., pp. 499-512 (1998).
http://www.gfredlee.com/wqchar_man.html

Lee, G. F., "Copper in San Francisco Bay: Where Is the Problem?" Letter to State Water Resources Control Board, Sacramento, CA, May (1994).
<http://www.gfredlee.com/pwwqual2.htm#sfbay>

Lee, G. F. and Jones-Lee, A., "Water Quality Issues for Copper in San Francisco Bay," Report of G. Fred Lee & Associates, El Macero, CA, 4pp, March (1993).

Lee, G. F. and Jones-Lee, A., "Appropriate Use of Numeric Chemical Water Quality Criteria," *Health and Ecological Risk Assessment*, 1:5-11 (1995). Letter to the Editor, Supplemental Discussion, 2:233-234 (1996).
<http://www.gfredlee.com/chemcri.htm>

Lee, G. F. and Jones-Lee, A., "Regulating Copper in San Francisco Bay: Importance of Appropriate Use of Aquatic Chemistry and Toxicology," Presented at the Fourth International Conference on the Biogeochemistry of Trace Elements, Berkeley, CA, June (1997).

Lee, G.F., and Jones-Lee, A., "Regulating Copper in Urban Stormwater Runoff," *Timely Topics, NorCal SETAC News* 11(2):10-11, June (2000a).
http://www.gfredlee.com/reg_copper_0600.pdf

Lee, G. F. and Jones-Lee, A., "Development of TMDLs and Wet Weather Standards for the Control of Heavy Metals in Urban Stormwater Runoff," *Proceedings WEFTECH 2000 Water Environment Federation annual meeting, Anaheim, CA, October (2000b).*

Lee, G. F. and Jones-Lee, A., "Appropriate Incorporation of Chemical Information in a Best Professional Judgment 'Triad' Weight of Evidence Evaluation of Sediment Quality," Presented at the 2002 Fifth International Conference on Sediment Quality

Assessment (SQA5), In: Munawar, M. (Ed.), *Aquatic Ecosystem Health and Management* 7(3):351-356 (2004).

<http://www.gfredlee.com/BPJWOpaper-pdf>

Lee, G. F. and Taylor, S., "Results of Heavy Metal Analysis Conducted during 2000 in the Upper Newport Bay Orange County, CA Watershed," Report of G. Fred Lee & Associates, El Macero, CA (2001a).

<http://www.members.aol.com/apple27298/Heavy-metals-319h.pdf>

Lee, G. F. and Taylor, S., "Results of Aquatic Toxicity Testing Conducted during 1997-2000 within the Upper Newport Bay Orange County, CA Watershed," Report of G. Fred Lee & Associates, El Macero, CA (2001b).

<http://www.members.aol.com/apple27298/295-319-tox-paper.pdf>

Lee, G. F., Jones, R. A. and Newbry, B. W., "Alternative Approach to Assessing Water Quality Impact of Wastewater Effluents," Proc. Ind. Waste Symposium, Water Pollution Control Federation (1982a).

Lee, G. F., Jones, A. and Newbry, B., "Water Quality Standards and Water Quality," *Journ. Water Pollut. Control Fed.* 54(7):1131-1138 (1982b).

<http://www.members.aol.com/LFandWQ/WQStds-WaterQuality.pdf>

Lee, G. F., Taylor, S. and County of Orange Public Facilities and Resources Department, "Upper Newport Bay Water Quality Enhancement Project, Final Report," Agreement Nos. 8-023-258-0 and 8-174-250-0, submitted to State Water Resources Control Board, Santa Ana Regional Water Quality Control Board and Orange County Public Facilities and Resources Department to meet the requirements of the US EPA 319(h) Project, G. Fred Lee & Associates, El Macero, CA and RBF Consulting, Irvine, CA, May (2001).

RWQCB SF Region, "Basin Plan Amendments Adopted by the Water Board: Site-Specific Objectives for Copper in San Francisco Bay," Regional Water Quality Control Board San Francisco Region, June (2007).

<http://www.swrcb.ca.gov/rwqcb2/basinplan.htm>

Sanchez, I., **Aqueous Environmental Chemistry of Copper**, PhD dissertation Water Chemistry, University of Wisconsin, Madison, Madison, WI (1971).

Stumm, W. and Morgan, J., **Aquatic Chemistry**, 3rd ed, Wiley, New York (1996).

USEPA, "CWA 303(d): Establishment of Phased Total Maximum Daily Loads (TMDLs) for Copper, Mercury, Nickel and Lead in New York-New Jersey Harbor," Federal Register: Volume 61, Number 16, Page 1930-1932, January 24 (1996)

<http://www.epa.gov/fedrgstr/EPA-WATER/1996/January/Day-24/pr-215.html>

US EPA, “Aquatic Life Ambient Freshwater Quality Criteria – Copper, 2007 Revision,”
United States Office of Water EPA-822-R-07-001 Environmental Protection 4304T,
February (2007).

<http://www.epa.gov/waterscience/criteria/copper/2007/criteria200702.pdf>