EVALUATION OF SURFACE WATER QUALITY IMPACTS OF HAZARDOUS CHEMICAL SITES[1]

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SUMMARY

Common deficiencies in the typical evaluation of the surface water quality impacts of hazardous chemical sites are discussed. Particular attention is given to deficiencies in monitoring stormwater runoff, as well as the input of contaminated groundwaters that lead to impairment of the beneficial uses of nearby surface waters due to site-derived hazardous and deleterious chemicals. An alternative approach, Evaluation Monitoring, is presented in this paper. Evaluation Monitoring shifts the monitoring program from periodic sampling and analysis of stormwater runoff as well as ambient waters for a suite of chemical parameters, to examining the receiving waters to determine what, if any, water quality use impairments are occurring in surface waters due to the runoff-associated constituents and shallow groundwater input.

INTRODUCTION

Increasing attention is being given to managing the water quality impacts of stormwater runoff and shallow groundwater discharges to surface waters from "superfund" and other sites where hazardous chemicals exist in the near-surface or surface soils. Stormwater runoff, as well as site-associated shallow groundwater inputs to surface waters, can cause significant water quality impairment in off-site surface and groundwaters. This paper is a condensation of a more complete discussion of this topic (Lee and Jones-Lee, 1997a). The stormwater runoff water quality portions of this paper are based on a recent review by Lee and Jones-Lee (1998a).

DEFICIENCIES IN TYPICAL STORMWATER RUNOFF AND AMBIENT WATER 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 (US EPA, 1990). 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 only compared to US EPA drinking water Maximum Contaminant Levels (MCLs) in an approach similar to that followed in superfund site groundwater monitoring. This technically deficient approach arises from the fact that, at many hazardous chemical sites, those responsible for developing and reviewing the water quality monitoring programs have little expertise in water quality evaluation and management. The typical drinking water standards

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approach ignores that 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 and shallow groundwater input to surface waters. Of particular importance is the evaluation of the impact of site-derived hazardous and deleterious chemicals on aquatic life and other designated beneficial uses of nearby surface waters. This is a basic component of developing a credible hazardous chemical site stormwater runoff and shallow groundwater input water quality monitoring program.

Inappropriate Analytical Methods

One of the areas of particular concern in developing technically valid stormwater runoff and ambient water quality monitoring programs is the selection of appropriate analytical methods. At some sites, 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 method 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.

Inadequate Sampling of Particulates

One of the problems that occurs in sampling stormwater runoff for the particulate chemical constituent content of the samples is that either the pumped sample associated with an automatic sampler in which tubing is extended into the flow and the grab samples in which samples are dipped from the flowing water properly sample the particulate load. In order to properly sample particulates in a flowing stream, it is necessary to practice isokinetic sampling in which the velocity of the water passing a sampling point is matched to the velocity of the inlet to the sampling tube or hose. If these two are not matched, then particulate constituents will not be sampled on a representative basis. Too low a tubing inlet velocity will exclude certain particles since they will be deflected away from the inlet; too high a velocity will take particles from the flow stream that would ordinarily not be sampled.

Part of this problem is that the velocity profiles in a stream or storm sewer vary with depth and therefore isokinetic sampling done at one depth will not appropriately sample particulates at another depth where the velocity of the flowing stream is different. Another problem with attempting to sample particulates is that flowing streams have a bedload of particulates that moves along the bed. This bedload can represent a significant part of the total particulate load. Few sampling programs sample rivers and streams and storm sewers reliably with respect to assessing bedload concentrations of constituents.

It is important to understand however, that the errors that routinely occur in sampling particulates in a stormwater runoff or other monitoring program are usually not of great significance in evaluating the water quality impacts of the runoff since with few exceptions, the particulate fraction of potential pollutants are in non-toxic, non-available forms. As a result, the errors made in sampling the particulates while they can be significant in terms of estimating total loads of constituents passing a sampling point, they are rarely significant in terms of estimating the water quality impacts of the particulates.

Another problem associated with the analysis of stormwater runoff samples as well as other types of ambient water samples where there is an attempt to assess the dissolved, potentially toxic forms of constituents is that the method used to distinguish between dissolved and particulate forms involving the use of a 0.45 µ pore size membrane filter does not reliably measure the true dissolved forms. Appreciable quantities of colloidal forms of potential pollutants can pass through a 0.45 µ pore size filter and be measured as “dissolved” yet not be thermodynamically true dissolved species. As recommended by Lee and Jones-Lee (1992), high speed centrifugation is needed to determine whether filtration-based dissolved constituent concentrations truly represent dissolved species that are potentially toxic or available to aquatic life.

Interpretation of Stormwater Runoff Data

Even if appropriate sampling and analytical methods are used in measuring stormwater runoff-associated constituents from hazardous chemical sites, shallow groundwater inputs to surface waters, and ambient waters receiving these inputs, and the data are properly compared to appropriate water quality criteria/standards designed to protect all beneficial uses, 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. As discussed by Jones-Lee and Lee (1998), the basic problem is that chemical concentration data in stormwater runoff or ambient waters cannot be translated to water quality impacts without significant site-specific investigations. It is for this reason that Evaluation Monitoring focuses on assessing chemical impacts on beneficial uses of waters, rather than on chemical concentrations or loads.

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 nearby receiving waters, including downstream waters. The designated beneficial uses of concern typically include 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. However, 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. These issues are discussed further by Jones-Lee and Lee (1998).

Use of US EPA Water Quality Criteria to Evaluate Water Quality

As discussed by Lee and Jones (1991), Lee and Jones-Lee (1994a, 1995, 1996a, 1997b, 1998b) and in references cited therein, the exceedance of a water quality criterion/standard in stormwater runoff waters or ambient 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 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 of concern to the public. Without these investigations, the exceedance of a water quality standard should be assumed to represent an impairment of the beneficial uses. The burden for conducting such studies should be placed on the hazardous chemical site owner and previous dischargers (PRPs).

Under-Protective Nature of Some US EPA Water Quality Criteria

There are a number of fairly common constituents associated with hazardous chemical sites where meeting US EPA water quality criteria may not be protective of aquatic life or other beneficial uses of a waterbody. Several situations of this type are summarized below.

Chromium. The US EPA water quality criterion of 10 µg/L for Cr VI is not necessarily protective of aquatic life in receiving waters in which there is limited dilution of the stormwater runoff, shallow groundwater input, 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 (1997c, 1998c) have reviewed the chromium chemistry/toxicity issues focusing on the deficiencies in the current regulatory approaches for control of chromium discharges to surface waters. They point out that some regulatory agencies allow chromium III (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.

It is important to understand that meeting the US EPA water quality criterion in ambient waters associated with stormwater runoff does not mean that the criterion constituent will not be adverse to some forms of aquatic life in the waterbody. 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* and/or *Ceriodaphnia*, at the point of discharge for stormwater runoff and wastewater inputs, as well as downstream from this discharge/runoff.

Arsenic. 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 with arsenic 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 as a new MCL, 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 at a hazardous chemical site surface water impact evaluation 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 or other constituents that have criteria currently under review. 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.

Mercury. Mercury is receiving increased attention as a hazardous chemical that, through bioaccumulation in fish, can represent a significant hazard to those who use fish with elevated concentrations of mercury as food. Of particular concern are fetuses and nursing infants. Typically in the past, stormwater and groundwater monitoring programs for mercury have used analytical procedures that do not detect mercury at the US EPA water quality criterion of 12 ng/L. This criterion is based on a worst-case evaluation for bioaccumulation of mercury in fish tissues that leads to excessive mercury residues in the fish compared to those that are considered to be adverse to human health. The US EPA, as part of its national mercury review, will likely decrease the national worst-case-based water quality criterion for mercury from 12 ng/L to 5 ng/L. This will make it even more difficult to measure mercury at potentially critical concentrations in stormwater runoff or ambient waters. A subsequent section of this paper discusses the appropriate approach that should be used to evaluate whether mercury or other potentially significant hazardous chemicals derived from a hazardous chemical site will bioaccumulate in fish to levels that are hazardous for the use of the fish as food.

Unregulated Chemicals

One of the areas that should be of primary concern associated with stormwater runoff and shallow groundwater discharges to surface waters 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 and groundwaters. 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 and many groundwaters 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 public health and environmental impacts. Therefore, it should not 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.

Risk Assessment Surrogate for Unregulated Constituents. Lee and Jones-Lee 1998(d) have discussed the importance of properly conducting a risk assessment for hazardous chemical sites which uses surrogate hazardous chemicals to represent the potential for some of the unregulated constituents present at sites to be adverse to public health or the environment. They recommend that with respect to protecting groundwater quality used for domestic water supplies, the assumed surrogate have a hazard to public health that would require a drinking water quality standard (MCL) of 0.01 µg/L and that this chemical be persistent and have the same mobility in groundwater systems as water. For surface water impacts, especially for stormwater runoff-associated constituents, the surrogate representing the unknown chemicals will need to have a much lower critical concentration to protect public health. Of particular concern are the unknown/unregulated hazardous chemicals that tend to bioaccumulate in fish tissue. Dioxins are the chemicals that at this time establish the potential hazards that can occur to public health through bioaccumulation in fish.

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, shallow groundwaters derived from the site, and the receiving waters for the runoff and groundwater inputs 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 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. As discussed in a subsequent section of this paper, toxicity testing of discharge in ambient waters can be used to screen for combined effects of potentially toxic regulated and unregulated chemicals on receiving water aquatic life.

Importance of Evaluating Aqueous Environmental Chemistry. Sufficient understanding of the aqueous environmental chemistry of the constituents of concern associated with hazardous chemical sites should be achieved to assess whether there are situations in which hazardous conditions can develop associated with non-hazardous chemical discharges. The conversion of mercury to methylmercury that bioaccumulates in fish is an example of this type of situation. Many of the particulate forms of mercury are normally only slowly converted to methylmercury in ambient water sediments. However, it is possible to discharge what would be considered nonhazardous chemicals such as particulate organics in wastewaters or stormwater runoff that exert a BOD in the receiving water sediments which promotes the conversion of particulate mercury in these sediments to methylmercury that bioaccumulates in fish to excessive concentrations. Evaluation of the potential water quality impacts of a hazardous chemical site must consider whether this type of situation is occurring in the ambient waters receiving stormwater runoff from a site.

Selection of Downstream Sampling Location. 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, regulated and unregulated hazardous chemicals and non-hazardous chemicals are converted to hazardous forms. An example of this type of situation can occur with Cr III, which some regulatory agencies allow to be discharged at 50 µg/L based on toxicity to humans. Generally, because of its low level of toxicity to aquatic life, Cr III is regulated based on drinking water standards of 50 µg/L. However, since Cr III can convert to Cr VI in aerobic surface waters, which can be toxic at about 0.5 µg/L, the discharge of Cr III at 50 µg/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 Cr III to Cr VI. As discussed by Lee and Jones-Lee (1997c), this conversion can take place in a few hours or over several days, depending primarily on receiving water conditions.

Another issue 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 to 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, *et al*. (1997) that elevated flow conditions have apparently scoured Cr III from sediments in the Sacramento River system that 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 in the sediments.

The Cr III discharge 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 aquatic life, 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 at the time of discharge, as well as in the future under different flow or other conditions that can exist in the receiving waters.

Regulatory agencies and dischargers often use an arbitrary fixed distance (such as 50 or 100 meters up and downstream from a discharge point) 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 in selecting downstream sampling stations.

Importance of “Non-Hazardous” Chemicals in Impacting Water Quality

Typically, RCRA and CERCLA focus hazardous chemical site investigation and remediation on a limited number of Priority Pollutants. This approach can lead to a highly distorted remediation/management approach where PRPs and regulatory agencies focus their efforts on some Priority Pollutants such as a chlorinated solvent, yet ignore a wide variety of other constituents present in the groundwaters derived from the hazardous chemical site which cause the groundwaters to be unusable or have a significantly impaired use for domestic and some other purposes. Jones-Lee and Lee (1993) have discussed the importance of remediating polluted groundwaters for the conventional pollutants that cause a groundwater to be unusable or impaired for use as a domestic water supply. Of concern are constituents that cause tastes and odors, staining, increased corrosion, scaling of plumbing and fixtures, etc. To a water utility or homeowner whose well is polluted by a Priority Pollutant and conventional pollutants, the remediation of the conventional pollutants is just as important as the Priority Pollutant remediation. It is inappropriate to only clean up Priority Pollutants and leave an unusable groundwater or surface water that receives hazardous chemical site stormwater runoff or groundwater input.

Aquatic plant nutrients such as nitrogen and phosphorus compounds are part of the conventional pollutants that while, except for concentrations of nitrate above 10 mg/L N, are of limited concern in impairing the use of groundwaters for domestic water supply. However, stormwater runoff of aquatic plant nutrients from a hazardous chemical site or groundwater transport of nitrate, including those at concentrations below the drinking water MCL, that reaches surface waters can be important sources of aquatic plant nutrients that cause significant water quality problems for domestic water supplies and the use of surface waters for recreational purposes. Soluble orthophosphate at concentrations above about 10 µg/L P can stimulate excessive growths of algae that cause severe taste and odor problems in domestic water supplies as well as interfere with contact and other recreation in waterbodies. For those waterbodies in which nitrogen is the element controlling excessive growths of algae, concentrations of nitrate nitrogen above about 50 µg/L N can stimulate excessive growths of algae which impair the beneficial uses of surface waters. A credible evaluation of the public heath and environmental impact of hazardous/deleterious chemicals from a hazardous chemical site must include an evaluation of whether potential pollutants, such as aquatic plant nutrients, could be discharged from the site in stormwater runoff or shallow groundwaters transported to surface waters to a sufficient extent to impair the beneficial uses of the surface waters. Further information on this topic is available from Lee and Jones-Lee (1997b).

It is also important to understand that the current approach used by the US EPA and states for defining what is a hazardous chemical involving TCLP extraction is based on political considerations designed to reduce the magnitude of the hazardous waste stream, rather than a proper evaluation of the real hazards that potentially hazardous chemicals represent to public health and/or the environment. These issues have recently been reviewed by Lee and Jones-Lee (1999).

Shallow Groundwater Discharges to Surface Waters as a Source of Hazardous Chemical Site Pollutants

Hazardous chemical sites located in shallow groundwater areas have the potential to pollute surface waters with hazardous or deleterious chemicals. It is essential in investigating the potential impact of a hazardous chemical site located where there are shallow groundwaters that discharge to surface water courses in the vicinity of the site to evaluate whether this discharge could carry hazardous/deleterious chemicals from the site to surface waters. The key issue is whether shallow groundwaters can transport hazardous/deleterious chemicals at a sufficient rate to be significantly adverse to the beneficial uses of these waters. The groundwater hydrology of hazardous chemical sites should be sufficiently well-defined so that the potential for transporting hazardous chemicals in shallow groundwaters to surface waters is appropriately evaluated.

This evaluation will typically involve developing a sufficient understanding of the site's stratigraphy, so that the potential flow paths for hazardous chemical-contaminated groundwaters are defined. If it is found that there is a potential for transport of hazardous chemicals from the site to surface waters, then a comprehensive shallow groundwater monitoring program should be undertaken to determine whether hazardous and/or deleterious chemicals are being transported from the site to off-site surface waters.

In addition to on-site monitoring of groundwaters, an extensive monitoring well array should be developed near the point of discharge to the surface waters for each of the potential flow paths for hazardous/deleterious chemical transport to the surface waters. Also, since the shallow groundwater plumes of hazardous chemicals may not necessarily have large lateral extent, it will typically be necessary to conduct comprehensive monitoring of the surface waters near where the potentially polluted groundwaters enter the surface waters. The expected transport rates in the shallow groundwater system from the areas where the hazardous chemicals are located on the site to the surface waters needs to be reliably evaluated. The sampling program should consider how rapidly hazardous chemicals that become associated with shallow groundwaters can be discharged to surface waters and the ability of the surface waters to assimilate the hazardous/deleterious chemicals without adversely impacting existing or potential beneficial uses of the waterbodies receiving or downstream of the discharge of the hazardous/deleterious chemicals to surface waters.

Of particular concern with respect to shallow groundwater pollution of surface waters are hazardous chemical sites such as former RCRA treatment facilities, municipal and/or industrial landfills, etc. where landfills have been used for waste disposal. The inevitable failure of non-hazardous as well as hazardous waste landfill liner/containment systems including both US EPA Subtitle C and D landfills, and the unreliability of the groundwater monitoring systems that are used at these landfills, means that ultimately, where shallow groundwater flow paths exist from the base of the landfill to surface water systems, on-site landfills will not only pollute groundwaters with hazardous/deleterious chemicals, but also surface waters. Since this pollution may not occur for many decades after closure of the landfill, it is essential that appropriate measures are taken, including the development of a dedicated trust fund of sufficient magnitude to provide funds, effectively forever, to monitor shallow groundwaters for the transport of hazardous and deleterious chemicals to surface waters.

The hazardous chemical site manager (PRP) should be required to develop reliable estimates of the ability of groundwater monitoring wells located downstream of a source of hazardous chemicals to intersect plumes of hazardous chemicals derived from specific parts of the hazardous chemical site. Of particular concern are on-site unlined and lined landfills. The approach that is typically used today of incorporating a few down groundwater gradient wells at somewhat arbitrary locations frequently produces groundwater monitoring programs of limited reliability in detecting polluted groundwaters before widespread off-site pollution occurs.

As part of developing a groundwater monitoring program for a hazardous chemical site, the site managers - PRPs and the regulatory agencies should conduct an independent, in-depth, public interactive, peer review analysis of the statistical reliability of the groundwater monitoring well placement and sampling characteristics relative to the expected characteristics of groundwater pollution plumes that could arise from releases of hazardous/deleterious chemicals to the groundwaters from landfills and other waste management units. This evaluation for plastic sheeting lined landfills should include consideration of the vertical and lateral spread from the point of initial leakage through the flexible membrane liner to the point of groundwater monitoring.

In accord with RCRA regulatory requirements for groundwater monitoring, the detection of groundwater pollution at the point of compliance for groundwater monitoring shall use sampling procedures and frequency that is protective of human health and the environment. It is suggested that initial leakage through two-foot long rips, tears or points of deterioration in the flexible membrane liner be considered the lateral extent of the source of the hazardous/deleterious chemicals that enter the groundwater system underlying the FML lined landfill unit. Lee and Jones-Lee (1998d,e and 1999) provide additional information on the long-term problems associated with municipal and industrial non-hazardous and hazardous waste landfills as threats to public health and the environment.

Another common problem with evaluating the potential for hazardous chemical sites with multiple waste management units to pollute ground and surface waters with hazardous or deleterious chemicals is the use of area-wide average upgradient concentrations in groundwaters to assess whether groundwater pollution is occurring by a particular waste management unit. Such an approach can readily lead to erroneous conclusions on the potential for a particular waste management unit/waste containing area to cause pollution that can lead to impairment of uses of groundwaters or surface waters. Each waste management unit should be treated as an individual source where upgradient and downgradient monitoring wells are appropriately sampled for constituents that could pollute/impair the groundwaters.

The evaluation of pollution should be based on determining whether there is a statistically significant increase in the concentrations of constituents as the groundwaters pass under or around a waste-containing area. Also, all constituents that could impair the beneficial uses of a groundwater, including increases in concentrations of TDS, hardness or other conventional pollutants independent of whether they exceed a drinking water MCL, should be considered in evaluating the pollution of a groundwater by a waste management unit/hazardous chemical area.. This evaluation should not be based just on the Priority Pollutant list.

AN ALTERNATIVE MONITORING/EVALUATION 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 a potential adverse impact that should be evaluated to determine if the potential impact is, in fact, manifested in the receiving waters for the runoff. Lee and Jones-Lee (1996a,b; 1997b,d) and Jones-Lee and Lee (1998) have reported on the development of 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. This approach can also detect some water quality problems due to unregulated chemicals and conventional pollutants.

EM focuses using monitoring resources to find a real water quality problem-use impairment in the receiving waters for the stormwater runoff or groundwater discharge, 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/groundwater discharge. 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 that aquatic life can receive to excessive concentrations of available forms of constituents in the receiving waters. Also, as discussed herein, meeting water quality criteria/standards for some constituents such as Cr VI may not be protective of certain forms of aquatic life.

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 or groundwater discharges from a particular location cause real, significant water quality problems in the receiving waters for the runoff/discharge. Where such problems are found, the stakeholders work together to control them in a technically valid, cost-effective manner. 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 EM approach to determine whether stormwater runoff or groundwater discharges from a hazardous chemical site are adversely impacting the beneficial uses of receiving waters for the runoff. Additional information on this topic is provided in the references listed for this paper.

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 (1991) and Lee and Jones-Lee (1994a,1996a,b,c) recommend that all stormwater runoff and ambient surface 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. The chronic toxicity endpoint should be used to detect potential toxicity that is of concern. While there are some PRPs that attempt to justify using only acute toxicity endpoints in stormwater runoff water quality impact evaluation, such approaches should not be followed unless an appropriate evaluation has been made of the duration of exposure that aquatic life can receive in a particular waterbody relative to the critical duration of exposure that can be adverse to aquatic life in a particular waterbody.

Appropriately conducted aquatic life toxicity tests can screen stormwater runoff and groundwater inputs to surface 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 or under-regulated chemicals in stormwater runoff and groundwater discharge. 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 the organophosphate pesticides, diazinon and chlorpyrifos, 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. Lee and Taylor (1997) and Lee *et al.* (1999a,b) have reviewed stormwater runoff organophosphate toxicity issues. Diazinon is one of the unregulated chemicals that is causing widespread aquatic life toxicity in receiving waters for stormwater runoff from urban areas and some commercial and agricultural areas. 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 portion of this diazinon is volatilized at the time of application and transported through the atmosphere. It becomes surface water runoff through atmospheric scouring associated with 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 organophosphate 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), Lee and Jones-Lee (1994b, 1996c) and Lee *et al.*(1999a,b), 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 and groundwater discharges to surface waters for potential adverse impacts associated with the discharge of potentially toxic regulated and unregulated chemicals in the stormwater runoff/groundwater discharge. 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), Lee and Taylor (1997) and Lee *et al.* (1999a,b) 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, PCBs, 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 (1997) adopted risk-based tissue concentrations which consider the potential hazard that a particular concentration of a hazardous chemical in an organism tissue represents through 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 not 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 (1996b,d) 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 determined 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. The technically valid, cost-effective approach for assessing excessive bioaccumulation is a direct measurement of edible aquatic organism tissue residues. This is the approach that Lee and Jones-Lee (1996a,b,d) recommend as part of implementing the EM approach for stormwater runoff and groundwater discharges to surface waters. 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 contribute 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 and groundwater discharge enter the waterbody, then it can be concluded that excessive bioaccumulation is not occurring and, most importantly, that the stormwater runoff/groundwater discharge 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/groundwater discharge 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/groundwater discharge is a significant contributor of the constituent of concern to cause or contribute to the excessive bioaccumulation problem. Lee and Jones-Lee (1996a,b; 1997b) 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 surface waters and groundwaters 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. The larger, 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 (1996d) 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 potentially 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/groundwater discharge-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; 1996f) 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, 1998) 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 15 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 in sediments 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, 1996f), 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 has announced that it will not develop chemically-based sediment quality criteria based on TOC normalized non-polar organic concentrations for constituents such as certain PAHs and organochlorine pesticides. Instead, the Agency plans to release sediment quality guidelines which do not have the same regulatory requirements as criteria. As discussed by Lee and Jones-Lee (1993, 1996f) 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 more 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 the purpose of evaluating whether sediment-associated constituents are in toxic forms.

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 (1996f,g,h) 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 or groundwater discharge-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 or groundwater discharge. 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 (1996f) 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, 1998) can be used for this purpose.

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, 1996i). 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 1994a,b; 1996a,b,c; 1997b,c). 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 EM 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.

The EM approach can be effective in detecting water quality problems due to hazardous chemical site polluted shallow groundwaters that discharge to surface waters. In addition to monitoring the receiving waters in the vicinity of where groundwaters associated with the hazardous chemical site discharge to surface waters, a comprehensive groundwater monitoring program designed to detect plumes of hazardous and deleterious chemicals derived from the site before they reach surface waters can and should be conducted. This approach would enable the initiation of groundwater remediation programs before the transport of hazardous/deleterious chemicals from the site impairs the beneficial uses of surface waters.

A key component of an appropriate stormwater runoff and groundwater discharge monitoring program is the examination of the runoff waters, groundwater discharge 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.

It is important in developing a stormwater runoff water quality 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 stormwater 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.

An area of concern that is often overlooked is the potential for the translocation of hazardous or deleterious chemicals from waste deposition areas through plant roots, flowers and leaves to the environment. Such translocation is becoming well-known to occur through the use of bioremediation of sites involving the use of trees and shrubs that take up hazardous chemicals through their roots and store them within their trunk and leaf structure. It is important that those responsible for managing a hazardous chemical site as well as those responsible for regulating this management continue to evaluate whether terrestrial vegetation could become a mode of transport of hazardous and deleterious chemicals that are buried below the surface of the soil to the soil surface areas due to translocation through plants.

While eventual reduction of stormwater runoff from stabilized chemical sites may be appropriate if translocation issues do not become important, it may not be appropriate for evaluation of the impacts of hazardous and deleterious chemicals that are transported to surface waters via shallow groundwater. Such transport can be slow and require many years between when the groundwaters under the areas where hazardous and deleterious chemicals are located on the site and where they are discharged to surface waters. As a result, intensive groundwater and ambient water monitoring must be conducted for as long as the constituents at the hazardous chemical site represent a threat to public health and the environment through groundwater transport to surface waters. For landfilled wastes, the period of time for this type of monitoring should be considered infinite, i.e. as long as the wastes in the landfill are a threat that can generate leachate that can pollute groundwater and surface 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 as well as site-associated groundwater discharges to surface waters are 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, surface and groundwater hydrology, and water quality. The US EPA's 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 and site-associated shallow groundwater discharges to surface waters monitoring programs must involve in-depth, reliable examination of the water quality characteristics of the receiving waters for the runoff. The EM 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 EM 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 and any groundwater discharge to surface waters.

Specific examples of stormwater runoff water quality monitoring programs for hazardous chemical sites that incorporate many of the issues discussed in this paper are provided by Lee (1998a,b).

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Copies of the authors' reports which serve as background to this paper are available from their web site (http://members.aol.com/gfredlee/gfl.htm).

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