Stormwater Runoff Water Quality Science/Engineering Newsletter
Devoted to Urban/Rural Stormwater Runoff
Water Quality Management Issues

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This issue of the Stormwater Runoff Water Quality Science/Engineering Newsletter (NL) is devoted to a review of **monitoring of water quality associated with stormwater runoff and discharges from irrigated agricultural lands.** It focuses on the situation that exists in the Central Valley of California where a major regulatory effort to control the water quality impacts of chemical constituents and pathogen indicator organisms in stormwater runoff and tailwater discharges from irrigated agriculture has been initiated. A discussion is presented in this Newsletter on some of the issues that need to be incorporated into a water quality monitoring program to develop reliable data that is useful in a water quality management program.

Proceedings of Symposium on Prevention of Pollution from Ships and Shipyards
A previous Newsletter provided information on an international symposium on prevention of pollution by ships and shipyards. This symposium was held in New Orleans in early November 2003. The symposium was organized my M. Champ of ATRP. This symposium consisted of 2.5 days of papers devoted to water quality management of releases/discharges from ships and shipyards. Particular attention was devoted to biocides used as antifoulants on boat hulls. It also included several papers on stormwater runoff impacts on port and harbor water quality. A future Newsletter will present information on the regulation of urban stormwater runoff impacts on port and harbor water quality.

The proceedings of the international symposium on pollution prevention from ships and shipyards will be published on a CD-ROM and will be distributed as part of the conference registration fee in mid-December. Those not registered for the Symposium in New Orleans, wishing to receive the Proceedings need to pay a fee of $185 to ATRP Corporation for processing, shipping and handling. Please send PO or Payment to ATRP Corporation, Attn: Charles Bakewell, 4913 Donovan Drive, Alexandria, VA 22304, Off: (703) 567-2405, Fax (703) 567-2406, cabakewell@atrp.com, www.atrp.com.

The CD-ROM will have the following five (5) Symposium and Workshop Proceedings on it:

<u>International Symposium on Pollution Prevention from Ships and Shipyards</u>. 2003. Held at the University of New Orleans, November 5-7, 2003, New Orleans, LA. Office of Naval Research. Vol. No. (1). Champ, M.A. and P.S. Seligman (Proceedings Editors).

<u>International Symposium on Pollution Prevention from Ships and Shipyards</u>. 2001. Oceanology International 2001 Conference. April 4-5, 2001. Miami, Florida. Office of Naval Research. Vol. No. (1). 351p. Champ, M.A. (Chairman and Proceedings Editor).

<u>Treatment of Regulated Discharges from Shipyards and Drydocks</u>. 1999. Proceedings of the Special Sessions held at Oceans '99 in Seattle Washington, Sept 13-16, 1999. The

Marine Technology Society, Washington, D.C. 20036. ISBN No. 0-933957-24-6. Office of Naval Research. Vol. No. (4). 223p. Champ, M.A., Fox, T.J., and A.J. Mearns (Co-Chairmen and Editors Special Volume).

Chemistry, Toxicity, and Bioavailability of Copper and its Relationship to Regulation in the Marine Environment. Seligman P.F., and A. Zirino (Editors). 1998. Office of Naval Research Workshop. SPAWAR Systems Center, San Diego. Technical Document 3044. 99p.

Copper Chemistry, Toxicity, and Bioavailability and its Relationship to Regulation in the Marine Environment. Zirino, A. and P.F. Seligman (Editors). 2002. Office of Naval Research 2nd Workshop. SPAWAR Systems Center, San Diego. Technical Document 3044. 80p.

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Monitoring the Water Quality Impacts of Irrigated Agricultural Stormwater Runoff and Tailwater Discharges

In early May 2003 the American Water Resources Association (AWRA) held a national specialty conference in Kansas City, Missouri, devoted to Agricultural Hydrology and Water Quality. The proceedings of this conference have recently become available on CD-ROM. The CD-ROM can be ordered at http://www.awra.org/proceedings/cd_proceedings.html#agr_hydro. This conference consisted of multiple concurrent sessions of papers concerned with various aspects of agricultural stormwater and irrigation water runoff/discharge impacts on water quality, and related topics. The focus of many of the conference papers was on the Midwestern US situation. There were some papers, such as the one by Drs. G. F. Lee and A. Jones-Lee, "Developing Central Valley, California, Agricultural Runoff/Discharges Water Quality Monitoring Programs," which covered similar issues in other parts of the country.

With respect to the paper by Lee and Jones-Lee, it focused on the approach that needs to be adopted to properly evaluate the water quality impacts of irrigated agricultural stormwater runoff and irrigation tailwater discharges on the beneficial uses of waterbodies in the Central Valley of California. This paper is available on the CD-ROM, as well as on the Lees' website, at www.gfredlee.com/AWRA_KC_Pap-Lee-web.pdf. The Lees have also made available a copy of the PowerPoint slides that they developed that summarize the key points of their presentation. Their paper was limited to six pages by AWRA. It represented a condensation of an approximately 150-page report that Lee and Jones-Lee (2002a) had developed for the state of California. This paper was summarized in Newsletter 6-1.

At this time, there is considerable discussion in California on the water quality monitoring program that should be developed as part of defining the water quality impacts of irrigated agricultural runoff/discharges on the water quality of Central Valley and other California waterbodies. The state of California water pollution control regulations (Porter-Cologne Act) have enabled the state regulatory authorities, such as the Central Valley Regional Water Quality Control Board, to allow agricultural discharges to be exempt from having to comply with water quality standards. This waiver of waste discharge requirements (WDRs) was terminated by the legislature based on the finding that there is pollution of the State's waters by agricultural discharges/runoff by currently used and "legacy" pesticides (such as the chlorinated hydrocarbon pesticides, including DDT, dieldrin, chlordane, toxaphene, etc.), nutrients (nitrogen and
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phosphorus compounds), sediments and potentially total organic carbon, which affects trihalomethane (THM) formation in water utilities' treated waters that use Central Valley surface waters as a source of water supply.

One of the major problems that have developed is that some agricultural interests object to conducting a comprehensive monitoring program that would define the magnitude of the water quality impacts associated with discharges from individual fields or groups of similar fields. As one agricultural representative indicated, in connection with commenting on the need for a comprehensive monitoring program, such a program could represent "spying" on agriculture by the regulatory agencies.

Environmental groups and others maintain the position that, in order to effectively define and then manage the water quality problems caused by agricultural runoff/discharges, it will be necessary to conduct comprehensive monitoring programs. Without them, the data that will be generated from some of the currently proposed monitoring programs will provide little new information beyond that which already exists, which shows that agricultural discharges and runoff contain constituents that are adverse to the beneficial uses of the State's waters.

Lee (2003a) has submitted a statement that indicates that, without the comprehensive monitoring programs, which include not only general watershed-based monitoring, but also edge-of-the-field monitoring for representative areas, for the suite of chemicals that are added to the land in agricultural production (such as pesticides, nutrients, etc.), that are generated on the land through agricultural activities (such as total organic carbon, suspended solids, total dissolved solids), or that are naturally present in some soils (such as selenium, boron, etc.) and are released from the land as a result of agricultural activities, it is not possible to reliably define the impacts of stormwater runoff and tailwater discharges from irrigated agriculture. These issues are discussed in the AWRA paper mentioned above, as well as in the Lee and Jones-Lee (2002a) comprehensive report on nonpoint source monitoring guidance.

The Central Valley Regional Water Quality Control Board (CVRWQCB, 2003) has established, as part of Order No. R5-2003-0826, the following table (Table 1) as the minimum requirements for the constituents to be monitored by the agricultural watershed Coalition Groups. Each monitoring group or individual is to develop a Monitoring Reporting Program (MRP). *"The MRP Plan must include a sufficient number of monitoring sites and surface water flow monitoring for each location to allow calculation of the load discharged for every parameter monitored. Method detection limits and practical quantitation limits shall be reported. All peaks detected on chromatograms shall be reported, including those which cannot be quantified and/or specifically identified. The Coalition Group shall use US EPA approved methods, provided the method can achieve method detection limits equal to or lower than analytical method quantitation limits specified in this Order. At a minimum, the MRP Plan must clearly demonstrate (1) compliance with requirement of all phases of monitoring as described in this MRP; (2) sufficient number of monitoring sites based on acreages and watershed characteristics, flow monitoring, and frequency of sample collection to allow for the calculation of load discharged for every waste parameter monitored; and (3) the use of proper sampling techniques and laboratory procedures to ensure a sample is representative of the site and is performed in the laboratory using approved methodologies."*

Table 1 Constituents to be Monitored[1]

Constituents	Quantitaion Limit	Reporting Unit
General Parameters		
Flow	N/A	cfs (ft^3/sec)
pH	N/A	pH units
Electrical Conductivity	N/A	µmhos/cm
Dissolved Oxygen	N/A	mg O_2/L
Temperature	N/A	Degrees Celsius
Color	N/A	ADMI
Turbidity	N/A	NTUs
Total Dissolved Solids	N/A	mg/L
Total Organic Carbon	N/A	mg/L
Drinking Water		
E. coli	(b)	MPN
Total Organic Carbon	(b)	mg/L
Chloroform	(b)	µg/L
Bromoform	(b)	µg/L
Dibromochloromethane	(b)	µg/L
Bromodichlormethane	(b)	µg/L
Toxicity Tests		
Water Column Toxicity	-	-
Sediment Toxicity	-	-
Pesticides (a)		
Carbamates	(b)	µg/L
Organochlorines	(b)	µg/L
Organophosphorus	(b)	µg/L
Pyrethroids	(b)	µg/L
Herbicides	(b)	µg/L
Metals (a)		
Cadmium	(b)	µg/L
Copper	(b)	µg/L
Lead	(b)	µg/L
Nickel	(b)	µg/L
Zinc	(b)	µg/L
Selenium	(b)	µg/L
Arsenic	(b)	µg/L
Boron	(b)	µg/L
Nutrients (a)		
Total Kjeldahl Nitrogen	(b)	mg/L
Phosphorus	(b)	µg/L
Potassium	(b)	µg/L

a. In addition to Toxicity Investigation Evaluations (TIEs), sites identified as toxic in the initial screen shall be re-sampled to estimate the duration of the toxicant in the waterbody. Additional samples upstream of the original site should also be collected to determine the potential source(s) of the toxicant in the watershed.

b. Quantitation limits must be lower than LC50 or other applicable federal or state toxic or risk limits.

[1] Adapted from CVRWQCB (2003)

"Bioassessment monitoring protocols are at the developing phase, and there are no Basin Plan requirements or standards addressing the results of bioassement monitoring. Coalition Groups are encouraged to conduct Bioassessments to collect data that may be used as reference sites and provide information for scientific and policy decision making in the future. Bioassessments may serve monitoring needs through three primary functions: (1) screening or initial assessment of conditions; (2) characterization of impairment and diagnosis; and (3) trend monitoring to evaluate improvements through the implementation of management practices. Bioassessment data from all wadeable impaired waterbodies may serve as an excellent benchmark for measuring both current biological conditions and success of management practices."

Lee (2003a) discussed that a number of the monitoring parameters and proposed approaches listed in Table 1 will lead to inadequate, unreliable, and in some cases, uninterpretable data on the characteristics of stormwater runoff and tailwater/subsurface drain water discharges from irrigated agricultural areas in the Central Valley. In order to use the funds spent on agricultural waiver water quality monitoring in a technically valid, cost-effective manner, it is essential that revisions be made in the monitoring program parameters to work toward achieving reliable, meaningful data from the monitoring program mandated by the agricultural waiver program. Since these same issues can occur in other monitoring programs, they are summarized below.

General Parameters

Flow. In order to reliably estimate potential pollutant loads, flow measurements must be made continuously, not intermittently at the time of sampling, as proposed. The intermittent time-of-sampling flow measurements can readily lead to significant errors in estimating the loads of a potential pollutant.

pH, DO and Temperature. Specifying that pH, DO and temperature be measured, without providing guidance as to the time of day when the measurements are to be made, is an inappropriate approach. For many waterbodies, especially agricultural drains, it would be expected that the time of day and the depth within the agricultural drain at which measurements are made will influence the pH, temperature, and dissolved oxygen values.

The CVRWQCB Basin Plan water quality objectives for pH and dissolved oxygen specify a concentration that should not be exceeded at any time or location in the waterbody. Since pH can change by several units from early morning to late afternoon, and DO can change by several mg/L from early morning to late afternoon, it is essential that, if compliance with the water quality objective for pH is to be evaluated, measurements at about 4:00 PM should be specified. If compliance with the water quality objective for DO is to be assessed, then measurements between 6:00 and 8:00 AM should be specified. These are typical times when these parameters will be at their maximum for pH, and minimum for DO. Allowing a discharger to measure pH and DO when it is convenient to them, or when the values are at their least or greatest, for pH and DO, respectively, leads to unreliable assessments of compliance with water quality objectives.

The time of day when temperature measurements are made is important and must be specified. Since, often, temperature change over a short period of time is a critical factor, the minimum temperature in early morning and maximum temperature in late afternoon should be measured.

Further, the temperature profile in the water column should be measured to determine if thermal stratification is occurring.

EC and TDS. Electrical conductivity is highly dependent on temperature. Some instruments attempt to correct for temperature. Others do not. This leads to the development of data where the electrical conductivity is dependent on the time of day, because the temperature can change with the time of day. Electrical conductivity should be corrected to 20 or 25°C, either automatically through temperature compensation in the conductivity instrument, or through determining, through laboratory studies, how EC for a particular water changes with temperature. The temperature of the corrected value should be included with the data.

With respect to requiring measurements of TDS and EC, a note should be added that indicates that after measuring TDS and EC on a particular water over a year or so, it will be possible to develop a factor that relates EC at 20°C to TDS. This then eliminates the need for further more expensive measurements of TDS in future monitoring.

Color. There are two forms of color: true color and apparent color. True color is obtained by filtering the sample, thereby removing turbidity. A list of monitoring parameters, such as Table 1, must specify whether true or apparent color is to be monitored. If it is true color, then the filter pore-size should be specified. Otherwise, essentially meaningless data will be generated.

Drinking Water Parameters

In Table 1, under Drinking Water, *E. coli* and Total Organic Carbon are listed. These are appropriate parameters. *E. coli* is important with respect not only to drinking water, but also to contact recreation. Also, dissolved organic carbon should be added to this list. The listing of chloroform, bromoform, dibromochloromethane and bromodichloromethane in this table will cause those doing the monitoring to waste funds making measurements of these parameters unless there are domestic wastewater discharges upstream of the monitoring location. These parameters are trihalomethanes (THMs) formed from the addition of chlorine as part of disinfecting water supplies. They would not be expected to be present in agricultural runoff, and even if they were present, they would not be an important parameter in the Central Valley that would justify spending funds for obtaining data on them, since THMs are rapidly lost from surface waters through volatilization and do not persist for long distances in surface waters.

TOC. While the US EPA has developed drinking water TOC concentration limits to control excessive THM formation, in order to regulate TOC discharges it is necessary to have these TOC limits adopted into the Basin Plan. It is known from past monitoring that both the mainstem and many of the tributaries of the Sacramento and San Joaquin Rivers have excessive TOC compared to the US EPA guideline values. As discussed by Lee and Jones-Lee (2003a) TOC measurements should be accompanied by planktonic algal chlorophyll and BOD measurements in order to determine the refractory versus labile TOC present in the samples. Agricultural interests and other dischargers of TOC should only be required to control TOC that is refractory – i.e., can reach a domestic water supply water treatment plant and thereby influence THM formation in the treated water supply. Some of the TOC discharged by agricultural and other sources in the Central Valley will, at times, not reach a domestic water supply intake, as a result of its degradation in transport from the source to the intake. These issues are reviewed by Lee and Jones-Lee (2003a).

Pesticides

In Table 1, under Pesticides, the organophosphorus and carbamate pesticides should be monitored, using low-level detection limit analytical procedures. Conventional procedures do not measure several of these parameters with sufficient sensitivity to determine if they are present at concentrations that are potentially adverse to aquatic life.

The July 11, 2003, final agricultural waiver monitoring program persists with requirements for measuring the organochlorine "legacy" pesticides, such as DDT, toxaphene, chlordane, dieldrin, etc., in water. As discussed by Lee and Jones-Lee (2002b), the approach that should be followed is to collect fish once during the year from the waterbody being sampled, and measure whether the fish tissue has excessive concentrations of these pesticides. As part of these measurements, PCBs should also be analyzed, since previous work on fish tissue residues from agricultural drain fish have shown that some of them have excessive PCBs. Based on a review that Drs. Lee and Jones-Lee conducted (Lee and Jones-Lee, 2002b) of the existing PCB fish tissue data, there are agricultural areas where PCBs have bioaccumulated in fish to excessive levels. Therefore, PCBs should be included in the chemicals that are examined as part of the agricultural waiver monitoring program.

Trying to measure organochlorine legacy pesticides and PCBs using chemical methods is a waste of time and money, since the analytical methods do not have the sensitivity to measure them at critical levels that can bioaccumulate to excessive levels in fish tissue, which represents a health threat to those who use the fish as food.

Another parameter that needs to be measured in fish, for at least some samples, is dioxins and furans. There are a variety of sources, including agricultural sources, of dioxins, which should be evaluated.

With respect to monitoring for pyrethroid pesticides and herbicides, large amounts of money could be spent attempting to monitor for these parameters, which would generate little or no useful data. The monitoring for these types of pesticides and herbicides should be based on their use in the watershed. Further, adequate sensitivity should be used to measure the pyrethroid pesticides at potentially toxic concentrations.

Appropriate pesticide monitoring should be part of the first phase of the monitoring program, where pesticides that have been used or are currently being used in a watershed are monitored as part of the Phase I efforts. This is based on the fact that toxicity measurements are not an effective screen for pesticide-caused aquatic life toxicity, except at high levels of pesticides. Pesticides, such as diazinon and chlorpyrifos, can be present in water at toxic levels and not cause toxicity to aquatic life in the standard tests specified in the monitoring requirements. The US EPA's approach for developing water quality criteria for potentially toxic substances involves estimating the "safe" concentration of the substance which should not cause toxicity to about 95 percent of aquatic life forms. This "safe" concentration (water quality criterion) is considerably less than the concentration that causes toxicity in a standard toxicity test.

In order to evaluate for toxicity at less than the levels that can be reliably assessed in a standard laboratory toxicity test, data are needed that would show whether diazinon, chlorpyrifos and a number of the carbamate pesticides are present at toxic levels. The measurement of these pesticides should be done with analytical methods that have a reliable quantitation limit (detection limit) of less than 0.1 times the LC_{50} for the test organism in the US EPA OPP Ecotoxicity Database that was used to register the pesticide. The issues of properly measuring pesticides and interpretation of the data from the water column, sediments and fish tissue are discussed in detail by Lee and Jones-Lee (2002b).

If fish in a particular agricultural discharge dominated waterbody contain excessive concentrations of organochlorine "legacy" pesticides, PCBs and/or dioxins, then the sediments from that waterbody and upstream should be assessed through the use of US EPA (2000) standardized bioaccumulation testing procedures. Lee, et al. (2002) have demonstrated the use of this approach for evaluating the bioavailable PCBs and organochlorine pesticides in city of Stockton Smith Canal waterway sediments.

Metals

Both total and dissolved metals should be monitored. While only the dissolved metals are regulated in the water column, the total metals are of importance because they can contribute to excessive metal concentrations in sediments.

Mercury should be analyzed in fish tissue from the waterbody being monitored to determine if there is a mercury source in the watershed that is leading to excessive mercury bioaccumulation in fish tissue. It is recommended that methylmercury be measured in waterbodies where the fish taken from the waterbody have been found to contain excessive mercury residues in edible tissue. Information on regulating mercury in water, fish tissue and sediments has recently been reviewed by Lee (2003b).

Nutrients

With respect to nutrients listed in Table 1, ammonia must be added to this list so that it is possible to calculate the organic nitrogen concentration from the ammonia and the TKN concentrations. Ammonia is also a toxicant that could be important in both the water column and sediments, and should be measured. In addition, ammonia is a source of oxygen demand that needs to be measured.

Phosphorus measurements should include both total phosphorus and soluble orthophosphate measurements. This information is essential to properly determining whether the phosphorus data are related to algal available P.

There is no reason to measure potassium. Any funds spent on measuring potassium will be a waste of money. Potassium is not a limiting nutrient in aquatic systems. There is always adequate potassium to meet algal and other aquatic plant needs.

As part of monitoring nutrients, planktonic algal chlorophyll, pheophytin and Secchi depth should be included as monitoring parameters. These parameters are needed to begin to evaluate the nutrient data.

Oxygen Demand Parameters

There is need to monitor oxygen demand parameters such as $BOD_{10,}$ ammonia, chlorophyll and pheophytin in any situation where there is a DO concentration below the water quality objective at the sampling location and downstream. BOD_{10} should be added to the list of monitoring parameters. BOD_{10} is specified rather than the traditional wastewater BOD_5 since low levels of BOD that typically occur in ambient waters are more reliably estimated in the 10-day BOD incubation. BOD_5 was found by Foe of the CVRWQCB to be about 65% of the BOD_{10} value.

Bioassessment

Bioassessment of benthic organism assemblages is a useful tool in water quality investigations in the right setting. However, it must be done correctly. It will be difficult to use bioassessment reliably in Central Valley waterbodies to evaluate the impacts of agricultural runoff/discharges on receiving water beneficial uses. There are no suitable reference waterbodies against which bioassessment data on an agricultural drain or agricultural discharge dominated waterbody can be evaluated. Large amounts of funds could be spent on conventional bioassessment measurements, yet gain little in definitive useful information. Lee and Jones-Lee (2002a) have discussed how bioassessment could potentially be used in evaluating the water quality impacts of agricultural runoff/discharges. Of particular concern is the approach of monitoring upstream and downstream of an agricultural discharge for assessing altered organism assemblages associated with the discharge. Also, short-term measurements should be made of benthic/epibenthic organism assemblages that address the impacts of toxic pulses in agricultural runoff/discharges.

Monitoring Locations and Duration

Monitoring should be required at river mainstem, basin, drain and representative edge-of-field locations. The monitoring at each location must be ongoing in perpetuity. One or two years of monitoring at a location is insufficient to properly characterize the water quality at that location, due to year-to-year variation in climate and agricultural practices. The comprehensive monitoring program must be initiated immediately, if the data needed to develop the revised final agricultural waiver monitoring program is to be available in the timeframe that the CVRWQCB has established.

Evaluation of the Water Quality Significance of Exceedance of a Water Quality Objective

Since the CVRWQCB chemical-specific numeric water quality objectives are based on worst-case (most toxic and available) conditions, it is necessary, in accordance with the Clean Water Act, to adjust the water quality objectives for site-specific conditions. Lee and Jones-Lee (2002a) have provided guidance on how this should be done. In the absence of site-specific studies, the worst-case-based water quality objectives will have to be used to regulate agricultural discharges/runoff. The funding of this program should include funding to cover the site-specific adjustments of water quality objectives.

Need for Guidance for Implementing Narrative Water Quality Objectives
The use of the CVRWQCB narrative water quality objectives, such as for nutrients (biostimulatory substances), sediments, etc., requires that additional site-specific information be developed through a site-specific evaluation of the regulatory requirements for the constituent(s) of concern. It is important to develop funding to accomplish the needed site-specific studies. These issues are discussed in Lee and Jones-Lee (2002a,c).

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