STORMWATER CHEMISTRY
AND WATER QUALITY

by

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1. Sources of Stormwater Pollutants

A considerable amount of research effort has been undertaken attempting to identify and quantify sources of stormwater pollution. This research has identified approximately eight major sources of common stormwater pollutants within drainage basins. Each of these sources is described briefly in the following sections.

1.1 Street Pavement

Components of road surface degradation are common constituents of urban runoff. Studies conducted in Europe have indicated that as much as 0.05-0. 10 inch of pavement surface is worn away from the roadway each year. The largest component of street pavement is the aggregate material itself, with additional smaller quantities originating from the asphalt binder, fillers and substances applied to the surface. The amount of material originating from roadway surfaces is dependent upon the age and type of surface, the climate of the area, and the average daily traffic loading.

1.2 Motor Vehicles

Motor vehicles contribute a wide variety of materials to runoff flow. Common constituents generated by motor vehicles include fuels, lubricants, particles from tires or brake lining. exhaust emissions which collect on the roadway surface, corrosion products, and larger broker, parts which fall from vehicles during operation. Although the actual quantity of material generated by the operation of motor vehicles is relatively small, the pollution potential is significant since many of these materials are toxic to aquatic life. Motor vehicles have been found to be the principle nonpoint source contributor of asbestos and many heavy metals including lead, zinc and copper. However, not all the pollutants generated by motor vehicles during rain events originate with the vehicle itself. A large portion of the pollutant loading consists of organics, nutrients and suspended solids which have become attached to the vehicle surface or underside and are washed onto the roadway surface by the action of the rain or splashing from street runoff.

1.3 Atmospheric Fallout

Atmospheric fallout originates as air pollution such as dust and particles from industrial processes, acid particles and heavy metals from fossil fuel power plants, dust emissions from automobiles and planes, and from exposed land. A large portion of the atmospheric fallout settles on the land surface and becomes entrained into the runoff flow during storm events. Another significant fraction of atmospheric fallout consists of smaller particles along with pollutants such as oxides of nitrogen and sulfur which become entrained into the rainfall prior to reaching the land surface. In some areas, atmospheric loadings of heavy metals and nutrients generated by direct rainfall exceed contributions generated from land surfaces.

Vegetation

Waste vegetation matter is an important source of organic and nutrient pollutants in urban stormwater. Organic matter such as leaves, grass, and other plant materials that fall or become deposited in urban areas may become part of stormwater runoff flows. Recent studies have suggested that soluble nutrients, particularly phosphorus, are released rapidly from plant matter after entering water.

Land Surface

Land use within a drainage basin is a primary factor in determining the characteristics of stormwater runoff generated within that basin. The type of ground cover found in the drainage basin as well as the amount of vehicular and pedestrian traffic is a function of land use and will have a direct effect on the quality of stormwater runoff generated within that area.

Litter

Litter consists of various kinds of discarded material such as food containers, packaging material and animal droppings. Many types of man-made litter do not constitute significant sources of pollution, although litter is highly visible and can be aesthetically unpleasing when discharged into a receiving waterbody. In some areas, animal droppings have been shown to be a major contributor of both nutrients and bacterial contamination in stormwater runoff.

Anti-Skid Compounds and Chemicals

Cities in cold weather regions often deploy large amounts of salts, sand, and ash which are designed to melt ice or provide better traction for motor vehicles during winter months. These materials accumulate along the roadway during the winter months and become part of the snow melt when spring arrives. In addition, chemicals such as fertilizers, insecticides and herbicides are often used for maintenance of roadside areas. Although the quantities of these chemicals which are used are relatively small, the enrichment and toxic effects of these chemicals often make them significant in a runoff flow.

1.8 Construction Sites

Erosion of soil from land disturbed during construction activities is a highly visible source of suspended matter in stormwater runoff. Soil erosion is a major source of stormwater solids for both urban and suburban areas.

2. Constituents in Stormwater Runoff

Although many different constituents can be found in urban runoff, the consistent presence of certain pollutants leads them to be considered "standard pollutants characterizing urban runoff". Such pollutants include:

- Suspended Solids (sediment)

- Nutrients
- Metals
- Oxygen Demanding Substances
- Oils, Greases and Hydrocarbons
- **Pathogens**

2.1 <u>Sediments</u>

Suspended matter, or sediment, is material such as sand, silt, clay and organic matter with a particle size larger than dissolved molecules or ions. Sediment is the largest contributor by volume to nonpoint source pollution in the United States. Suspended matter is generated primarily through erosion processes during rain events. Erosion results from rainfall and runoff when soil and other particles are removed from the land surface and transported into conveyance systems and waterbodies. Since land surface erosion is the principle source of sediment, the type of soil, land cover, and hydrologic conditions are major factors in determining the severity and extent of sedimentation problems. Although erosion is a natural process, it is frequently exacerbated by the activities of man, in both urban and rural environments. Nonpoint sources of suspended solids contribute approximately 95% of the average daily loading of sediments to receiving waters in the U.S. Sources and impacts of sediment pollution are summarized in Table 1 .

Sediment particles vary greatly in size and density, but may be roughly divided by particle diameter and behavior into suspended solids and colloidal particles. In the laboratory, the distinction between suspended solids and colloidal particles is often defined arbitrarily by the ability of particles to be trapped on a specific filter. Particles which are trapped by a 0.45 micron filter are considered to be suspended solids, while those passing through the filter are colloidal. The settleability of a particular solid particle depends to a large degree on particle diameter and density. Suspended particles are usually large enough to be removed by settling in quiescent waters, while colloidal particles often do not settle at significant rates and may remain in suspension indefinitely.

TABLE 1

SOURCES AND WATER QUALITY IMPACTS OF SUSPENDED SOLIDS (SEDIMENTS)

NONPOINT <u>SOURCE(S)</u>	**WATER QUALITY AND ASSOCIATED IMPACTS**
Agriculture Silviculture Urban Runoff Construction Mining-	Causes a decrease in transmission of light through water: - Decreases primary productivity of aquatic plants and phytoplankton upon which other species feed - Obscures sources of food, habitat, hiding places, and nesting sites - Interferes with mating activities that rely on sight and delays reproductive timing <u>May have</u> direct effects <u>on respiration and digestion of aquatic species</u> Decreases survival rates of fish eggs and sizes of fish populations which may alter species <u>composition</u> Increases temperature of surface layer of water which increases stratification and reduces

oxygen availability to lower layers

Decreases value for recreational and commercial activities:

- Reduced aesthetic value
- Reduced sport and commercial fish populations
- Decreased boating and swimming activities
- Interference with navigation

May affect surface water sources used for drinking water

Increases drinking water costs
Deposition can clog conveyance systems and reduce water storage

Many studies have indicated that other pollutants contributed by nonpoint sources are often bound or adsorbed onto suspended particles, a phenomenon which has been observed for phosphorus, heavy metals and organic compounds. This association significantly alters the water quality impacts of the bound pollutants. For example, the biological availability of phosphorus, nitrogen, pesticides and heavy metals is decreased substantially when these pollutants are bound to suspended matter. In addition, as sediments settle out, the associated pollutants also settle out, further reducing biological availability. Whether or not sediment-pollutant associations continue to mitigate the effects of contaminants depends on a number of factors, including how easily and quickly the pollutant will dissolve into solution, chemistry of the sediment layers, and the degree to which future storm events stir up bottom sediments and stimulate processes leading to release of bound pollutants.

'The receiving water impacts of Nonpoint source generated sediment loads depends upon the nature of the waterbody to which they are delivered. Slow-flushing lakes, reservoirs, ponds and estuaries may retain the sediment associated pollutants delivered to them for long periods of time. Such waterbodies may be particularly vulnerable to sediment deposition. Sediment buildup, coupled with accumulating nutrient pollution, can hasten the eutrophication of impounded waters. The suspended solids in urban runoff can also exert deleterious physical effects by sedimenting over egg deposition sites, smothering juvenile species of fish and aquatic insects, and altering benthic communities.

On an annual loading basis, contributions of suspended solids from urban runoff in the United States are approximately an order of magnitude or more greater than those from secondary sewage treatment plants. However, the nature of the suspended solids in urban runoff is different from those in treatment plant discharges, with urban runoff being higher in mineral and man-made products and somewhat lower in organic particulates. Also, the solids in urban runoff are more likely to have other contaminants adsorbed onto them.

2.2 Nutrients

Plant nutrients, such as nitrogen and phosphorus, are common constituents of nonpoint source runoff. The introduction of nutrients into receiving waters stimulates the growth of algae and other aquatic plants and accelerates the process of eutrophication. Nutrients enter runoff through sources such as fertilizers, plant matter, detergents and washing fluids, bulk precipitation, soil leeching, animal wastes, and seepage from septic tanks. Sources and impacts of nutrient pollution are summarized in Table 2.

Nutrients in stormwater may be present as either dissolved ions or in a particulate form. In general, about 40-50 percent of nitrogen and phosphorus in runoff is in a dissolved form, while 50-60 percent exists in a

particulate form. However, after entering a stormwater management system or receiving water, particulate forms may break down and decompose into dissolved species which may increase the percentage of dissolved forms. Dissolved forms of nitrogen include ammonia, nitrate and nitrite. Nitrogen incorporated into organic matter is the
most common. organic nitrogen form. Several dissolved forms of phosphorus have been measured in runoff, but the most common and important form is orthophosphorus, which is a form directly available for uptake by algae and other plants. Particulate phosphorus is present as both inert and organic solids.

Because nutrients are present in both dissolved and particulate forms, an effective stormwater management system must include provisions for settling of particulate forms and uptake mechanisms such as biological assimilation or adsorption for the dissolved forms. Uptake of dissolved nutrient forms in waterbodies, especially phosphorus, is relatively rapid.

TABLE 2

SOURCES AND WATER QUALITY IMPACTS OF NUTRIENTS (PHOSPHORUS, NITROGEN)

NONPOINT SOURCE(S)	**WATER QUALITY AND ASSOCIATED IMPACTS**
Agriculture	Nutrients promote premature aging of lakes and estuaries (eutrophication):
Silviculture	
Urban Runoff Construction Septic Tanks	- Algal blooms caused by nutrients and the resulting, decay of organic materials create turbid conditions that eliminate submerged aquatic vegetation and destroy habitat and food sources for aquatic animals and waterfowl
	- Blooms of toxic algae, such as blue-green species, can affect health of swimmers and aesthetic qualities of waterbodies
	- Excess algal growth favors survival of less desirable fish species over commercially/recreationally more desirable/sensitive species
	- Interference with boating and fishing activities
	- Reduced quality of water supplies, including addition of tastes and odors
	- Reduced dissolved oxygen levels can suffocate fish species
	- Reduction of waterfront property values
	Toxic Effects:
	Ammonia may be toxic to aquatic species at pH levels above 9.5 to 10.0

2.3 Heavy Metals

Heavy metals in stormwater runoff originate from the operation of motor vehicles, direct fallout, and the degradation of highway materials. Transportation related sources of metals include gasoline (Pb), diesel fuel (Cd), exhaust emissions (Pb, Ni), crankcase and lubricating oils (Pb, Ni, Zn), grease (Zn, Pb), tire wear (Cd, Zn), wear on moving parts (Cu, Pb), decorative and protective coatings (Al, Cd, Cu, Zn, Ni, Fe), brake lining wear (Cu, Cr, Ni), moving engine parts (Fe, Mn, Cr, Co), and asphalt paving wear (Ni, V). Sources and water quality impacts of heavy metals are summarized in Table 3.

The most abundant heavy metals in stormwater are lead, zinc and copper which together account for about 90 percent of dissolved heavy metals and 90-98 percent of total metal concentrations (Harper, 1985). Except for copper and cadmium, most metal species are present in particulate form. Consequently, very good removal efficiencies (60-95 percent) can be obtained in stormwater management systems which allow adequate detention time for sedimentation to occur. In general, the quantities of heavy metals in runoff and the forms in which they exist depend to a large degree on the physical and chemical nature of the specific elements.

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TABLE 3

SOURCES AND WATER QUALITY IMPACTS OF HEAVY METALS

NONPOINT SOURCE(S)	**WATER QUALITY AND ASSOCIATED IMPACTS**
Transportation Urban Runoff Mining Agriculture Construction	Dissolved metal species can create both short-term and long-term toxic impacts to receiving waters Heavy metals accumulate in bottom sediments, posing risks to bottom-feeding organisms and their predators Heavy metals can bioaccumulate in animal tissues Heavy metals can affect reproduction rates and life spans of aquatic species Heavy metals may disrupt food chains in aquatic systems Heavy metals can affect recreational and commercial fishing Heavy metals can affect water supplies

Although substantial research has been conducted on the effects of heavy metals on aquatic communities, prediction of toxic effects remains difficult. Predictions are complicated by the fact that dissolved heavy metals can exist in many different chemical speciations, each of which exhibits a unique toxicity and method of movement in the environment. Many inorganic and organic molecules and ions can form stable complexes with metal species in natural waters. The type of metal complexes affects both the toxicity and the potential for removal from the water column by adsorption, exchange or precipitation reactions.

The Nationwide Urban Runoff Program (NURP) (U.S. EPA, 1983) determined that heavy metals, especially copper, lead and zinc, are by far the most prevalent priority pollutants found in urban runoff. On a national basis, freshwater acute toxicity criteria for copper were exceeded in 47 percent of the samples and for lead in 23 percent of the samples. Freshwater chronic toxicity exceedances were common for lead (94 percent), copper (82 percent), zinc (77 percent) and cadmium (48 percent).

2.4 0xygen Demanding Substances

Oxygen demanding substances include numerous organic materials which are decomposed by microorganisms thereby creating a need for oxygen. There are many organic compounds which may be utilized by microorganisms in waterbodies as sources of energy and chemicals necessary for growth. Metabolic processes responsible for these transformations under aerobic conditions cause the breakdown of organic constituents to simpler compounds according to the following generalized reaction:

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$$C.H_bO_cN_d + \frac{(4a+b-2c-3d)}{4} O_2 - aCO_2 + \underline{(b-3d)}\ H_2 0 + dNH_3$$

This biochemical reaction results in utilization of oxygen dissolved in the water, imposing a BOD (biochemical oxygen demand) on the limited oxygen resources available in watercourses. The amount of BOD exerted depends on the types and amounts of organic chemicals present, numbers and types of organisms in the water, temperature, pH, presence of nutrients and trace elements necessary for growth, and many other environmental factors. Oxygen used in the biochemical reactions can be replenished through reaeration of oxygen from the atmosphere into the water and by photosynthetic production of oxygen by algae and other aquatic green plants. A summary of nonpoint source water quality impacts for oxygen demanding substances is given in Table 4.

TABLE 4

NONPOINT SOURCE WATER QUALITY IMPACTS FOR OXYGEN DEMANDING SUBSTANCES

NONPOINT SOURCE(S)	WATER QUALITY AND ASSOCIATED IMPACTS
Agriculture Silviculture Urban Runoff Septic Tanks	May cause oxygen depletion and fish kills if introduced in high concentrations
	May alter species composition to species more tolerant of low dissolved oxygen conditions
	May increase growth of anaerobic microorganisms which produce by-products responsible for odors in water
	Low oxygen levels may increase solubility of phosphorus and heavy metals in the water column

A stream or lake can tolerate the introduction of a limited amount of BOD without serious upset of its dissolved oxygen balance. However, when dissolved oxygen is used faster than it can be replenished by reaeration and photosynthesis, the concentration of dissolved oxygen in the water decreases. Reduction of dissolved oxygen to less than 3-5 mg/l can cause an adverse impact on fish that require a relatively high oxygen concentration to meet their metabolic needs. A further increase in BOD loading would result in an even lower dissolved oxygen concentration and progressively worse conditions for fish and other aquatic life. The addition of enough oxygen demanding materials to the watercourse could cause the total depletion of dissolved oxygen and the death of all fish. Furthermore, the absence of dissolved oxygen could result in the growth of microorganisms that produce by-products which cause foul odors in the water.

2.5 Oils, Greases and Hydrocarbons

Unlike the oxygen demanding substances, which are of concern because of oxygen depletion caused by rapid decomposition in a waterbody, other types of organic chemicals cause concern because they cannot be easily decomposed through biological action and may persist for long periods. Examples of such compounds include the low-boiling hydrocarbon fractions of oils and greases resulting from transportation and industrial sources, benzene from gasoline, synthetic detergents, pesticides, herbicides, wood preservatives, and a wide range of synthetic organic industrial chemicals. Many of these compounds exhibit acute or toxic effects on aquatic life at concentrations found in urban runoff. Because there is no-mechanism by which nature can rapidly cleanse itself of these constituents, even low input concentrations of these compounds may gradually accumulate in the environment and ultimately may reach objectionable concentrations in the water or in aquatic life. A summary of nonpoint source water quality impacts for oils, greases and hydrocarbons is given in Table 5.

TABLE 5

NON-POINT SOURCE WATER QUALITY IMPACTS FOR OILS, GREASES AND HYDROCARBONS (PESTICIDES AND HERBICIDES)

NONPOINT <u>SOURCE(S)</u>	**WATER QUALITY AND ASSOCIATED IMPACTS**
Agriculture Silviculture Urban Runoff Construction	All compounds can hinder photosynthesis in aquatic plants
	Sub-lethal effects lower resistance of organisms and increase susceptibility to other environmental stresses
	Some chemicals can affect reproduction, respiration, growth and development in aquatic species as well as reduce food supply and destroy habitat for aquatic species
	By definition, these chemicals are poisons; if released to the aquatic environment before degradation, many compounds can kill non-target fish and other aquatic species
	Some pesticides/herbicides can bioaccumulate in tissues of fish and other species
	Some pesticides/herbicides are carcinogenic and mutagenic
	Reduces commercial/sport fishing and other recreational values
	Health hazard from <u>human</u> consumption of contaminated fish/water
	Oils can create undesirable surface films on water
	Greases may accumulate in sediments with potential toxic effects
	May cause tainting of fish flesh or tastes in water supplies
	Volatile <u>hydrocarbons may be lethal</u> or toxic to fish or birds

Some chlorinated hydrocarbons are highly resistant to decomposition and may have acute or chronic health effects on humans. Because they are so persistent and are strongly adsorbed by cell materials, they often bioaccumulate in microorganisms to concentrations many times greater than concentrations in the water column. The consumption of those organisms by other organisms higher in the food chain and the subsequent repetition of that process can produce ever-higher concentrations at each step and, ultimately, may result in bioaccumulations to levels hundreds or even thousands of times that in the water. This sometimes produces concentrations in fish high enough to make them unacceptable as food, although concentration of the chemical in water itself may not be high enough to cause concern. Some of the thousands of persistent organics in existence today are objectionable because of known harmful effects on humans, fish or wildlife. Others are considered objectionable because of adverse effects that are suspected but whose -nature and extent are unclear.

2.6 <u>Pathogens</u>

This category includes a wide variety of organisms such as bacteria, fungi, viruses and protozoans capable of transmitting disease and having an adverse impact on human health. The primary source of pathogens in stormwater include animal wastes, illegal wastewater connections into stormsewer lines, seepage of groundwater containing pathogens into stormsewer lines, and septic tanks. A summary of nonpoint source water quality impacts for pathogens is given in Table 6.

TABLE 6

NONPOINT SOURCE WATER QUALITY IMPACTS FOR PATHOGENS (BACTERIA, FUNGI, VIRUSES, PROTOZOANS)

NONPOINT SOURCE(S)	WATER QUALITY AND ASSOCIATED IMPACTS
Agriculture	Introduction of disease-bearing organisms to surface waters
Urban Runoff	
Septic Tanks	Reduced recreational usage
	Increase in treatment costs for drinking water
	Human health hazards

Pathogens of primary concern in stormwater are those which are directly implicated in human health issues. These include bacteria, viruses, and other types of pathogenic organisms known to be transmitted through the water route. It is widely recognized that water is a key vehicle in direct transmission of the infectious agents of several diseases, including cholera, typhoid fever, salmonella, dysentery and diarrheal diseases. Water also is vitally important in the routes of many diseases in which it plays indirect but necessary roles, including some of the leading killers of people: malaria, yellow fever, filiariasis, and schistosomiasis.

The principle indicator of pathogen contamination is coliform bacteria. Coliform bacteria are generally accepted to be a useful indicator of the possible presence of human pathogens when the source of contamination is sanitary sewage. However, no such relationship has been conclusively demonstrated for urban runoff. Therefore, the use of coliforms as an indicator of human health risk when the sole source of contamination is urban runoff warrants further investigation. Unfortunately, pathogens are seldom measured in runoff studies. The NURP study reported that coliform bacteria are present at high levels in urban runoff and may exceed water quality criteria during and immediately after storm events in receiving waterbodies. Coliform bacteria in urban runoff can cause violations of criteria for the recreational use of lakes. When unusually high fecal coliform counts are observed, they may be partially attributable to sanitary sewage contamination, in which case significant health risks may be involved.

3. Concentrations of Pollutants in Stormwater

Concentrations of pollutants in stormwater runoff have been shown to vary considerably during a storm event, as well as from event to event at a given site, and from site to site within a given city and from city to city across the country. This variability is the natural result of high variations in rainfall intensity and frequency of occurrence, soil types, land use, weather patterns and intensity of watershed activities. The event mean concentration(EMC), defined as the total constituent mass discharge divided by the total runoff volume, is generally accepted as the primary measure of the characteristic pollutant concentration for individual storm events. Most research suggests that event mean concentrations of pollutants are characterized by log-normal distributions.

Since the probability distributions of pollutant concentrations in stormwater are often log-normal, the appropriate statistic to employ for comparisons between individual sites or groups of sites is the median value, because it is less influenced by the small number of large values typical of log-normal distributions and is a more robust measure of central tendency. However, the majority of published data on stormwater runoff reports mean values.

3.1 NURP Study Finding

A summary of median EMCs for all sites included in the NURP study by land use category is given in Table 7. In general, residential land uses were found to have the highest median EMCs for many pollutants **including BOD, COD,** TSS, total lead, total copper, TKN, nitrate, total P and soluble P.

Although not shown in Table 7, the NURP study found bacteria concentrations in stormwater to be significant. Coliform bacteria were found to be present at high levels in urban runoff which caused exceedances of water quality criteria during and immediately after storm events in many surface waters, even those providing high degrees of dilution. Fecal coliform counts in urban runoff were typically in the tens to hundreds of thousands per 100 ml during warm weather conditions, with the median for all sites being around 21,000/100 ml. During cold weather, fecal coliform counts were more typically in the 1, 000/ 100 ml range, which is the median for all sites. Thus, violations of fecal coliform standards were reported by a number of NURP projects.

TABLE 7

MEDIAN EVENT MEAN CONCENTRATIONS (EMCs) FOR ALL SITES IN THE NURP STUDY BY LAND USE CATEGORY

POLLUTANT	UNITS	RESIDENTIAL	MIXED	COMMERCIAL	OPEN/ NON-URBAN
Soluble P	ug	143	56	80	26
Total P	ug	383	263	201	121
NO2-N + N03-N	ug	736	558	572	543
TKN	ug	1900	1288	1179	965
Total N	ug	2636	1846	1751	1508
BOD	mg/I	10.0	7.8	9.3	
COD	mg/l	73	65	57	40
TSS	mg/l	101	67	69	70
Total copper		33	27	29	
Total Lead	ug/l	144	114	104	30
Total Zinc	ug/l	135	154	226	195

SOURCE: Environmental Protection Agency. Final Report of the Nationwide Urban Runoff Program, Final Draft, Vol. 1. WH-554. Water Planning Division, December 1983.

A summary of the most frequently detected priority pollutants in NURP urban runoff samples is given in Table 8. Heavy metals are by far the most prevalent priority pollutant constituents of urban runoff. All 14 inorganics (13 metals, plus cyanide; asbestos excluded) were detected, and all but three at frequencies of detection greater than 10 percent. Most often detected among the metals were copper, lead and zinc, all of which were found in at least 91 percent of the samples, with maximum concentrations of 100, 460 and 2,400 ug/l, respectively. Other frequently detected organics included arsenic, chromium, cadmium, nickel and cyanide.

In general, the organic pollutants were detected less frequently and at lower concentrations than the inorganic pollutants. Sixty-three of a possible 106 organics were detected. The most commonly found organic was the plasticizer bis (2-ethylhexyl) phthalate (22 percent) followed by the pesticide alpha-hexachlorocyclohexane (alpha-BHQ (20 percent). An additional 11 organic pollutants were reported with detection frequencies between 10 and 20 percent, including 3 pesticides, 3 phenols, 4 polycyclic aromatics and a single halogenated aliphatic.

TABLE 8

MOST FREQUENTLY DETECTED PRIORITY POLLUTANTS IN NURP RUNOFF SAMPLES*

DETECTION RATE	INORGANICS	ORGANICS
Detected in 75 % or more	Lead (94 %)	None
of the NURP samples	Zinc (94 %)	
	Copper (91 %)	
Detected in 50-74%	Chromium (58%)	None
of the NURP samples	Arsenic (52%)	
Detected in 20-49%	Cadmium (48%)	Bis (2-ethylhexyl) phthyalate (22%)
of the NURP samples	Nickel (43 %)	alpha-hexachlorocyclohexane (20%)
	Cyanide (23%)	
Detected in 10-19%	Antimony (13%)	alpha-Endosulfan (19%)
of the NURP samples	Beryllium (12%)	Pentachlorophenol (19%)
	Selenium (I I %)	Chlordane (17 %)
		gamma-Hexachlorociclohexane (Lindane) (15%)
		Pyrene (15%)
		Phenol (14%)
		Phenanthrene (12%)
		Dichloromethane (Methylene Chloride) (I I %)
		4-Nitrophenol (10%)
		Chrysene (10%)
		Fluoranthene (16%)

Based on 121 sample results received as of September 30, 1983; adjusted for quality control review. Does not include special metals samples.

SOURCE: Environmental Protection Agency. Final Report of the Nationwide Urban Runoff Program Final Draft, Vol. 1. W11-554. Water Planning Division, December 1983.

Criteria exceedances were less frequently observed among the organics than the inorganics. Freshwater chronic criteria exceedances were observed for pentachlorophenol, bis (2-ethylhexyl) phthalate, gamma-hexachlorocyclohexane (Lindane), alpha-endosulfan, and chlordane. All other organic exceedances were in the human carcinogen category and were most serious for alpha-hexachlorocyclohexane (alpha-BHC), gamma-hexachlorocyclohexane (gamma-BHC or Lindane), chlordane, phenanthrene, pyrene, and chrysene.

3.2 Characteristics of Stormwater Runoff in Florida

A compilation of stormwater characteristics representative of Central and South Florida conditions was recently performed by Harper (1994) based on a literature search of previous research projects and studies which measured and summarized stormwater pollutant concentrations or loading rates for various land use types. This search included publications and studies conducted within the State of Florida only. A total of 10 land use types and 8 pollutant categories were included. Approximately 100 reports and publications were reviewed with 40 reports actually used in development of pollutant characteristics. A summary of the results from this study is given in Table 9. In general, concentrations presented in Table 9 represent event mean concentrations (EMCs) for each parameter.

Concentrations of most pollutants listed in Table 9 are similar to those reported by the NURP study with the exceptions of lead and zinc which appear to be higher in value in the NURP data. Differences in levels of lead in the NURP data can be explained by changes in the lead content of gasoline from the late 1970s and early 1980s, when most of the NURP data was collected, to the mid to late 1980s when many of the studies represented in Table 9 were conducted.

Based on the literature review, microbiological parameters are rarely measured in stormwater studies. However, when these parameters are measured, elevated levels of coliform bacteria are frequently observed in runoff studies conducted within the State of Florida. It is not uncommon to find total coliform concentrations in the range of 10-6-10-8/100 Ml in heavily urbanized areas, even in stormsewer systems with no apparent illicit connections or cross connections with wastewater systems. Although the specific sources of coliform contamination in stormwater are not clearly understood, many researchers have suggested that pet wastes may play a significant role in introducing coliform bacteria into runoff. Other potential sources include groundwater inflow into the stormsewer system from septic tanks and surface flow from septic tank systems operated under high water table conditions. Unfortunately, the extreme variability observed in measured bacterial concentrations in stormwater runoff makes it extremely difficult to assign a meaningful average concentration for this pollution category. As a result, microbiological parameters are not included in the parameters listed in Table 9.

4. Estimation of Pollutant Loadings from Stormwater Runoff

Although absolute pollutant concentrations are important in determining water quality characteristics and potential toxic effects in the immediate vicinity of stormwater outfalls, overall toxic effects on receiving waterbodies can only be addressed by evaluation of total mass inputs for each pollutant. Estimation of mass inputs requires knowledge of stormwater quantity as well as quality. It is generally recognized that as the percentage of impervious area increases within a watershed, both the volume and the rate of stormwater discharge increase. Typical changes in runoff flows resulting from increases in impervious surfaces are illustrated in Figure 1.

TABLE 9

SUMMARY OF LITERATURE-BASED RUNOFF CONCENTRATIONS FOR SELECTED LAND USE CATEGORIES IN CENTRAL AND SOUTH FLORIDA

LAND USE CATEGORY	TYPICAL RUNOFF CONCENTRATION (mg/1) TOTAL N	ORTHO-P	TOTAL P	BOD	TSS	TOTAL Zn	TOTAL Pb	PERCENT IMPERVIOUS	RUNOFF COEFFICIENT
1. Low Density Residential [1]	1.77	0.077	0.177	4.4	19.1	0.032	0.037	14.7	0.268
2. Single-Family	2.29	0.15	0.30	7.4	27.0	0.057	0.048	27.8	0.373
3. Multifamily	2.42	0.27	0.49	11.0	71.7	0.055	0.087	67.0	0.675
4. Low-Intensity Commercial	1.18	0.03	0.15	8.2	81.0	0.111	0.136	91.0	0.837
5. High Intensity Commercial	2.83	0.33	0.43	7.2	94.3	0.170	0.214	97.5	0.887
6. Industrial	1.79	0.13	0.31	9.6	93.9	0.122	0.202	86.8	0.793
7. Highway	2.08	0.14	0.34	5.6	50.3	0.134	0.189	85.0	0.783
8. Agricultural									
a. Pasture	2.48	0.349	0.476	5.1	94.3			0.00	0.355
b. Citrus	2.05	0.088	0.140	2.55	16.3			0.00	0.282
c. Row Crops	2.68	0.398	0.562					0.00	0.204
d. General Agriculture	2.32	0.227	0.344	3.8	55.3			0.00	0.304
9. Recreational/Open Space	1.25	0.004	0.053	1.45	11.1	0.006 [2]	0.025	1.50	0.163
10. Mining	1.18	0.07 [3]	0.15	9.6 [4]	93.9 [4]	0.122 [4]	0.202[4]	23.0	0.361
11. Wetland	1.60	0.13	0.19	4.63	10.2	0.006	0.025	0.00	0.225
12. Open Water/Lake	1.25	0.05 [3]	0.11	1.6	3.1	0.028	0.025 [2]	100	0.500

1. Average of single-family and recreational/open space loading rates
2. Runoff concentrations assumed equal to wetland values for these parameters
3. Orthophosphorus concentrations assumed to equal 50% of average total phosphorus
4. Runoff concentrations assumed equal to industrial values for these parameters

A better understanding of the receiving water impacts resulting from stormwater runoff can often be obtained by evaluating mass loadings, which reflect the total runoff volume as well as the chemical characteristics of the runoff. Estimates of annual mass loadings were calculated for each pollutant category listed in Table 9 by multiplying the listed event mean runoff concentrations times estimates of annual runoff volumes for each land use type. Estimates of annual runoff volumes per unit surface area were obtained using the runoff coefficients given in Table 9, an estimated annual rainfall of 50 inches and a unit area of 1 acre. The resulting estimates of annual mass loading rates, in terms of kilograms of pollutant per acre per year, are given in Table 10.

Evaluation of pollutant loadings on a mass basis provides a somewhat different picture of potential impacts than might be obtained from evaluating concentration based data only. For example, the typical runoff concentration for total nitrogen in single-family land use given in Table 9 is 2.29 mg/l. Low intensity commercial land use exhibits a much lower typical nitrogen concentration of 1. 18 mg/l. This difference may lead to the initial conclusion that single-family land use is a larger contributor of nitrogen to receiving waters than low intensity commercial use. However, due to differences in annual runoff volumes generated within each land use, low intensity commercial areas contribute an average of 5.18 kilograms of nitrogen per acre per year, while single-family land use contributes 4.68 kg/acre per year. Knowledge of mass loading rates is also important in evaluating the pollutant attenuation capabilities of various stormwater management practices since many of the removal efficiencies reported in the literature are based on annual mass removal rather than on reductions in concentration.

Estimates of pollutant loadings from watershed areas are often included in various types of stormwater evaluations. If pollutant loadings based upon actual field and laboratory analyses are not available, estimates of pollutant loadings can be obtained for planning or comparison purposes by using the concentration-based runoff characteristics listed in Table 9 or the areal pollutant loading rates for various land use categories listed in Table 10. If the area within each land use category is known for a particular drainage basin, estimates of event-based or annual pollutant mass loadings can be performed using a standard spreadsheet program. Since the estimated concentrations and areal loading rates presented in Tables 9 and 10 do not include the effects of stormwater management systems or attenuation during migration through open channel conveyance systems, pollutant attenuation must also be incorporated into the analysis to obtain the most realistic estimate of pollutant loadings actually reaching the receiving waterbody.

Although it is easier to estimate pollutant loadings using the areal pollutant loading rates presented in Table 10, combined with estimates of the area within each land use category, this method of estimation may not always produce the most accurate results. This method estimates pollutant loadings based upon estimates of both runoff concentrations and hydrologic characteristics, which are assumed to be the same for all areas in a particular land use category. A more accurate method of generating estimates of pollutant loadings from a drainage basin area is to combine the concentration-based values presented in Table 9 with site-specific hydrologic characteristics which can be used to generate estimates of annual runoff volumes discharging from each land use category. This approach will allow consideration of parameters such as soil type, percentage of impervious areas, soil moisture characteristics, and other site-specific parameters, resulting in a more reliable estimate of annual pollutant loadings for the basin under consideration. It should be emphasized that it is inappropriate to use rational formula runoff coefficients (C values) for estimation of annual runoff from land use types since these textbook values are designed to reflect runoff conditions under 10-year, 25-year or 100-year storm conditions and will result in a gross over-estimation of the total annual runoff volume discharging from a particular land use type on an annual basis.

TABLE 10

SUMMARY OF CALCULATED AREAL POLLUTANT LOADING RATES FOR CENTRAL AND SOUTH FLORIDA

LAND USE CATEGORY	AREAL LOADING RATE (kg/ac-yr)						
	TOTAL N	ORTHO-P	TOTAL P	BOD	TSS	TOTAL Zn	TOTAL Pb
1. Low Density Residential	2.88	0.169	0.320	7.63	31.9	0.064	0.052
2. Single-Family	4.68	0.335	0.594	14.3	56.1	0.122	0.083
3. Multi Family	8.51	0.924	1.72	38.4	256	0.188	0.299
4. Low-Intensity Commercial	5.18	0.157	0.650	36.1	343	0.511	0.635
5. High Intensity Commercial	13.0	1.52	1.96	79.3	435	0.782	0.985
6. Industrial	7.30	0.519	1.24	39.5	383	0.543	0.872
7. Highway	6.69	0.361	1.32	21.9	182	0.508	0.727
8. Agricultural							
a. Pasture	4.54	0.732	0.876	7.99	126		
b. Citrus	2.91	0.123	0.197	3.60	21.9		
c. Row Crops	2.84	0.421	0.595				
d. General Agriculture	3.62	0.380	0.551	5.80	74.0		
9. Recreational/Open Space	1.07	0.003	0.046	0.956	7.60	0.005	0.021
10. Mining	2.21	0.131	0.281	18.0	176	0.229	0.378
11. Wetland	1.81	0.204	0.222	4.96	11.2	0.009	0.039
12. Open Water/Lake	3.23	0.130	0.273	4.02	8.05	0.073	0.065

1. Average of single-family and recreational/open space loading rates

5. Removal of Stormwater Pollutants

There are many distinct physical and chemical processes which occur in stormwater management systems to remove pollutants from the water column. The exact nature of the processes involved depends upon the type of pollutant, whether the pollutant exists as a particle or in an ionic form, affinity for adsorption or biological uptake, chemical reactions, volatilization, and others. However, in spite of this complexity, removal processes can be divided into those mechanisms which affect particulate forms and those processes which affect dissolved or ionic forms.

5.1 Removal of Particulate Pollutants

The primary mechanism for removal of suspended matter in water is the unhindered settling of discrete particles according to Newton's Law (for turbulent conditions) or Stoke's Law (for larninar conditions), often termed Type I settling. These processes are extremely important pollutant removal mechanisms since they not only remove suspended matter but also other pollutants which may be bound or adsorbed onto the suspended matter. The following factors seem to be of significance in describing the settling characteristics of suspended solids and associated pollutants:

- Type of pollutant load in the stormwater
- Percentage of settleable pollutants
- Particle size distribution
- Particle settling velocities
- Particle volume distribution of the solids
- The density of the settleable pollutants
- The pH of the water
- The heavy metal content of the water

A study of the distribution of particle settling velocities in urban runoff was conducted by EPA (1986) based on laboratory studies of 50 different runoff samples from seven different sites around the U.S. The results of this survey are summarized in Figure 2. Approximately 20 percent of the solids exhibited settling velocities less than 101 cm/sec, corresponding roughly to particle sizes less than 10 microns. Under ideal quiescent conditions, a particle settling at a rate of 10-1 cm/sec will travel approximately 5.7 feet in 48 hours and should be effectively removed from a water column of this approximate depth over a period of 48 hours. Particle sizes less than 10 microns, generally considered to be in the colloidal or clay range, cannot be effectively removed by sedimentation.

Unfortunately, conditions within detention basins are often turbulent due to the inflow and outflow of water and wave action. As a result, small diameter particles capable of settling can be maintained in suspension and may even resuspend from the bottom of the basin in shallow systems. These naturally occurring processes can reduce the measured sediment removal efficiencies of stormwater management systems. Pollutants which are attached to suspended matter are often associated with these smaller particle sizes which reduces the removal of associated pollutants as well.

One of the most comprehensive evaluations of sedimentation for stormwater runoff was conducted by Randall, et al. (1982) in laboratory settling tests of seven urban stormwater samples. A summary of his results for suspended solids, COD, total P and lead is given in Figure 3. Settling processes for these particulate associated pollutants appear to be virtually complete after 24-48 hours with good removals achieved for all parameters. Removal of dissolved ions by sedimentation was generally poor. However, these results represent optimum settling under laboratory conditions. Actual observed settling in a stormwater management system may be less than these reported laboratory values.

To maximize removal of suspended matter, designs for retention or detention facilities should provide physical configurations which encourage a reduction in flow velocity to promote particle sedimentation, maximize the flow length from inlets to the discharge point, prevent short circuiting of flows and hydraulically dead zones, and include suitable aquatic plants to promote removal of dissolved pollutants.

5.2 <u>Removal of Dissolved Pollutants</u>

A wide variety of chemical, physical and biological processes are responsible for removal of dissolved pollutants from runoff in stormwater treatment systems. These processes include chemical precipitation, adsorption onto plant surfaces, adsorption onto suspended solids, adsorption onto the sediment surface, cation exchange, complexation with organic matter, volatilization, biological uptake by algae, macrophytes and aquatic animals, coagulation and flocculation, chemical transformations, and bacterial decomposition. The type and extent of these processes is highly dependent upon the type of pollutant and the nature of the environment provided by the stormwater treatment process.

5.2.1 Nutrients

Dissolved stormwater pollutants such as nutrients and oxygen demanding wastes are removed primarily through biologically mediated processes although physical adsorption onto inert surfaces may occur to a limited degree. Removal of these pollutants is generally optimized in systems which maintain permanent pools, diverse biota, and are well oxygenated. Removal of dissolved phosphorus in these systems is generally excellent since orthophosphorus, which is rapidly taken up by algae in the water column, is the primary dissolved form of phosphorus in runoff.

Several forms of dissolved nitrogen are present in runoff such as ammonia, nitrate and dissolved organic complexes. Ammonia can be utilized by some algae and higher plants and can also take part in exchange or adsorption processes onto solid surfaces. Nitrate is also a plant nutrient but does not generally participate in other physical processes. Unfortunately, concentrations of both ammonia and nitrate in runoff are generally well in excess of the uptake capabilities of the biota. Organic nitrogen is generally not biologically available and does not adsorb well onto other substances. However, organic nitrogen can be assimilated by bacteria under aerobic conditions and converted into ammonia, but the significance of this process in stormwater systems is probably low. In general, removal of dissolved nitrogen in stormwater management systems is much less than that observed for phosphorus.

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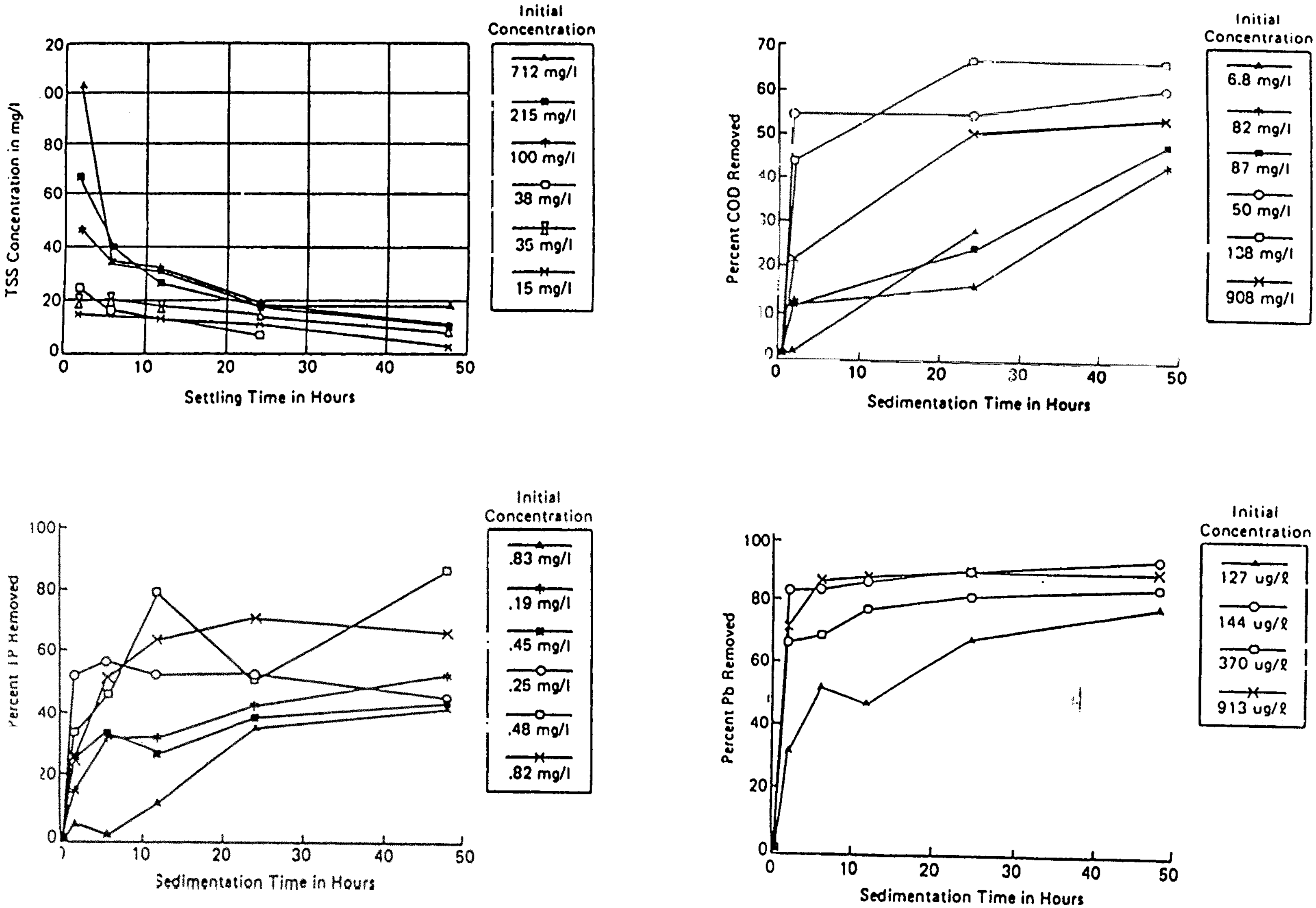

Figure 3. Removal of TSS, COD, Total P, and Total Pb Versus Sedimentation Time (Randall, et al., 1982).

5.2.2 Oxygen Demanding Wastes

Removal of oxygen demanding wastes occurs through simple oxidation of organic matter by aerobic bacteria and fungi. This process is generally complete in 3-5 days. Therefore, to optimize removal of oxygen demanding substances, stormwater systems must provide adequate supplies of oxygen and sufficient detention time for decomposition processes to occur. The system design should include mechanisms to maintain high oxygen levels and prevent the formation of anaerobic conditions. These mechanisms can be natural such as shallow water depths (less than 10-15 feet), a high length to width ratio to induce wind mixing, or artificial aeration. The adequacy of these design features for maintaining-aerobic conditions is highly dependent upon the magnitude of the BOD loading to the system.

5.2.3 Heavy Metals

Dissolved heavy metals are removed from the water phase of stormwater management systems primarily by physical and chemical processes. Virtually all heavy metals can be biologically assimilated in small amounts, but this is relatively insignificant as a removal mechanism for all metals except copper. Important chemical and physical processes for heavy metals include chemical precipitation as hydroxides, carbonates and sulfides; adsorption onto negatively charged anionic sites in clay minerals; sorption and coprecipitation on hydrous oxides of iron and manganese; complexation with organics followed by coagulation and flocculation; and sorption onto carbonates and phosphates.

Most removal processes for heavy metals result in deposition of the metals into the sediments. To keep metals bound to sediments, it is important that the sediment pH be kept in the pH range of 6-8 and that the sediments be aerobic. Under these conditions, metal-sediment associations are relatively inert with virtually no tendency for release into the water column or into groundwaters. However, substantial decreases in sediment pH, and to a lesser extent redox potential as well, will cause some metals to solubilize from the sediments. For this reason, it is important to monitor the accumulation of sediment and decaying organic matter within stormwater ponds since this accumulation can result in lowered sediment pH and possible anaerobic conditions.

5.2.4 Pathogens

The fate of pathogens in stormwater management systems is poorly understood since most studies have ignored this pollutant category. The limited research available in this area suggests that concentrations of coliform bacteria can be reduced in stormwater management systems. Suspected removal mechanisms include die-off, coagulation, predation by zooplankton, and adsorption onto suspended matter with subsequent deposition into the bottom sediments. Perhaps the best treatment technique for excessive coliform levels is to investigate and reduce the sources within the watershed.

5.2.5 Oils, Greases and Hydrocarbons

Oils, greases and hydrocarbons are removed primarily by physical and chemical processes, since biological uptake is relatively limited. Low boiling hydrocarbons often float on the water surface and are removed by volatilization. Greases generally accumulate into the sediments where they may undergo gradual microbial decomposition. Many pesticides are relatively insoluble in water, as well as hydrophobic, and readily adsorb onto soil particles.

Oils and greases can be effectively retained in stormwater management systems by using oil skimmers at the discharge weir. The best technique for reducing pesticides is to control the sources of these compounds within the watershed.

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What is an Illicit Discharge? ï‚¡ Georgetown County Stormwater Ordinance defines an Illicit Discharge as: ï¬ â€œAny activity which results in a discharge to the Georgetown County Storm Water System or receiving waters that is not composed entirely of storm water, except a discharge pursuant to an NPDES permit and other allowable discharges as defined in this Ordinance.â€Â Soil erosion is a major source of stormwater solids for both urban and suburban areas. Components of Stormwater Runoff ï‚¡ Suspended Solids (Sediment) ï‚¡ Nutrients ï‚¡ Metals ï‚¡ Oxygen Demanding Substances ï‚¡ Oils, Greases and Hydrocarbons ï‚¡ Pathogens Suspended Solids (Sediment) ï‚¡ ï‚¡ ï‚¡ Material such as sand, silt, clay and organic matter with a particle size larger than dissolved molecules or ions. Stormwater, also spelled storm water, is water that originates from rain, including snow and ice melt. Stormwater can soak into the soil (infiltrate), be stored on the land surface in ponds and puddles, evaporate, or runoff. Most runoff is conveyed directly to nearby streams, rivers, or other water bodies (surface water) without treatment. In natural landscapes, such as forests, soil absorbs much of the stormwater. Plants also reduce stormwater by improving infiltration, intercepting precipitation as Soil Chemistry and Fertility. Water quality and chemistry. Soil chemistry and biology.