Development of a Stormwater Runoff Water Quality Evaluation and Management Program for Hazardous Chemical Sites

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ABSTRACT

Some of the common deficiencies in stormwater runoff water quality monitoring from hazardous chemical sites in assessing water quality impacts are discussed. An alternative approach for monitoring (Evaluation Monitoring, EM) that shifts the monitoring program from periodic sampling and analysis of stormwater runoff for a suite of chemical parameters to examining the receiving waters to determine what, if any, water quality use impairments are occurring due to the runoff-associated constituents is presented. Rather than measuring potentially toxic constituents such as heavy metals in runoff, the EM program determines whether there is aquatic life toxicity in the receiving waters associated with the stormwater runoff. If toxicity is found, its water quality significance and its cause is determined. The source of the constituents causing the toxicity is identified through forensic analysis. Based on this information, site-specific, technically valid stormwater runoff management programs can be developed that will control real water quality impacts caused by stormwater runoff-associated constituents.

KEYWORDS: hazardous chemical site, stormwater runoff monitoring, water quality impact evaluation

Introduction

Increasing attention is being given to managing the water quality impacts of stormwater runoff from "superfund" and other sites where hazardous chemicals exist in the near-surface or surface soils. Stormwater runoff from these areas could cause significant water quality impairment in off-site surface and groundwaters. This paper is a condensation of a more complete discussion of this topic. The more comprehensive review includes discussion of translocation as a source of stormwater runoff hazardous chemicals, cooperative watershed-based receiving water studies, aquatic sediment issues, atmospheric sources of toxic chemicals, importance of non-hazardous chemicals, wastewater discharges from site, groundwater recharge, data management and presentation, and duration of stormwater runoff monitoring. Information on these topics, as well as others, is available from Lee and Jones-Lee (1997a).

Deficiencies in Typical Stormwater Runoff Water Quality Monitoring Programs

In accord with US EPA stormwater runoff water quality regulatory requirements, the stormwater manager for the site is supposed to conduct analyses for any constituent that is likely to be present in stormwater runoff that could impair receiving water quality. For those sites complying with the minimum federal/state industrial site stormwater monitoring requirements, measurements are made of a stormwater sample's TDS, pH, TSS and TOC. For sites at which a wide variety of potentially hazardous chemicals have been manufactured, used, managed or disposed of, the stormwater runoff could justifiably be analyzed for the suite of Priority Pollutants.

Inappropriate Standards

At some hazardous chemical sites, drinking water quality is the focus of the site investigation where the stormwater runoff data are compared to drinking water MCLs in an approach similar to that followed in superfund site groundwater monitoring. For many of the heavy metals and some organics, the critical concentrations of constituents that are adverse to aquatic life are orders of magnitude lower than the concentrations that are acceptable in domestic water supplies. It is, therefore, important to consider the full range of potential impacts of stormwater runoff-associated constituents on the beneficial uses of the receiving waters for the stormwater runoff.

Inappropriate Analytical Methods

One of the areas of particular concern in developing technically valid stormwater runoff water quality monitoring programs is the selection of analytical methods, where methods that are typically suitable for groundwater investigation are also used for surface water runoff. Such an approach can generate large amounts of "non-detect" data in which the detection limits are well above the potentially significant critical concentrations for adverse impacts of chemical constituents in the stormwater runoff to aquatic life in the receiving waters for the runoff.

An area that is often not adequately investigated in stormwater runoff from hazardous chemical sites is the potential for some of the runoff-associated constituents, such as chlorinated hydrocarbon pesticides, PCBs, dioxins and mercury, to bioaccumulate to excessive concentrations in the receiving water aquatic organisms to render these organisms unsuitable for use as human food because of an increased cancer risk or, in the case of mercury, neurological damage to those who consume the organisms. For many constituents, the concentrations in water that can lead to excessive bioaccumulation in fish are well below the analytical methods detection limits typically used in "superfund" site investigations. This can lead to the superfund contractor incorrectly reporting that no water quality problems are associated with stormwater runoff from the site, since the concentrations of constituents found in the stormwater runoff are below the detection limits of the analytical methods used. Yet the fish in the waters receiving the stormwater runoff have bioaccumulated sufficient concentrations of hazardous chemicals derived from the site, as well as possibly elsewhere, to be hazardous for human consumption. These fish may also be hazardous for consumption by higher trophic level organisms such as fish-eating birds and mammals.

Even if appropriate analytical methods are used in measuring stormwater runoff-associated constituents from hazardous chemical sites and the data are properly compared to appropriate water quality criteria/standards designed to protect all beneficial uses such as fish and aquatic life, domestic water supply, agricultural water supply, etc., and an adequate sampling program has been conducted to measure the first-flush characteristics as well as the concentrations of constituents at other times during the runoff event for representative storms, it is still not possible to determine, from such monitoring programs what, if any, significant adverse impacts are occurring in the receiving waters for the stormwater runoff due to chemical constituents derived from the site in runoff waters.

Interpretation of Stormwater Runoff Data

The objective of a stormwater runoff water quality monitoring and evaluation program should be to determine whether the chemical constituents and/or pathogenic organisms in the runoff waters, when mixed into the receiving waters for the runoff, cause an impairment of the designated beneficial uses of the receiving waters, including downstream waters. The designated beneficial uses of concern are typically domestic water supply, fish and aquatic life, contact and other recreation, wildlife habitat, agricultural water supplies, etc. The typical approach used to determine whether stormwater runoff from a hazardous chemical or other site is adverse to the beneficial uses of the receiving waters involves comparing the concentrations of constituents found in the runoff waters to water quality criteria/standards. If an exceedance of the standard is found in the runoff waters, then it is often said that the stormwater runoff-associated constituent causing the exceedance is adverse to the beneficial uses of the receiving waters.

In order to properly evaluate whether an exceedance of a water quality criterion/standard for a regulated chemical is adverse to fish and aquatic life in the receiving waters for the stormwater runoff, it is necessary to determine the concentrations of toxic/available forms of the constituent of concern in the receiving waters for the runoff at the point of mixing and downstream relative to the concentrations of this constituent that are known to be adverse to the forms of aquatic life present in, or that could be present in, receiving waters of concern for the site stormwater runoff waters. Also, the duration of exposure of the aquatic organism to toxic/available forms of the constituents in the runoff waters and in the receiving waters must be evaluated.

Use of US EPA Water Quality Criteria

As discussed by Lee and Jones (1991), Lee and Jones-Lee (1994a, 1995, 1996a,b,c) and in references cited therein, the exceedance of a water quality criterion/standard in stormwater runoff waters should not be interpreted to mean that a real water quality use impairment is occurring in the receiving waters for the runoff. Aquatic life-based water quality criteria/standards are typically developed based on worst-case, or near worst-case situations with respect to the constituent being adverse to the aquatic life. Normally, these criteria and standards assume that the constituents of concern are in 100% toxic/available forms and the potentially impacted organisms received extended-chronic exposures to these forms. The typical stormwater runoff event is normally of short duration relative to the critical duration-concentrations of toxic/available forms for aquatic life. Further, many of the chemical constituents in stormwater runoff are associated with particulates and are, therefore, in non-toxic, non-available forms. In some instances, the concentrations of constituents in stormwater runoff can be orders of magnitude above the water quality criterion/standard and not be adverse to the aquatic life-related beneficial uses of the receiving waters for the stormwater runoff. It cannot, however, be assumed that because this situation occurs at some locations that it will always occur at all locations and at all times. Site specific investigations must be conducted to determine if the exceedance of a water quality standard represents a real water quality use impairment.

Under-Protective Nature of Some US EPA Water Quality Criteria

The authors have recently encountered a situation with Cr VI, where the US EPA water quality criterion of 10 µg/L would not necessarily be protective of aquatic life in receiving waters in which there is limited dilution of the stormwater runoff or wastewater discharges to a waterbody. Certain forms of aquatic life, such as zooplankton, which serve as important components of larval fish food, have been found to be adversely impacted by Cr VI at less than 0.5 µg/L. Lee and Jones-Lee (1996c, 1997b) have reviewed the chromium chemistry/toxicity issues. Some regulatory agencies allow Cr III to be discharged in wastewaters and stormwaters at 50 µg/L, i.e. the chromium drinking water MCL. Such practice, however, can readily lead to chromium toxicity to aquatic life since Cr III can convert to Cr VI in some aquatic systems. There is need for the US EPA and the states to update the water quality criterion for Cr VI as well as to consider the conversion of Cr III to Cr VI in permitting wastewater discharges and stormwater runoff in order for the criterion to be protective of important forms of aquatic life. In light of the information available today, it is appropriate to limit the total chromium concentration in a waterbody to 0.5 µg/L unless it can be shown that concentrations above this level are non-toxic to zooplankton, such as *Daphnia,* at the point of discharge for stormwater runoff and wastewater inputs, as well as downstream from this discharge/runoff.

There are a number of chemicals, such as arsenic, which are regulated as hazardous chemicals that will likely have their water quality standard significantly decreased within a few years. Arsenic has been used widely as a pesticide and herbicide. There are many former and current agricultural soils and some industrial areas that have sufficient arsenic in the surface soil to be of concern with respect to stormwater transport from the area. There is widespread recognition that arsenic at 50 µg/L (current drinking water MCL) represents a significant potential to cause cancer in people who consume domestic water supplies at or near these concentrations. The US EPA is reviewing the development of new, stricter drinking water standards for arsenic. The concentrations being considered are 0.2, 2.0, and 20 µg/L. It appears likely that a value of a few µg/L will be adopted, even though that value would still represent a significant cancer risk to those who consume waters with that concentration compared to the one in a million cancer risk that is typically accepted today as an appropriate risk for domestic water supplies.

The arsenic drinking water standard situation points to an important issue that needs to be considered in developing stormwater runoff water quality monitoring programs. Typically today, those establishing such programs only consider arsenic concentrations above 50 µg/L to be of potential concern with respect to water quality impacts. With new, stricter arsenic standards likely to be promulgated in the next few years, it is important to be certain that the analytical methods used are appropriate not only for today's regulatory situation but for those that can be reasonably expected to occur in the foreseeable future. Those conducting stormwater runoff monitoring programs from hazardous chemical sites should be cognizant of not only existing water quality criteria for water supplies, aquatic life, etc., but also of proposed changes such as will likely occur within a few years for arsenic. If, as in the case of arsenic, proposed lower concentration levels exist, then the stormwater managers should be using analytical methods that will measure the constituent at levels below the proposed criterion.

Unregulated Chemicals

One of the areas that should be of primary concern associated with stormwater runoff from a hazardous chemical site is the evaluation of the potential adverse impacts of the large number of potentially hazardous unregulated chemicals present in stormwater runoff. Typically, a comparison between the total organic carbon content of runoff waters and the total concentrations of specific organics measured in the runoff waters as determined by a Priority Pollutant scan shows that most of the organics in stormwater runoff are not identified/characterized. It is known that there are over 75,000 chemicals used in the US today. Only about 100 to 200 of these are regulated. Further, many chemicals can be transformed to other chemicals through chemical/biochemical processes that are also of concern with respect to impacting water quality as part of the unregulated chemicals in stormwater runoff. It is also known that each year newly developed and discovered hazardous chemicals are added to the list of hazardous chemicals that need to be regulated as a result of acquiring new information on their potential impacts. Therefore, it should never be assumed that because a stormwater runoff contains no constituents that cause an exceedance of a water quality criterion/standard in the runoff waters or receiving waters that the runoff-associated constituents from a hazardous chemical site or other area where complex mixtures of hazardous chemicals are present will not have an adverse impact on aquatic life and other beneficial uses of the receiving waters for the runoff.

A properly developed stormwater runoff impact evaluation and management program will include not only examination of the runoff waters and receiving waters for the regulated chemicals, but also include determining if the presence of unregulated, as well as regulated, chemicals in the runoff waters and the receiving waters are adversely impacting aquatic life and other beneficial uses of the receiving waters for the runoff. In evaluating the impact of stormwater runoff-associated constituents on receiving water quality, it is important to examine the combined impacts of constituents in the stormwater runoff when mixed with constituents in the receiving waters. It is possible that adverse impacts will occur even though no impacts are potentially predicted based on examining the concentrations of regulated chemicals in the runoff waters. A combination of regulated and unregulated chemicals in the runoff waters and receiving waters could have an adverse impact that would not occur in either water alone.

In addition, it is necessary to consider not only potential impacts at the point of mixing of the runoff waters with the receiving waters, but also downstream of this point where, associated with chemical/biochemical transformations of regulated and unregulated chemicals, non-hazardous chemicals are converted to hazardous forms. An example of this type of situation occurs with chromium III which some regulatory agencies allow to be discharged at 50 ug/L based on toxicity to humans and aquatic life. However, since chromium III can convert to chromium VI in aerobic surface waters, which can be toxic at about 0.5 µg/L, the discharge of chromium III at 50 ug/L, which is non-toxic at the point of discharge, can lead to aquatic life toxicity in the receiving waters downstream of the discharge due to the conversion of chromium III to chromium VI. This conversion can take place in a few hours or over several days, depending primarily on receiving water conditions.

Generally, because of its low level of toxicity, Cr III is regulated based on drinking water standards of 50 ug/L. Another issues of concern with respect to the discharge of Cr III to a waterbody is the accumulation of the Cr III in the waterbody sediments. Cr III has a strong tendency to sorb two particulates and precipitate. This tends to cause Cr III particulate forms to accumulate in receiving water sediments during low-flow conditions. These areas of accumulation can, however, be scoured into the water column during high-flow conditions suspending the particulate Cr III into the water column. This could cause significantly elevated levels of Cr III to pass downstream during elevated flow conditions. It was recently reported by Gunther (1997) that elevated flow conditions have apparently scoured Cr III from sediments in the Sacramento River system and have bioaccumulated in mussels in San Francisco Bay.

This situation raises the question of whether the scoured Cr III, either through bioaccumulation or through conversion to Cr VI, is adverse to the beneficial uses of downstream waters where Cr III has accumulated. This situation provides another example of the inappropriateness of assuming that just because stormwater runoff contains constituents that, in the runoff or at the point of mixing with the receiving waters, are not adverse to the aquatic life, that these constituents will not be adverse to aquatic life at some time in the future under a different flow regime. It is essential that receiving water studies be conducted to determine whether adverse conditions are found in the receiving waters due to stormwater runoff derived constituents.

Regulatory agencies and dischargers often use an arbitrary fixed distance (such as 50 or 100 meters) for sampling the receiving waters for discharges. The downstream sampling station should be selected based on a site specific evaluation of mixing distances at various receiving water flows. Since the distance for mixing is dependent upon the receiving water velocity, consideration must be given to how the velocity of the receiving waters changes as a function of flow in selecting downstream sampling stations. Further, the rates of reactions of potential concern, such as the conversion of Cr III to Cr VI, must be considered.

An Alternative Monitoring Approach

In order to be protective of aquatic life and other beneficial uses of receiving waters for stormwater runoff, it should be assumed that the exceedance of a water quality criterion/standard due to runoff-associated constituents from a hazardous chemical site represents an adverse impact that should be evaluated by the stormwater manager to determine if the potential impact is, in fact, manifested in the receiving waters for the runoff. Lee and Jones-Lee (1996a,b,c) have developed an Evaluation Monitoring (EM) approach that can be used to determine whether exceedances of water quality criteria/standards in stormwater runoff are causing real water quality use impairments in the receiving waters for the runoff. It can also detect some water quality problems due to unregulated chemicals. Evaluation Monitoring focuses on finding a real water quality problem-use impairment in the receiving waters for the stormwater runoff, identifying its cause and determining whether stormwater runoff-associated constituents derived from a particular site cause a water quality use impairment(s) in the receiving waters for the runoff. It should not be assumed, as it is often done, that an exceedance of a water quality standard represents a real water quality use impairment. Exceedances can readily reflect the overly protective nature of many water quality criteria/standards which fail to consider the toxic, available forms of the constituents in runoff waters as well as the duration of exposure to excessive concentrations of available forms of constituents in the receiving waters.

The EM approach should be implemented as a watershed-based water quality management program in which all stakeholders (dischargers, regulatory agencies and potentially impacted parties) work together to define whether stormwater runoff from a particular location causes real, significant water quality problems in the receiving waters for the runoff. Where such problems are found, the stakeholders work together to control them. All of the designated beneficial uses for the receiving waters are considered in implementing the EM approach. These may include domestic water supply, fish and aquatic life, public health, contact and other recreation, wildlife habitat, agricultural water supply, groundwater recharge, excessive fertilization, etc. Presented below is a summary of some of the issues that need to be considered in implementing the Evaluation Monitoring approach to determine whether stormwater runoff from a hazardous chemical site is adversely impacting some of the beneficial uses of receiving waters for the runoff.

Aquatic Life Toxicity

There are basically two concerns for the protection of aquatic life and their use as food associated with the discharge of hazardous/deleterious chemicals from hazardous chemical sites and other areas where there are complex mixtures of regulated and unregulated chemicals. One of these is aquatic life toxicity; the other is excessive bioaccumulation. Lee and Jones-Lee (1996a,b,c) recommend that all stormwater runoff water quality evaluation programs include measurement of the aquatic life toxicity to sensitive forms of aquatic life in the stormwater runoff waters as well as the receiving waters mixed with the stormwater runoff near the point of mixing and downstream thereof.

Appropriately conducted aquatic life toxicity tests can screen stormwater runoff waters for potential adverse impacts of all regulated and unregulated chemical constituents that are of concern with respect to being potentially toxic to aquatic life in the receiving waters. Such tests can and usually show that exceedances of water quality criteria for potentially toxic regulated chemicals in stormwater runoff do not necessarily translate to toxicity in the receiving waters for the runoff that is adverse to aquatic life in these waters. Further, such testing, if appropriately conducted, can detect toxic components in the unregulated chemicals in the stormwater runoff. Aquatic life toxicity testing using standardized US EPA toxicity test methods for freshwater systems using fathead minnow larvae and *Ceriodaphnia* (Lewis, *et al.*, 1994) is a powerful tool that should be used on a routine basis to determine whether potentially toxic regulated and unregulated chemicals in stormwater runoff cause significant toxicity in receiving waters for the runoff.

Toxicity testing of the stormwater runoff waters should be done for at least two storms each season. In addition to testing the runoff waters for aquatic life toxicity, the receiving waters should be sampled and tested for aquatic life toxicity just downstream of where the runoff waters enter and are mixed with the receiving waters. The degree of mixing should be established at that point by measurements of specific conductance and/or temperature in the receiving waters. Further, toxicity testing should be done further downstream to detect whether non-toxic constituents in the runoff waters convert to toxic constituents in the receiving waters in sufficient amounts to be toxic to aquatic life, i.e. Cr III to Cr VI conversion.

It was through the use of aquatic life toxicity testing of stormwater runoff that diazinon and chlorpyrifos, organophosphorus pesticides that are widely used in urban areas and in agriculture, were found to cause potentially significant aquatic life toxicity due to their presence in stormwater runoff from urban areas, highways and some rural areas. Diazinon is one of the unregulated chemicals that is causing widespread aquatic life toxicity in receiving waters for stormwater runoff. There are periods of time for several weeks each year in north-central California where diazinon applied to orchards as a dormant spray causes significant aquatic life toxicity in all runoff waters from urban and rural areas. A significant portion of this diazinon is volatilized at the time of application and transported through the atmosphere. It returns through the surface in rainfall and fogfall. Similarly, urban area stormwater runoff has been found to contain diazinon and chlorpyrifos toxicity due to homeowner structural and landscape use of these chemicals. There are other organophosphorus and carbamate pesticides that are not now being adequately regulated which are likely causing similar problems in stormwater runoff from urban and rural areas.

It is important, when using aquatic life toxicity testing, to properly interpret the results of such tests. It should not be assumed that because aquatic life toxicity is found in the stormwater runoff waters that this will lead to significant aquatic life toxicity in the receiving waters for the runoff. As discussed by Lee and Jones (1991) and Lee and Jones-Lee (1994b, 1996d), the short-term episodic nature of stormwater runoff events coupled with the approach used in aquatic life toxicity testing where the tests are conducted for approximately one week, can over-estimate toxicity that occurs in the receiving waters due to the discharge of toxic stormwater runoff. Typical aquatic life toxicity testing requires several days to about a week duration of test organism exposure. It is unusual in a stormwater runoff event for aquatic organisms to receive a week-long duration of exposure to toxic conditions. There are, however, significant differences in the rate at which various types of chemicals exert a toxic effect. There are fast-acting chemicals where, at elevated concentrations, the toxicity can be manifested within a few hours. There are other chemicals where, either due to low concentrations or the typical rate at which toxicity is manifested, several days of exposure must occur before the organisms are adversely impacted.

The recommended approach is to use the standard toxicity test to screen stormwater runoff for potential adverse impacts associated with the discharge of potentially toxic regulated and unregulated chemicals in the stormwater runoff. If toxicity is found in the runoff waters that persists for a sufficient period of time in the receiving waters to be potentially adverse to aquatic life, then additional toxicity testing should be conducted in which the toxicity-duration of exposure relationship that occurs in the receiving waters for the runoff is mimicked in the toxicity test. Lee and Jones (1991) provide additional information on this topic.

Bioaccumulation

The bioaccumulation of hazardous chemicals in aquatic life tissue is one of the major adverse impacts that can occur due to stormwater runoff constituents. The chemicals of greatest concern for excessive bioaccumulation are the chlorinated hydrocarbon pesticides such as DDT and chlordane, PCB's, dioxins, and mercury. These chemicals have been found to bioaccumulate to a sufficient extent in aquatic life tissue to cause the use of aquatic organisms as food to be hazardous due to increased cancer risk or other adverse impacts on human health. For many years, the Food and Drug Administration (FDA) Action Levels were used to determine excessive concentrations of hazardous chemicals in aquatic life tissue. The US EPA (1994) adopted risk-based tissue concentrations which consider the potential hazard that a particular concentration of a hazardous chemical in an organism tissue represents, considering its cancer potency as well as the amount of tissue consumed. Generally, the risk-based excessive concentrations of hazardous chemicals are one or more orders of magnitude lower than the FDA Action Levels. This has created a situation where concentrations of hazardous chemicals in stormwater runoff that were considered to have adverse impacts in the past are now being recognized as a potential significant source of excessive concentrations of the chemicals in fish tissue. Lee and Jones-Lee (1996a,c) have provided guidance on assessing excessive bioaccumulation of chemicals in aquatic organisms associated with stormwater runoff situations.

Similar problems occur with mercury where mercury is analyzed with analytical methods that do not have the necessary sensitivity to determine whether, under worst-case conditions such as those used by the US EPA in developing bioaccumulation-based water quality criteria, measured concentrations could result in excessive bioaccumulation in the receiving water organisms. It may be necessary, in some instances for some types of bioaccumulatable chemicals where the analytical methods do not have sufficient sensitivity to detect the concentrations of the chemical in the runoff waters that can lead to excessive bioaccumulation in receiving water aquatic organisms, to rely on measurement of the concentrations of the chemicals in the receiving water aquatic organisms as a measure of excessive bioaccumulation.

This is the approach that Lee and Jones-Lee (1996a,c) recommend as part of implementing the EM approach for stormwater runoff. Direct measurements of excessive bioaccumulation can readily be accomplished with the analytical methods available today. Such measurements provide information that can be used to determine whether all sources of a bioaccumulatable chemical in fish tissue contributes sufficient amounts of the chemical to the waterbody in available forms to lead to a bioaccumulation-caused use impairment of the waterbody. If the concentrations of chlordane, mercury or some other constituent are below excessive levels within aquatic organisms taken within the waterbody and downstream of the point at which the stormwater runoff enters the waterbody, then it can be concluded that excessive bioaccumulation is not occurring and, most importantly, that the stormwater runoff does not contain sufficient concentrations of a potential bioaccumulatable chemical to cause a water quality use impairment in the receiving waters due to that chemical.

If, however, the fish and/or other aquatic organisms used as human food in the receiving waters potentially impacted by stormwater runoff from a hazardous chemical site contain excessive concentrations of a chemical such as chlordane or mercury, then it is necessary to conduct additional studies to determine whether the stormwater runoff is a significant contributor of the constituent of concern to cause or contribute to the excessive bioaccumulation problem. Lee and Jones-Lee (1996a,c) have discussed the use of forensic procedures with caged organisms and/or laboratory studies that can determine whether stormwater runoff-associated potentially bioaccumulatable constituents could be significant contributors to excessive bioaccumulation in receiving water aquatic organisms. The bioaccumulation studies of stormwater derived from hazardous chemical sites should involve measurement of receiving water aquatic organism tissue levels for the conventional suite of potentially significant bioaccumulatable chemicals, such as the chlorinated hydrocarbon pesticides, PCBs, dioxins and mercury for a several-year period. The bioaccumulation studies should be conducted each spring and fall to examine seasonal differences. Higher trophic level predator organisms should be sampled as well as the organisms that tend to have higher concentrations of fat in their tissue. Generally, the chlorinated hydrocarbon pesticides and PCBs accumulate in high lipid content tissue to a greater degree. The lipid content of the tissues collected and analyzed should also be determined.

Caution must be exercised in using US EPA water quality criteria, such as the US EPA (1987) "Gold Book" criteria, in predicting bioaccumulation that will occur in receiving waters for stormwater runoff. The US EPA water quality criteria for bioaccumulation are based on worst-case conditions which tend to over-estimate the actual bioaccumulation that will occur in many waterbodies. Lee and Jones-Lee (1996e) have discussed the current information in using chemical concentration data in water and/or sediments to estimate excessive bioaccumulation that occurs in receiving water aquatic organisms. There are a wide variety of factors which influence whether a particular chemical constituent, as typically measured by standard water quality monitoring analytical procedures, will bioaccumulate to excessive levels. The most important factor is the aqueous environmental chemistry of the constituent. Many of the bioaccumulatable chemicals exist in a variety of chemical forms which are non-available to bioaccumulate within aquatic organisms. Since the analytical methods typically used in water quality investigations rarely only measure available forms of constituents, most measurements of bioaccumulatable chemicals tend to over-estimate the actual bioaccumulation that will occur when the concentrations are used with US EPA bioaccumulation factors. It is for this reason that the primary tool for determining whether excessive bioaccumulation occurs in a waterbody due to stormwater runoff-associated constituents is the actual bioaccumulation in aquatic organisms in the receiving waters. This is a more reliable approach than the approach that is typically used today of trying to measure concentrations of bioaccumulatable chemicals in runoff waters and then extrapolating these concentrations to excessive concentrations in receiving water aquatic organisms.

Aquatic Sediment Issues

The transport of hazardous chemicals from superfund and other hazardous chemical sites occurs with dissolved chemicals and chemicals attached to particulate matter. The dissolved chemicals can interact with the receiving water particulates to become part of the particulate-associated hazardous chemicals derived from the site. Since the particulate-associated chemicals are transported differently and represent significantly different hazards in the environment, it is important to determine whether hazardous conditions exist in the receiving waters due to the release of hazardous chemicals from the site that are in particulate forms or become particulate in the receiving waters.

Generally, particulate forms of hazardous chemicals are non-toxic and non-available and therefore represent minimal hazards in the environment. There are situations, however, where the accumulation of particulate forms in bedded sediments represents a potential cause of water quality deterioration due to either aquatic life toxicity to benthic or epibenthic organisms, or serve as a source of bioaccumulatable chemicals that can be adverse to the beneficial uses of a waterbody through causing a health hazard to humans who use the aquatic life as food. There is also the potential for the bioaccumulation of hazardous chemicals to be adverse to higher trophic level organisms, such as fish-eating birds and terrestrial mammals.

The US EPA (1995) has officially recognized that particulate forms of many heavy metals are non-toxic and non-available and now recommends regulating these heavy metals based on ambient water dissolved forms. The Agency should adopt the same approach for many of the potentially toxic organics and other constituents that tend to become associated with particulates. The Agency still recommends measuring total recoverable metals in discharge waters and the use of a generic or site-specific translator to translate dissolved forms of metals to particulate forms and vice versa in the ambient waters receiving the heavy metal input. This is based on the concern that particulate forms present in the discharge would convert to dissolved forms in the receiving waters. It is the authors' experience that such a conversion would be extremely rare.

As discussed by Lee and Jones (1992a), Lee and Jones-Lee (1993; 1994b,c; 1996g) in the 1970s, the US Army Corps of Engineers conducted the Dredged Material Research Program (DMRP) for the purpose of determining the water quality significance of chemicals associated with open water disposal of contaminated dredged sediments. This was a $30 million, five-year effort that served as the information base for the US EPA and the Corps of Engineers to develop the current dredged sediment management program that is used in the US to evaluate and manage contaminated dredged sediments. Of particular concern was whether sediments could be dredged and deposited in deeper water without significant adverse impact on the beneficial uses of these waters. The DMRP research results supported what had been known since the 1960s--that there is no relationship between the total concentration of a constituent in sediments and its toxicity or its ability to serve as a source of bioaccumulatable chemicals for higher trophic level organisms. The US EPA and Corps (US EPA/COE 1991, 1994) adopted a biological assessment approach in which toxicity tests are used to determine whether excessive concentrations of a potentially toxic constituent exist in a sediment that could be adverse to aquatic life and the beneficial uses of the waterbody in which the sediments are located.

While the US EPA and Corps of Engineers provide guidance on estimating bioaccumulation of constituents from contaminated sediments, the estimation approaches typically over-estimate the actual bioaccumulation that will occur in higher trophic level organisms in a waterbody in contact with the contaminated sediments. Based on the results of the DMRP, the authors (Lee and Jones, 1992a) recommended that any predicted excessive bioaccumulation associated with evaluation of a dredged sediment be confirmed by actual bioaccumulation measurements in the organisms of interest whose consumption would be adverse to human health or wildlife.

In the mid-1980s, the US EPA initiated a regulatory and associated research program designed to develop chemically-based sediment quality criteria. The Agency adopted this approach, even though various professionals with expertise in the topic and professional organizations recommended against this approach (Dickson, *et al*., 1987; Lee and Jones, 1987). The Agency was informed that chemically-based approaches would not likely be reliable for determining excessive concentrations of constituents in sediments. It was recommended that the Agency adopt the biological effects-based approach that had been adopted by another part of the Agency and the Corps of Engineers for regulating contaminated dredged sediments. The Agency ignored the recommendations and has over the last ten years been struggling with trying to develop reliable, chemically-based sediment quality criteria.

In the early 1990s, the US EPA formulated an equilibrium partitioning approach (US EPA, 1993) which attempted to adjust (normalize) the total concentrations of constituents of concern in sediments based on one of the detoxification factors that tend to make certain types of chemical constituents non-toxic and non-available. The equilibrium partitioning approach is a modeling approach in which an attempt is made through normalizing sediment concentrations of constituents to estimate the concentration of interstitial water-dissolved forms of potentially hazardous chemicals. It assumes that if the interstitial water-dissolved concentration is in excess of the US EPA's water quality criterion, the chemical would be adverse to benthic forms of aquatic life. Some laboratory studies have provided support for this approach (US EPA, 1993). For certain non-polar organics, the total organic carbon (TOC) content of the sediment is the normalizing factor. For certain heavy metals, the acid volatile sulfide (AVS) content of the sediments is used to normalize the heavy metal concentrations in sediments in order to estimate whether there would be free heavy metals in the sediments' interstitial water that would be available to be adverse to aquatic life. Lee and Jones (1992b) developed a comprehensive discussion of why the US EPA's proposed equilibrium partitioning approach would not be a reliable regulatory tool. This is the result of the fact that there are many other factors than AVS and TOC which tend to detoxify chemical constituents in aquatic sediments. Further, there are many factors that tend to cause so-called dissolved forms of constituents in sediment interstitial water to be non-toxic.

As discussed by Lee and Jones-Lee (1993, 1996g), there is growing recognition that while equilibrium partitioning approaches for estimating toxicity of sediment-associated constituents are more valid than trying to make the same estimate based on total constituent concentrations, they are not sufficiently reliable to be used as a regulatory approach. The Agency has admitted this deficiency with respect to trying to use AVS normalized heavy metals for developing sediment quality criteria. As discussed by Lee and Jones (1992b), AVS normalization is useful as part of a Toxicity Investigation Evaluation (TIE) where excess AVS over heavy metals is a reliable indication of a lack of heavy metal toxicity. Excess heavy metals over AVS, however, is not a reliable indicator of toxicity due to the fact that there are many other factors in sediments which neutralize heavy metal toxicity than sulfide precipitation. Of particular importance under oxic conditions is the role of hydrous iron oxide as a heavy metal and organic scavenger (Lee, 1975).

At this time, the Agency is still trying to utilize TOC normalized non-polar organic concentrations for certain constituents as a basis for developing chemically-based sediment quality criteria for certain chlorinated hydrocarbon pesticides and PAHs. This approach, however, is technically invalid and will lead to gross over-regulation of these chemicals in sediments due to the fact that there are a variety of factors other than TOC content of sediments which cause these chemicals to be non-toxic. Again, as with AVS, TOC normalization can be used in a TIE to determine whether there is a *potential* for these chemicals to be toxic to aquatic life. However, as discussed by Lee and Jones-Lee (1993, 1996g) and in numerous references cited therein, the reliable approach for estimating whether chemical constituents in sediments are, in fact, toxic is to use a suite of appropriately sensitive aquatic organisms to directly assess aquatic life toxicity. This is a reliable approach than chemically-based approaches where, with or without normalization, the concentration of a chemical in sediments is used to try to predict whether it will be toxic to aquatic life. Sediment toxicity testing procedures are well-established and readily implementable and should be used directly for this purpose.

Long and Morgan (1990) have developed a co-occurrence-based so-called relationship between the total sediment concentration of a constituent and potential adverse impacts of that constituent on sediment quality. However, the Long and Morgan co-occurrence-based approaches, as well as various modifications of these approaches, are not technically valid and have repeatedly been shown to be unreliable for predicting aquatic life toxicity in sediments. Lee and Jones-Lee (1996g,h,i) have discussed the unreliability of co-occurrence-based approaches for estimating sediment toxicity. Such approaches should not be used for any purpose, including screening sediments for potential toxicity. Basically, total concentration data for constituents in sediments are only reliable to indicate that an increase in concentration of a constituent compared to background has occurred. It provides no reliable information on the potential significance of the elevated concentration with respect to water quality issues.

The investigation of hazardous chemical sites with respect to assessment of stormwater runoff-associated constituents on receiving water quality should include measurement of sediment toxicity at various locations upstream and downstream of where the stormwater from the site enters the waterbody. If sediment toxicity is found, then TIE studies of the type described by Ankley, *et al.* (1991) should be used to try to determine the cause of the toxicity. The US EPA Duluth, Minnesota laboratory (Ankley) is developing revised TIE guidance for constituents in sediments. Further, forensic studies should be used to determine if the toxicity is associated with chemical constituents derived from the hazardous chemical site stormwater runoff. These measurements should be made in the spring and fall in order to examine potential seasonal differences. Also, appropriately developed reference sites should be used in evaluating the sediment toxicity. Lee and Jones-Lee (1996g) have provided guidance on a number of the issues that need to be considered in evaluating whether measured aquatic sediment toxicity is important in determining whether water quality use impairments are occurring in the receiving waters in which the sediments are located.

The potential for stormwater runoff transport of hazardous chemicals that accumulate in receiving water sediments that are a threat to excessive bioaccumulation in receiving water organisms can be evaluated best by first determining whether excessive bioaccumulation is a problem in the receiving waters for the site stormwater runoff. If excessive bioaccumulation is not a problem in the receiving water organisms, then there is no need for further studies of the receiving water sediments to determine whether constituents present in the stormwater runoff from the site are a cause of this problem due to bioaccumulatable chemicals. If excessive bioaccumulation is found in the receiving water aquatic organisms, then studies designed to evaluate whether receiving water sediments are a significant source of bioaccumulatable chemicals should be undertaken. Techniques similar to those described by the US EPA/COE (1991, 1994) can be used for this purpose.

Atmospheric Sources of Hazardous Chemicals in Stormwater Runoff

Increasing evidence is accumulating that certain agricultural practices involving the application of pesticides are causing widespread aquatic life toxicity in stormwater runoff from many areas at considerable distances from the locations where the pesticides were applied. The most notable example of this kind of a problem is associated with the use of diazinon as a dormant spray in orchards. Connor (1995) has reported finding diazinon-caused toxicity in stormwater runoff at many locations in north central California (Sacramento Valley). Toxicity has been traced to atmospheric transport of diazinon that causes rainfall and fogfall to be highly toxic to some forms of aquatic life for several weeks after the application of this chemical to orchards. Majewski (1996) of the USGS, Sacramento is conducting a pesticide air sampling program in the Sacramento, California region. His studies will help to provide information on the atmospheric transport of various pesticides that could, through rainfall and fogfall, cause aquatic life toxicity in the waters of a region that are not directly subject to runoff from the areas where the pesticides are applied. This situation could cause hazardous chemical sites and other areas to have toxicity in stormwater runoff that is not due to chemicals associated with past activities at the site. It is, therefore, important that if toxicity is found in stormwater runoff from a particular site that atmospheric collection of rainfall samples should be practiced to determine whether the toxicity is derived from off-site sources.

A similar situation could occur from stormwater run-on to the hazardous chemical site which carries with it hazardous chemicals from other areas. A stormwater monitoring program for a hazardous chemical site should include sampling of any run-on waters to examine whether off-site sources are contributing to the impairment of the stormwater runoff from the site.

Importance of "Non-Hazardous" Chemicals

The US EPA Superfund program focuses site investigation and remediation on a narrow, somewhat inappropriately developed group of so-called hazardous chemicals (Priority Pollutants). A review of how the Priority Pollutant list was developed in the 1970s shows that it did not then, nor does it today, represent the most important chemicals that could impact public health and the environment through water and/or soil contact. The Priority Pollutant list evolved out of a court order without public or US EPA peer review. It was recognized then that many of the chemicals that are on this list are of minor importance to public health and the environment. There are chemicals not on this list that are of importance. Further, and most importantly, there are many so-called "non-hazardous" chemicals that can be significantly detrimental to the beneficial uses of a waterbody. It is important in conducting hazardous chemical site stormwater runoff monitoring programs to consider not only the impacts of the so-called hazardous chemicals but also the potential impacts of conventional pollutants and other chemicals that can be adverse to the beneficial uses of receiving waters.

One of the areas of concern is the discharge of chemicals that can cause tastes and odors in the receiving waters that would be used for domestic water supply as well as to cause off-flavors in receiving water fish. Many state regulations require that dischargers control the discharge of chemicals that could impair the use of a fisheries resource such as causing the fish to be undesirable for use as food because of taste. Issues of this type need to be considered and then properly developed and implemented in a stormwater runoff water quality monitoring and management program for hazardous chemical sites in order to comply with state and local regulations governing water quality protection in the receiving waters for stormwater runoff from the site.

A new area which is emerging as an important area in managing stormwater runoff from hazardous chemical sites is the presence of elevated levels of total organic carbon (TOC) as well as dissolved organic carbon (DOC) in the runoff waters. TOC and DOC are becoming recognized as important pollutants that adversely impact the use of a water for domestic water supply purposes. Hazardous chemical sites that contain high levels of, what has been considered in the past, innocuous TOC/DOC soon will be recognized as important sources of pollutants that can cause a domestic water supply purveyor to provide additional treatment for TOC/DOC removal in order to reduce the total trihalomethane (TTHM) content of the treated water. The US EPA will soon adopt regulations that will require that dischargers of high levels of TOC/DOC above a few mg/L reduce the concentrations in the discharge in order to protect the use of the water for domestic water supply purposes.

The excessive fertilization of waterbodies by stormwater runoff-associated aquatic plant nutrients is one of the most common problems attributable to stormwater runoff from various areas. Often aquatic plant nutrients (nitrogen and phosphorus compounds) are monitored in stormwater runoff from hazardous chemical and other sites. The evaluation of whether a certain concentration of nitrate and ammonia as well as phosphate in stormwater runoff represents a threat to receiving water quality requires considerable knowledge about how nutrients influence the growth of algae and other aquatic plants. There are no reliable chemically-based water quality criteria or standards that can be applied to runoff waters and/or receiving waters to determine whether excessive nutrient runoff is occurring.

As discussed by Lee and Jones-Lee (1996a,c; 1997d), the approach to follow in evaluating whether stormwater runoff from a particular area is contributing to excessive fertilization of the receiving waters for the stormwater runoff is to first determine whether there is an excessive fertilization problem in the receiving waters and downstream that is significantly impairing the beneficial uses of the waterbodies. If there is no problem, then there is little need to be concerned about the discharge of nutrients in the stormwater runoff independent of their concentrations. If, however, there is a problem of excessive fertilization in the receiving waters and/or downstream, then special purpose studies need to be conducted to determine whether the nutrients derived from a particular location are causing or significantly contributing to the eutrophication-related water quality use impairment problem. Lee and Jones-Lee (1996a,c; 1997d) and in references contained therein provide guidance on how to determine whether nitrogen and/or phosphorus derived from a particular area in stormwater runoff and/or wastewater inputs is a significant contributor to excessive fertilization problems. Factors such as the characteristics of the excessive aquatic plant growth problem, the limiting nutrient vs. when the water quality problem occurs, the hydrodynamics of the waterbody, etc. all must be considered.

Another area of concern in such programs is the monitoring in the runoff waters as well as in the receiving waters for constituents that could influence the toxicity/availability of chemical constituents in the runoff waters as well as in the receiving waters for the runoff. Total organic carbon, alkalinity, hardness, TDS, oxygen demanding materials, etc. can all impact, either directly or indirectly, the water quality of a waterbody. A stormwater runoff water quality monitoring program from a hazardous chemical site should consider these issues and make appropriate measurements of the runoff waters and of the receiving waters for the suite of commonly measured chemical constituents that influence chemical constituent toxicity or availability.

Overview of Recommended Stormwater Monitoring for Hazardous Chemical Sites

Typically, stormwater runoff from urban areas and highways has been found to have limited adverse impact on the beneficial uses of the receiving waters for stormwater runoff (Lee and Jones-Lee 1996f). However, this is not necessarily the situation for stormwater runoff from hazardous chemical sites or other areas where large amounts of potentially hazardous chemicals are used in such a way as to possibly be present in elevated concentrations in stormwater runoff from the area. Sites of this type deserve special monitoring and proper interpretation of the US EPA's General Industrial Permit requirements for monitoring for "toxic" chemicals that could be present in the stormwater runoff. There is growing recognition that conventional end-of-the-pipe/edge-of-the-pavement/property monitoring of stormwater runoff for the conventional as well as the Priority Pollutants provides limited information on the impact of the stormwater runoff on receiving water quality-beneficial uses (Lee and Jones-Lee 1996a,b,c,e; 1997c,d). There is widespread recognition that the conventional monitoring approach for stormwater runoff needs to be shifted from runoff water monitoring to receiving water monitoring and evaluation. The Evaluation Monitoring approach, in which the regulated entity (the PRP for a hazardous chemical site under remediation), regulatory agencies and the impacted community work together in a watershed-based water quality evaluation and management program to define what, if any, real water quality use impairments are occurring in the receiving waters for the stormwater runoff, if implemented properly, can be a technically valid, cost-effective approach. As discussed herein, a key component of a technically valid, cost-effective stormwater runoff monitoring program is the examination of the runoff waters and receiving waters for aquatic life toxicity and excessive bioaccumulation of hazardous chemicals that cause receiving water organisms to be considered hazardous for use as human food.

Table 1 presents a summary of many of the components of a hazardous chemical site stormwater runoff monitoring program. It is important in developing a stormwater evaluation and management program for a hazardous chemical site to not over-regulate stormwater discharges and thereby waste public and private funds in unnecessary monitoring. In situations where adequate monitoring and evaluation have been conducted which show with a high degree of certainty that there is limited likelihood of significant adverse impacts on the beneficial uses of the receiving waters for the runoff, there is no point in continuing intensive monitoring and management programs. A low-level, on-going monitoring program should be continued in order to be certain that new problems do not occur in the future that were not detected previously or that the site characteristics changed sufficiently to significantly change the concentrations of constituents in the stormwater runoff.

Table 1

Hazardous Chemical Site Stormwater Runoff Monitoring

Aquatic Life Toxicity

Monitor stormwater runoff waters at the point of discharge for at least two storms per season for:

- Suite of conventional pollutants and Priority Pollutants
- Aquatic life toxicity using fathead minnow larvae and *Ceriodaphnia*

All toxicity measurements should be for chronic toxicity to the test organisms.

- The stormwater runoff event hydrograph should be developed for each storm.

The monitoring of stormwater runoff should be done during the first hour of a runoff event.

All stormwater runoff points from a hazardous chemical site, including stormwater entering the sanitary sewerage system, should be monitored.

The emphasis in this monitoring program is the monitoring of the receiving waters for water quality use impairments rather than the stormwater runoff from the site. The monitoring program should include monitoring the receiving waters upstream of the runoff waters, as well as at the point of mixing of the runoff waters with the receiving waters where the two are 90% mixed for conventional pollutants and Priority Pollutants.

The degree of mixing can be estimated through the use of temperature and/or conductivity measurements. Information on the flow of streams and rivers that are the receiving waters for the stormwater runoff should be obtained. If the receiving water is a lake, reservoir, estuary or ocean, an estimate of the current (water movement) magnitude and direction in the vicinity of the stormwater runoff area should be obtained. This can be done through the use of drogues, i.e. devices that are designed to move with the runoff waters in the receiving waters.

The receiving waters should be monitored for conventional pollutants, Priority Pollutants and aquatic life toxicity. During the first two years, the receiving water monitoring should be done twice each quarter and should include not only sampling at the point of mixing, but also at an estimated one-hour, 12-hour and one-day travel time downstream of the point of mixing. If after two years no toxicity is found in the receiving waters for the stormwater runoff, then the frequency of monitoring receiving waters for aquatic life toxicity can be reduced to one storm each quarter. If after five years of such monitoring, no toxicity in the receiving waters is found, then the frequency of receiving water monitoring can be reduced to once each spring and late summer-fall. If, however, major disturbances of the soil or structures or other activities which could influence the chemical characteristics of stormwater runoff occur at the site, then the frequency of stormwater runoff and receiving water monitoring should be changed to the initial program, i.e. twice per quarter.

Bedded sediments in the receiving waters should be analyzed just upstream and downstream and at several locations further downstream for aquatic life toxicity using several sensitive forms of aquatic life that are used to test for sediment toxicity. This testing should be done in the spring and the fall.

Bioaccumulation

Edible forms of aquatic life upstream in the vicinity of the hazardous chemical site stormwater runoff and at one "upstream" location and two locations "downstream" of the stormwater runoff point should be collected and analyzed for chlorinated hydrocarbon pesticides, PCBs, dioxins and mercury for discharges to lakes, bays or near-shore marine waters. "Upstream" should be a reference site that has characteristics as close as possible to the receiving water that is not influenced by the stormwater runoff, and "downstream" would be along the path of the plume that is developed by the stormwater runoff entering the waterbody. This sampling should be done in the spring and the fall.

Other Water Quality Impacts of Stormwater Runoff

The receiving waters should be examined for potential water quality use impairments, such as excessive fertilization, siltation, contact recreation, etc., that could be caused by hazardous chemical site stormwater runoff-derived constituents. This examination should be conducted in a watershed-based, cooperative water quality stakeholder administered program. If water quality problems are found that could be derived from stormwater runoff from the hazardous chemical site, then forensic studies should be conducted to determine whether the constituents responsible for the use impairments are derived to any significant extent from the hazardous chemical site.

Stormwater Discharge to the Sanitary Sewer

If stormwater from the site enters the local sanitary sewerage system and the local treatment works discharge is large compared to low-flow conditions in the receiving waters, then the impact of the local treatment works discharges on the receiving water quality should be monitored. This monitoring should include sampling the treated effluent for the conventional pollutants and Priority Pollutants, including measurement of aquatic life toxicity for fathead minnow larvae and *Ceriodaphnia*. These measurements should be made during non-stormwater runoff situations as well as during and following stormwater runoff events.

Selection of Analytical Methods

All analytical methods used should be sufficiently sensitive to measure the parameters of concern at potentially significant water quality impact levels. If this is not possible for bioaccumulatable chemicals, then excessive concentrations in the aquatic life tissue should be used to potentially indicate whether excessive discharge of hazardous chemicals is occurring from the site in stormwater runoff.

Long-Term Stormwater Runoff Monitoring Program

If no aquatic life toxicity or bioaccumulation is found in the receiving waters for the hazardous chemical site stormwater runoff and there are no major conventional pollutants in the stormwater runoff that adversely impact the beneficial uses of the receiving waters for the runoff, then as long as the site remains stable, i.e. no new activities or construction occurs, the monitoring of the receiving waters for site stormwater runoff can be reduced to one storm runoff event per quarter. Further, after several years of quarterly monitoring of receiving waters and the site is "stabilized," then the frequency of monitoring of stormwater runoff and receiving waters can be reduced to one sampling event in the spring and one in the fall. Further, if no aquatic life toxicity in the receiving water column or sediments or excessive bioaccumulation is found in the receiving water aquatic life and the concentrations of Priority Pollutants found in the receiving waters do not approach or exceed drinking water MCLs for freshwater systems, then the monitoring of Priority Pollutants in the runoff waters and receiving waters can be significantly reduced. The aquatic life toxicity testing and bioaccumulation monitoring should be continued to be practiced to screen for potential new problems that arise from stormwater runoff at the site or a combination of runoff-associated constituents with receiving water constituents that lead to problems that impact the beneficial uses of the receiving waters.

The overall approach that should be used in a monitoring and management program of hazardous chemical sites is to err on the side of public health and environmental protection in those situations where definitive information on the impact of runoff from a site is lacking. Regulatory agencies should require that the burden of proof should be on the PRP - stormwater discharger to reliably demonstrate that stormwater runoff from the site is not adverse to the beneficial uses of the receiving waters.

Conclusions

The development of a technically valid, cost-effective stormwater runoff monitoring and evaluation program for a hazardous chemical site requires a high degree of understanding of aquatic chemistry, aquatic toxicology, hydrodynamics and water quality. The General Industrial Permit stormwater runoff monitoring program will not ordinarily provide adequate monitoring to ensure that hazardous chemical site stormwater runoff-associated constituents do not have an adverse impact on the beneficial uses of the receiving waters for the runoff. Credible stormwater runoff monitoring programs must involve in-depth, reliable examination of the water quality characteristics of the receiving waters for the runoff. The Evaluation Monitoring approach provides a focused examination of receiving waters in which these waters are examined for water quality use impairments of potential concern to the public and others who utilize these waters. If properly implemented, the Evaluation Monitoring approach can significantly reduce the cost of monitoring of hazardous chemical sites stormwater runoff and focus the funds spent on monitoring on detecting real water quality problems that need to be addressed in order to protect the designated beneficial uses of the receiving waters for the stormwater runoff.

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Presentation Slides Follow:

Development of a Stormwater Runoff Water Quality Evaluation and Management Program for Hazardous Chemical Sites

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Inadequacy of Current Stormwater Runoff Monitoring for Assessing Water Quality Impacts

Recommend Alternative Approach -- Evaluation Monitoring

Conventional Stormwater Runoff "Water Quality" Monitoring

Many Hazardous Chemical Sites Contain Surface and Near-Surface Hazardous Chemicals That Can Be Transported in Stormwater Runoff

- Stormwater Runoff from Hazardous Chemical Site Could Readily Contain Chemicals That Are Significantly Adverse to the Beneficial Uses of a Receiving Water for the Runoff
- Current Approach: Conduct Runoff Monitoring Program to Focus on about 100 Priority Pollutants - Inadequate and Unreliable

PRPs and Consultants Do Not Want to Find Additional Public Health and Environmental Problems

- Often Fail to Consider Full Range of Potential Impacts Due to Stormwater Runoff from Hazardous Chemical Site
- Focus on a Few Priority Pollutants
- Ignore Conventional Pollutants, Unregulated Hazardous Constituents, etc.

Regulatory Agency Personnel Responsible for Site Review Often Do Not Have Adequate Expertise in Surface Water Quality to Provide Guidance on Developing Reliable Stormwater Runoff Monitoring

Conventional Hazardous Chemical Stormwater Runoff Monitoring

Typical Monitoring Approaches Involve Sampling Stormwater Runoff for Several Storms per Year

- Measure Suite of Chemical Parameters
- Compare Result to Water Quality Standards

Conventional Stormwater Runoff Monitoring Based on NPDES Wastewater Discharge Permit Compliance Monitoring

- Is There a Violation of Permit Conditions?
- Not Designed to Evaluate Impact of Discharge/Runoff on Receiving Water Beneficial Uses
- Conventional Monitoring/Regulation Focuses on Determining Chemical Concentrations/Loads

Should Focus on Impacts of Chemical

Potential Problems with Conventional Monitoring Approach

If Properly Implemented:

- Tends to Over-Regulate Regulated Chemicals

For Most Chemicals, e.g., Heavy Metals, Exceedance of a Water Quality Standard Is Poor Measure of Water Quality/Use Impairment - Pollution

- Fails to Regulate Unregulated Chemicals, i.e., Those without Water Quality Standards

Only Regulate about 100 of the 75,000 Chemicals in Use Today

- Fails to Use Aquatic Life Standards in Evaluating Water Quality Significance of Runoff-Associated Constituents

Typically Uses Groundwater - Drinking Water Standards

For Non-Carcinogens, Aquatic Life Standards Are Generally Lower Than Drinking Water Standards

US EPA Criteria and State Standards Based on Those Criteria Over-Regulate -- Not Developed for or Applicable to Stormwater Runoff Situations

Toxic/Available Forms

Short Duration of Exposure

- Fails to Use Sufficiently Sensitive Analytical Methods to Measure Chemical Constituents at Potentially Significant Concentrations

Typically Uses Analytical Procedures Suitable for Groundwaters for Surface Water Monitoring -- Often Inadequate

- Fails to Measure Aquatic Life Toxicity in Runoff Waters and at Appropriate Locations in Receiving Waters for Runoff

Screen for Regulated and Unregulated Chemicals That Cause Aquatic Life Toxicity

- Fails to Measure Bioaccumulation of Hazardous Chemicals in Receiving-Water Organisms

Fish Tissue Measurements Screen for Excessive Bioaccumulation of Hazardous Chemicals in Organisms Used as Food

- Cannot Extrapolate from Runoff Concentration/Loads to Receiving Water Impact

To Extrapolate, Must Conduct Site-Specific Studies to Evaluate

- Physics of Mixing and Transport
- Thermodynamics and Kinetics of Aquatic Chemistry Reactions
- Duration of Exposure of Sensitive Organisms

Generally Recognized That Conventional End-of-the-Pipe Stormwater Monitoring Is Largely a Waste of Funds and Unreliable for Developing Technically Valid, Cost-Effective Control of Water Quality Impacts of Stormwater-Associated Chemical Constituents in Hazardous Chemical Site Stormwater Runoff

Must Shift Monitoring Resources to Receiving-Water Impact Evaluation

Alternative Approaches:

Conventional Receiving Water Monitoring Measures Set of Chemicals at Arbitrarily Selected Intervals over 1 Year and Tries to Determine if Use-Impairment Is Occurring

Not Reliable for Assessing Stormwater Runoff Impacts

May Not See Episodic Impacts

Results Often Inconclusive on Role of Stormwater Runoff Constituents on Receiving Water Beneficial Use Impairment

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Evaluation Monitoring

Developed as Alternative to Conventional End-of-the-Pipe and Receiving Water Monitoring

Watershed-Based, Technical Stakeholder-Driven, Consensus Evaluation of the Water Quality/Use-Impairment of Receiving Waters

Overall Approach

Examine Receiving Water for Stormwater Runoff Impacts to:

- Drinking Water Use-Impairment - Surface and Groundwater
- Aquatic Life Toxicity in Water Column and/or Sediments
- Excessive Bioaccumulation - Threat to Human Health and/or Wildlife

- Sediment - Turbidity - Siltation - Habitat Impacts
- Excessive Fertilization/Eutrophication - Nutrients - N & P
- Pathogenic Organism Indicators - Contact Recreation and Shellfish Harvesting
- Low Dissolved Oxygen
- Aesthetics - Litter, Debris, Oil Sheen, etc.

If Impairment Found, Determine Its Cause and Whether the Hazardous Chemical Site Is a Significant Source of Constituent(s) Responsible for Use-Impairment

If Use-Impairment Due to Hazardous Chemical Site Stormwater Runoff-Derived Constituents Is Found, Adjust Site Management Program to Control Use-Impairment

If Over-Regulation of Stormwater Runoff-Derived Constituents Is Occurring, Adjust Regulatory Program to Protect Beneficial Uses of Receiving Waters without Significant Unnecessary Expenditures for Chemical Constituent Control

Evaluation Monitoring Used in Orange County Upper Newport Bay and Sacramento River Watershed Programs

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Examples of Evaluation Monitoring Application

Mercury in Stormwater Runoff

Concern Because of Excessive Bioaccumulation in Fish

Typically, Stormwater Runoff from Hazardous Chemical Sites and Other Areas Monitored for Suite of Heavy Metals, Including Mercury

Mercury Analytical Methods Used Do Not Have Adequate Sensitivity to Measure Mercury at the Current Regulatory Standard of 12 ng/L.

Cannot Determine if Mercury in Stormwater Runoff Is Potentially Bioaccumulating to Excessive Levels in Receiving-Water Aquatic Life

While Consultants for PRPs Often Report No Water Quality Problems Due to Mercury in the Stormwater Runoff, Such Reporting Can Be Unreliable Because of Inadequacies in Stormwater Runoff Monitoring Program

Typically, Measurement of Total Mercury in Aquatic Systems Unreliable for Assessing Potential Bioaccumulation

New US EPA Water Quality Criterion for Mercury Likely to Be 5 ng/L

Evaluation Monitoring Approach Screens Receiving Water Aquatic Life for Excessive Mercury in Edible Tissue

If Mercury Level below Regulatory Levels, Mercury Is Not a Problem from Any Source, Including Hazardous Chemical Site Runoff

If Mercury Has Bioaccumulated to Excessive Levels, Conduct Forensic Studies to Determine Source(s) of

Mercury That Is Bioaccumulating to Concentrations That Cause Receiving Water Aquatic Organisms to Be Judged Hazardous for Use as Food

Similar Issues and Approaches Applicable to Chlorinated Hydrocarbon Pesticides, PCBs, and Dioxins

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Examples of Evaluation Monitoring Application

Organophosphate Pesticides

OP Pesticides Highly Toxic to Some Forms of Aquatic Life, Especially Certain Zooplankton

Diazinon and Chlorpyrifos Are Widely Used for Urban, Industrial, and Agricultural Pest Control

Stormwater Runoff from Areas Where Pesticides Are Used or to Which They Have Been Transported via Airborne Transport Is Typically Toxic to *Ceriodaphnia*, a US EPA Standard Toxicity Test Organism

Diazinon and Chlorpyrifos Are Among the Unregulated Chemicals That Are Causing Widespread Aquatic Life Toxicity in Stormwater Runoff

Their Toxicity Is Typically Unrecognized Since They Are Not on the Priority Pollutant List and Are Not Monitored for in Hazardous Chemical Site Stormwater Monitoring Programs

Should Monitor Hazardous Chemical Site Stormwater Runoff for Aquatic Life Toxicity Using Standard US EPA Test Procedures

Where Toxicity Is Found, Examine, through Toxicity Investigation Evaluation (TIE), Whether It Is Due to Organophosphate Pesticides

If Toxicity Is Found, Determine Its Significance to Beneficial Uses of the Receiving Waters and, Through Forensic Studies, Its Sources

Control Toxicity at Source

Conclusions

- Current Stormwater Runoff Water Quality Monitoring of Hazardous Chemicals Inadequate to Define the Water Quality Impacts of the Residual Chemicals in Stormwater Runoff

Tends to Over-Regulate Priority Pollutants

Fails to Regulate Chemicals without Water Quality Standards

- Should Shift Monitoring Effort to Determine if Stormwater Runoff from Hazardous Chemical Site Is Causing a Real Water Quality/Use-Impairment in the Receiving Waters for the Runoff

Evaluation Monitoring Has Been Found to Be a Highly Effective Approach for Monitoring Stormwater Runoff That Should Be Used at Hazardous Chemical Sites and Other Sites