



Northeast Coastal and Barrier Network Assessment of Contaminant Threats

Sagamore Hill National Park

Natural Resource Technical Report NPS/NCBN/NRTR—2010/344



ON THE COVER

Winter sunrise behind Theodore Roosevelt's home at Sagamore Hill National Park
Photo taken by Brian Forseth

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Contents

	Page
Figures.....	v
Tables.....	vii
List of Abbreviations	ix
Introduction.....	1
General Physical Characteristics	1
Biological Habitats	4
Source Inputs at Sagamore Hill National Historic Site (SAHI)	5
Onsite Inputs.....	5
<i>Terrestrial Soil</i>	5
<i>Surface Water</i>	7
<i>Groundwater</i>	9
Offsite Inputs	9
<i>Surface Water</i>	9
<i>Terrestrial Sources</i>	10
Chemicals of Concern in Different Matrixes.....	13
Surface Water Analysis	13
Oyster Bay and Cold Spring Harbor Sediment Toxicity and COCs	13
Groundwater	16
Monitoring Recommendations Based on Risk Evaluations.....	21
Management Recommendations.....	22
Conclusion	25
Literature Cited	27

Appendix 1: Hazard Quotient Approaches and Sampling Protocols for Screening Level Evaluations for Chemicals of Concern at National Parks.....	39
Appendix 2: Hazard Quotient Approaches and Sampling Protocols (continued)	73

Figures

	Page
Figure 1. Location of SAHI on Long Island, New York.	2
Figure 2. Map of SAHI on Long Island, New York.	2
Figure 3. Topographical Map and Nature Trail Route.....	3
Figure 4. Hazardous Waste Sites near SAHI.	12
Figure 5. Sampling Locations in Oyster Bay (#11) and Cold Spring Harbor (#7).	16

Tables

	Page
Table 1. Detection of Pesticides Applied to Estuarine Environment.	6
Table 2. EPA Water Quality Criteria Analysis for Entire SAHI Study Area.	14
Table 3. NOAA Sediment Data for Metals in Sites near SAHI.	17
Table 4. NOAA Sediment Data for Organic Chemicals.	18
Table 5. Recommendations for Sampling to Examine COCs in Different Matrix in SAHI.....	23

List of Abbreviations

atm	Atmospheres
AUF	Area Use Factor
BAF	Bioaccumulation Factor
BCF	Bioconcentration Factor
BW	Body Weight
CFC	Chlorofluorocarbon
CFR	Code of Federal Regulations
COC	Chemical of Concern
CRC	Contamination Reduction Corridor
CRZ	Contamination Reduction Zone
DDE	Primary persistent metabolite of DDT
DDT	Broad spectrum pesticide
DOT	Department of Transportation
EEE	Eastern Equine Encephalitis
EPA	Environmental Protection Agency
ERL	Expected Response Low
ERM	Expected Response Moderate
FCM	Food Chain Multiplier
FIR	Food Intake Ratio
GFCI	Ground Fault Circuit Interrupter
GPS	Global Positioning System
HQ	Hazard Quotient
IR	Ingestion Rate
K _{ow}	Octanol/water partitioning Coefficient
LD ₅₀	Lethal Dose resulting in 50% death
LOAEL	Low Observable Adverse Effects Level
MHQ	Matrix concentration quotient
MTBE	Methyltetbutylether (gasoline additive)
MPN	Most Probable Number (bacteria)
NCBN	National and Coastal Barrier Network
NOAEL	No Observed Adverse Effects Level
NPS	National Park Service
PAH	Polyaromatic hydrocarbons
PCB	Polychlorinated biphenyl
PEL	Probable Effects Level
pH	Concentration of hydrogen ions
PM _{2.5}	Particulate Matter 2.5 microns in size
PM ₁₀	Particulate Matter 10 microns in size
ppb	Parts per billion (ug/Kg or ug/L)
ppm	Parts per million (mg/Kg or mg/L or atmospheric # atoms/cubic meter air)
QA	Quality Assurance
QAWP	Quality Assurance Work Plans
QC	Quality Control

List of Abbreviations (continued)

RI/FS	Remedial Investigation/Feasibility Study
ROD	Record of Decision
SAHI	Sagamore Hill National Park
SOP	Standard Operating Procedure
SQuiRT	Screening Quick References Tables
TDI	Total Daily Intake (of a compound)
TEL	Threshold Effects Level
TBT	Tributyltin
THQ	Threshold Hazard Quotient
TOC	Total Organic Carbon
TRI	Toxic Reporting Inventory
USEPA	United States Environmental Protection Agency
VOA	Volatile Organic Analysis
VOC	Volatile Organic Compounds

Introduction

The purpose for this report is to review existing contaminant data from all sources (state, U.S. Environmental Protection Agency, National Park Service, U.S. Corps of Engineers etc.) and produce a data synthesis report for Sagamore Hill National Park (SAHI). Site visits and interviews with NPS staff were carried out to evaluate sources and threats and assess the ecological setting at each park. A park specific baseline inventory and monitoring plan which will include recommendations for frequency of sampling, sampling locations, sample analytes, analytical methods and sampling methods based on the information collected from Task 1 and 2 will be prepared and recommendations of contaminant assessments that should be conducted to evaluate threats to natural resources to document impairment will be submitted. The recommendations are based on the current data sets that may be limited due to minimal sampling for specific chemical contaminants at the park and in the surrounding area.

The approach taken in this and other reports will utilize a hazard quotient (HQ) approach. A detailed discussion of this approach is presented in Appendix 1. The basic principle is that detected levels in a matrix (sediment, soil, water or tissue) that are greater than a given benchmark concentration or dose that is considered a threshold for toxicity results in a HQ greater than one. HQ greater than one for a compound would result in that compound being considered a chemical of concern (COC). In the case where there are no data from a site, but there is literature or personnel observations that would suggest the specific activities could contribute to chemical loading that could impact park wildlife, then sampling is suggested to be carried out to confirm or refute such an assertion.

General Physical Characteristics

SAHI is an 83 acre park located in an urban and suburban environment in Oyster Bay, Long Island, New York. The park is part of the Oyster Bay National Wildlife Refuge that encompasses Oyster Bay Harbor and a portion of Cold Spring Harbor (Figure 1). The park is approximately 35 miles from New York City and is in an urban residential setting. The park is located in the central portion of the Cove Neck Peninsula. The peninsula is surrounded by Oyster Bay and Cold Spring Harbor. Both of these water bodies are saltwater and receive freshwater inputs from streams and creeks, and soil inputs from surface runoff.

There is good tidal exchange between Long Island Sound and these more protected bays. The lands surrounding the bay are generally at a higher elevation with drainage into creeks that enter the bays, resulting in this bay complex acting as a sink for terrestrial borne contaminants. In specific areas along the shoreline there are estuarine marshes and sandy beaches intermixed with residential and commercial activities. The offshore waters are heavily utilized by recreational boaters. The upland areas are primarily second growth forests and residential areas (Figure 2). The park's variety of habitats—woodlands, open fields, beaches and salt marshes—provide a great deal of diversity in plant and animal life. There are two freshwater ponds (Heron and Woodpile) located in the upland woodlands. In spite of the surrounding urbanization, SAHI has a relatively rare and intact stand of native oak-tulip tree forest in the northwest corner of the park. The park also includes a hydrologically intact maritime complex consisting of high and low salt marshes, a tidal creek, dunes, and beach. The park's beach-salt-marsh-tidal-creek habitat complex is part of the larger Oyster Bay and Cold Spring Harbor system.



Figure 1. Location of SAHI on Long Island, New York.

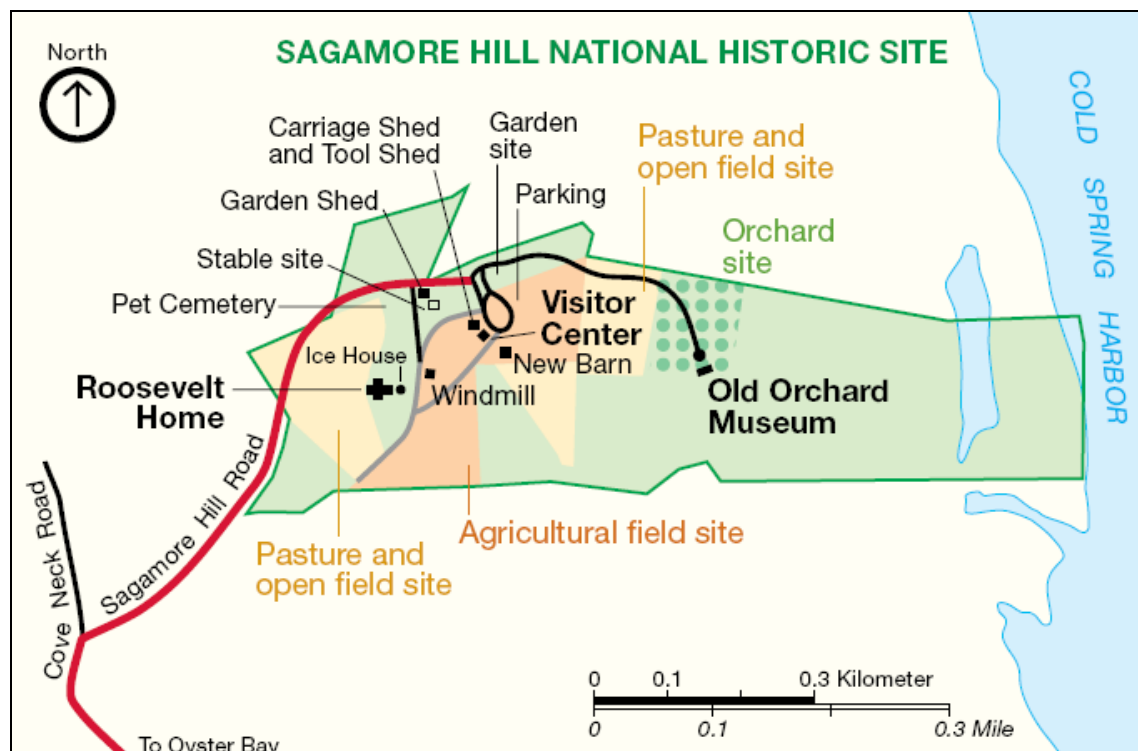


Figure 2. Map of SAHI on Long Island, New York.

The residences in the area are primarily large family-type estates on large acreage of grass fields and forested areas. The area surrounding the park would be considered suburban with residential

areas having well maintained lawns. There are small urban centers such as Oyster Bay and many small village type communities.

The soil can be best described as sandy with a layer of plant humus on the surface. Beneath the sandy soil is bedrock. Because of the sandy nature of the soil leachable compounds will move with the groundwater and potentially concentrate into the ponds or marsh area because they are down-slope from the buildings and grounds. The bedrock will act as a barrier to deeper penetrations of chemicals. Although there is limited onsite application of chemicals, the ponds and marsh area will act as naturally occurring retention basins. The sediments in the ponds and in the marsh area could act as sinks for persistent contaminants.

The beach and marsh area are on the down-slope of the park and borders Cold Spring Harbor (Figure 3). The marsh area is fed both by freshwater from the upland area and saltwater from the tidal action in the bay. The beach is connected to the upland area by a walkway that crosses the marsh area. Adjacent to the beach area, on the southern edge, there is a small inlet, which has a bulkhead and a dock along with several gasoline powered watercrafts.

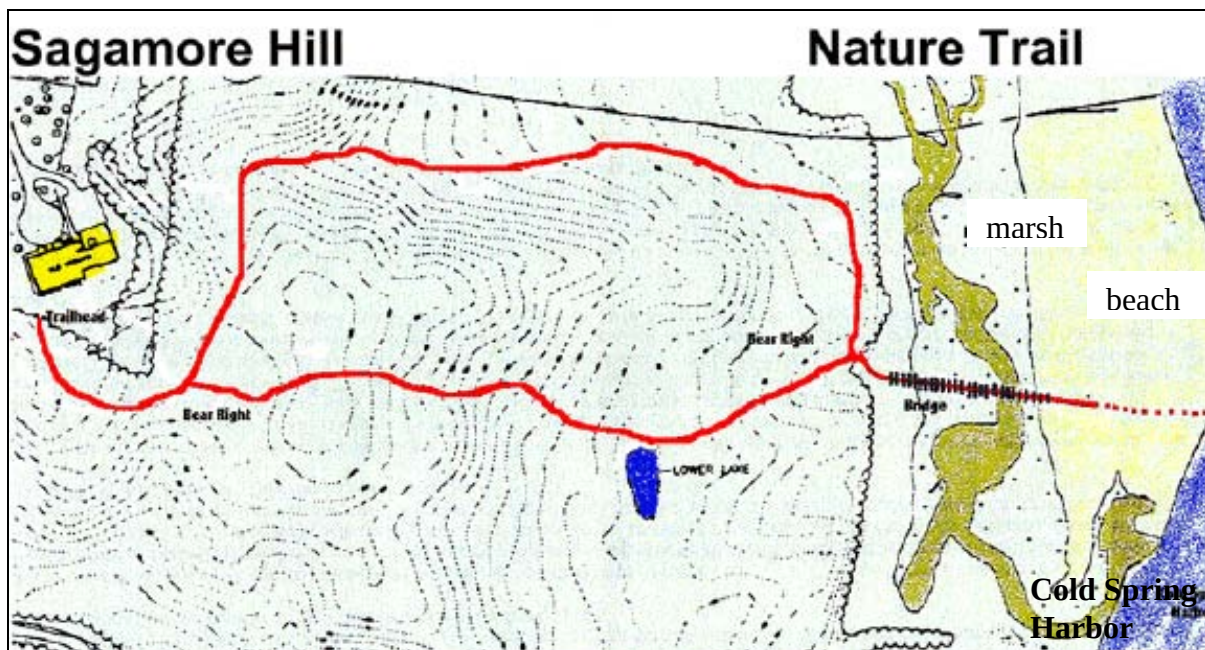


Figure 3. Topographical Map and Nature Trail Route.

Biological Habitats

Due to its small size, SAHI does not contain large, contiguous areas comprised of a single vegetation type. However, the site's many vegetation types are utilized by a variety of wildlife, including rare species. The park's fauna consist of a variety of urban tolerant species, but some species like the spotted salamander (*Ambystoma maculatum*), frogs (green frogs, [*Rana clamitans*], bullfrogs [*R. catesbeiana*], gray tree frogs [*Hyla versicolor*]), and Eastern box turtle (*Terapene carolina carolina*), which are uncommon in developed areas. The park also houses 21 species of dragonflies and damselflies including the rare comet darner (*Anax longipes*). The presence of dragonflies and damselflies would indicate that the waters they are breeding in are relatively pristine because these insects are very sensitive to metals, pesticides, and organic compounds. Their presence in a stream is used as a gauge of low level contamination and therefore they are considered an indicator species (May 2004). The two ponds (Heron and Woodpile) are the only freshwater wetlands in the park and exhibit high species diversity. The ponds are critical for obligate vernal pool breeders like wood frogs (*Rana sylvatica*), spotted salamanders, spring peepers (*Pseudacris crucifer*), and grey tree frogs. There are no fish within these ponds.

The salt marshes attract the diamond-backed terrapin (*Malaclemys terrapin*) that comes ashore in spring and lays eggs in holes dug in loose sand. There is a flyway for migratory birds moving along the east coast. There are a total of 116 species of birds seen in SAHI. Notable species found here are the winter wren (*Troglodytes troglodytes*), great crested flycatcher (*Myiarchus crinitus*), yellow billed cuckoo ([*Coccyzus americanus*](#)), and the ruby crowned kinglet (*Regulus calendula*). Below the beach waterline and in the marsh area are a number of molluscan species (bivalve and gastropods) present in the intertidal area and in the back marsh. Invertebrate species such as sandworms are present along the shoreline along with other seasonal species. These invertebrate species and lower vertebrates serve as an important source of energy for the migratory and resident birds.

Source Inputs at Sagamore Hill National Historic Site (SAHI)

SAHI is a small park with minimal large industry impacting the local environments (Figure 4). The potential COC inputs to the park can include both offsite and onsite activities. The COC inputs can reach the park through air, land, and water routes. However, without actual measurements of the compounds onsite we are making assumptions concerning the potential for the COCs to be present and having an impact on wildlife and flora. Table 1 summarizes the potential factors that could impact the park's flora and fauna both from activities carried out within the park as well as offsite activities. Each one of these areas will be discussed as it relates to potential COCs. Based on the limited information that is available, the potential for an activity or COC to affect the wildlife or flora of the park will be discussed.

Onsite Inputs

The onsite activities at this park are relatively straight forward due to its size and lack of non-park related activities within the park boundaries. Even in this small park there are activities that could result in chemical exposure to flora and fauna and produce adverse effects.

Terrestrial Soil

According to discussions with park personnel, the age and proper functioning of the septic systems has resulted in areas of water pooling and enriched plant growth. The impacts of nutrient enrichment are being evaluated by other groups and will not be discussed in this report. There are several septic systems on park property, and they are adjacent to each building. These septic systems could be a source for increased chemicals entering the ground and surface runoff water, especially during peak season when the system is at maximum capacity. The compounds of concern from these systems include nitrogen, phosphorous, trace metals, pharmaceuticals, personal care products and a wide variety of organic compounds (surfactants 1.2-6.5 mg/L, alkylphenol polyethoxylates, 1,4-dichlorobenzene, xylenes, 1,1-dichloroethane, 1,1,1-trichloroethane and dimethylketone). The widespread occurrence of these organic compounds is due to their presence in household solvents and cleaners (USEPA 2000). An example of concentrations of metals reported in septic tank effluents include the following: arsenic (6-59 ug/L), barium (400-1310 ug/L), cadmium (30-330 ug/l), chromium 960-1400 ug/L, lead (0-2700 ug/L), mercury (1-3 ug/L), nickel (0-4000 ug/L) and selenium (3-39 ug/L). The presence of septic systems in sandy environments will result in chronic low level releases of compounds into groundwater and surface waters. Septic systems are how waste water is treated at the park and the majority of private homes in the area. It is estimated that 189 to 265 liters per person per day is generated. USEPA estimated that 19 liter per person per day would be the volume of water contributed to a septic system for a visitor's center. Contaminants entering the groundwater aquifers by these systems could pose a serious threat to the small ponds (Heron and Woodpile) and salt marsh area. It is critical to determine the concentration of metals and organic compounds being introduced into the shallow groundwater system.

The slope of the upland areas would result in the chemicals applied on the grass and asphalt areas in the uplands migrating down slope into the freshwater ponds and ultimately entering the salt marsh areas behind the beach. The marsh wetlands are fed both from the upland freshwater but also from the bayside (Figure 3).

Gasoline was being stored in underground tanks before the year 2000. There was a contract to remove it when it was noticed that one of the tanks was leaking, hence the tank was removed along with some surrounding soil. There are no data regarding how much leakage occurred and no sampling was done in that area. This is unlikely to be a problem today.

The buildings are heated with fuel oil (S. Gurney, personal communication, January 2006). Underground storage tanks for heating oil pose a potential threat if a leak should occur. The extent of any spill would be minimal because the storage tanks have alarms that are activated when a spill occurs. The question would be how quickly the spill could be contained. Above-ground storage tanks with spill catchments would be less of a risk than below-ground tanks. However, a massive breach of an above-ground tank can overwhelm catchments and spread rapidly over the soil surface.

Gasoline and oils in the parking area and in the surrounding areas drain into the two ponds. It can be assumed that cars and buses in the parking area contribute to a hydrocarbon film, local atmospheric releases, and trace metals, which collect on the pavement. When it rains, the contaminants will run off the pavement into the surrounding soil. A short list of contaminants that are known to be released from combustion engines include: carbon monoxide; nitrogen dioxide; sulphur dioxide; suspended particles including particulate matter 10 microns in size (PM₁₀) and particulate matter 2.5 microns in size (PM_{2.5}); benzene; formaldehyde; polyaromatic hydrocarbons (PAHs); and fuel additives like methyltetbutylether (MTBE). The COC components of these materials are likely not the mono-aromatic components, but the polycyclic compounds with higher vapor pressures. Even though MTBE has been banned from New York, as of 2005 the additive was still being used in neighboring states. From historical usage and continued reduced use, MTBE may be detected in the runoff and surrounding soil. Because MTBE has high water solubility and leachability, it is a common groundwater contaminant. It must be realized that there are a number of other contaminants that are released from gasoline and diesel exhausts that could impact the fauna inhabiting the small receiving pond. These compounds could be of concern especially during peak season, or when there have been long periods of little or no rain, which allows compounds to accumulate on the surface. The metals that have been deposited for many years may also have begun to accumulate in the sediment areas in the ponds.

Table 1. Detection of Pesticides Applied to Estuarine Environment.

Compound	Percentage Detected	Range of Detected Concentrations (ng/L)	Detection Limit (ng/L)
Malathion & Sumithrin ¹	0 (0/72)	NA	<5 ng/L
PBO	33.0 (24/72)	35 – 59,800	<5 ng/L
Resmethrin	11.1 (8/72)	6 -293	<5 ng/L
Methoprene	9.7 (7/72)	39-9.030	<5 ng/L
Methoprene Acid	2.4 (1/41)	1,710	<20 ng/L

¹ Neither compound was applied and or detected in this study.

Historic use of pesticides at the park may have left residues in the soil at specific locations. One area could be the orchard area where arsenical pesticides have been used quite extensively (Figure 2). Background levels of arsenic in uncontaminated soils in the USA are 7.4 mg/kg dry weight (Jorgensen et al. 1991). Orchards treated with arsenical pesticides had a mean of 165 mg/kg dry weight in the USA (Eisler 1988). The typical use rates were 4.00-60.00 kg/ha until the mid to late 1940s. This compound is very persistent and if applied, is likely to be present in historical soils. A single composite sample from this area should be analyzed for arsenic (AA Furnace 7060). The use of chlorodane (termiticides initial deposit of 500 mg/kg as a barrier) and DDT/DDE at the site are likely, but the residual levels are expected to be below levels of concern. There has also been reported use of RoundupTM (active ingredient glyphosate) to control weeds at the park. It can also be noticed that the neighboring lands are residential with well-maintained lawns. There could be inputs from pesticide (RoundupTM and 2, 4-D) entering the local streams, but migration onto the park is unlikely with the exception of the homes directly abutting onto the park properties.

Because of the historical use of lead based paints on exterior trim and walls, the soil next to older buildings often have higher levels of lead due to paint flaking off and accumulating in the soil. The lead used in paints is insoluble. The lead would not be mobile and would pose little or no concern to wildlife.

Surface Water

The park area has a small beach and wetland that is contiguous with Cold Spring Harbor. Although sediment samples have been shown to be toxic from samples in Oyster Bay and Cold Spring Harbor, no onsite samples have been collected and analyzed for inorganic or organic chemicals.

Gasoline was reported to be released from motor crafts near the shore. Although the amounts are likely quite small, chronic exposure could result in subtle effects on invertebrates living in the intertidal area. The shift in the formulation to unleaded gasoline was made in part as a response to the amount of lead that was accumulating in flora and fauna in the environment and the need for low lead fuel for catalytic converters to work properly. Unleaded gasoline may contain up to 0.013 g/L lead in the USA (Reese and Kimbrough 1993), and since 1986, leaded gasoline cannot contain more than 0.025 g/L lead in the USA

In addition to the lead in gasoline, there are also volatile organic compounds (VOCs) that are released. Gasoline is a highly volatile petroleum product comprised primarily of light hydrocarbons, alkenes, benzene and alkyl substituted benzenes, toluene, o,p,m-xylenes, and ethylbenzene (Calabrese and Kostecki 1991). Benzene, toluene, ethylbenzene, and xylene are commonly referred to as BTEX. Three of the more common oxygenated fuel additives that have been used with unleaded gasoline are methanol, ethanol, and MTBE. In present formulation up to 50% of a premium gasoline blend can be aromatic compounds, both mono and polycyclic aromatic compounds. Although these mono-aromatic compounds are considered sparingly soluble in water, their solubility are above toxic effect levels. When a spill occurs there are two main processes occurring at the same time; evaporation and dissolution into the water or soil. Gasoline also contains a small but significant amount of PAHs including naphthalene and alkyl naphthalenes. Naphthalenes are particularly hazardous PAHs due to their particular combination of mobility, toxicity, and general environmental hazard. Alkyl naphthalenes pose similar hazards

and are usually found in the same petroleum products as naphthalenes, often in higher concentration than the parent compound (naphthalene). The parent compound naphthalene is the first to degrade. So as petroleum products age, the percentage of alkyl naphthalenes vs. naphthalene increases. Heavier and more persistent PAHs are also found in gasoline (Heath 1993). Although PAHs make up a small percentage of gasoline, they are more persistent than most other constituents of gasoline and tend to have greater carcinogenic and other chronic impact potential. As the gasoline spreads out over the surface, an oil-sheen is formed that contains all the components of gasoline. There is also enrichment at the surface due to a lipid enriched bi-layer at the surface of the water and the air interface. Both BTEX and substituted naphthalenes can cause these effects. Organisms living at the air/water interface will also be affected. Gasoline and its BTEX components clearly exhibit short-term toxicity effects to a variety of aquatic organisms, especially in freshly spilled gasoline.

Gasoline possesses high acute toxicity to biota. Long-term (chronic) potential hazards of some of the lighter, more volatile and water soluble aromatic compounds in gasoline include contamination of surface water and entrainment in sediment. Sediment low effect levels on an mg/kg dry wt. basis for benzene is 0.34, ethylbenzene 1.4, tetrachloroethylene 0.45, toluene 2.5, and trichloroethylene 1.6 (NJDEP 2006). Chronic effects associated with the lighter aromatic components of gasoline are mainly due to very high exposures or from chronic small releases that exposes a population of organisms. For example, in the case of benzene, high concentrations can result in aplastic anaemia in both lower vertebrates and higher vertebrates, which may result in abnormal blood disorders. Chronic effects of some of the constituents in gasoline (benzene, toluene, xylene, naphthalenes, alkyl benzenes, and various alkyl PAHs) include changes in the function of the liver or the kidneys. Although PAHs, particularly heavy PAHs, do not make up a large percentage of gasoline, they are still detrimental to the environment. Due to their relative persistence and potential for various chronic effects, specific PAHs (such as B(a)P), can contribute to long-term (chronic) hazards in exposed organisms.

Gasoline additive MTBE tends to volatilize quickly; like most ethers it also dissolves readily in water (ATSDR 1995b). Higher concentrations of MTBE in surface waters tend to be in marinas, where two cycle engines release MTBE along with gasoline and oil. In addition, many of the outboard motors need motor oil added to the gasoline which contributes even more to the introduction of higher molecular weight PAHs into the engine exhaust water. In a marina at California's Lake Shasta, concentrations as high as 84 ppb MTBE have been found along with BTEX concentrations of about 30 ppb. The potential for gasoline or its components to reach the ponds onsite and the beach area from motor craft would indicate that these are COCs.

The walkway leading down to the beach is constructed from chromium, copper, and arsenic (CCA) treated wood and could be a source metal contaminants in areas under and adjacent to the walkway.

SAHI uses integrated pest management (IPM) procedures on the whole of the park site. Attempts are made to limit pesticide and herbicide use on the park property. For example, sanitary methods are used to avoid mosquito breeding. However, there could be contamination from chemicals used to prevent mosquito breeding in the neighboring areas of Suffolk County. The use of water management practices, mosquito eating fish, the use of pre-emergent baits, and limited aerial spraying reduces the potential impact of these activities by the county on the park's

wildlife and flora. The use of malathion in marsh areas for control of mosquitoes carrying Eastern Equine Encephalitis (EEE) or West Nile would result in non-target species being impacted. Malathion would be a COC if used on or around park properties. This assumption is in agreement with a large risk assessment study conducted by Suffolk County.

Groundwater

Currently there is no drinking-water well or irrigation well located at the site. The water supply to the park is a municipal water supply. As the sole source for freshwater to the park, the municipal drinking water must meet current drinking water standards (USEPA Drinking Water Standards). These standards are designed to protect humans and not wildlife. It is known that the chlorination process produces compounds that are toxic to certain aquatic species (e.g., fish sensitivity to chloramines) and other invertebrate species if there is direct contact prior to loss of chlorinated products. It is possible that groundwater could contribute metals and VOCs into the freshwater ponds from the septic systems onsite (see above).

Offsite Inputs

Surface Water

The Oyster Bay/Cold Spring Harbor region is the receiving water body for watershed areas including Tiffany Creek and Mill Neck Creek in Northeastern Nassau County. The receiving water bodies are classified as SA. This classification states that this water body is suitable for shellfish for market purposes, primary and secondary contact recreation, and fishing. The waters are suitable for fish propagation and survival. It is important to note that these bodies of water were listed for TMDL development by New York State 303(d) list in 2002, because of polychlorinated biphenyls (PCBs) present in fish and pathogenic bacteria in shellfish. One of the sources of the PCBs is from the closed shipyard, and the bacteria are from septic tanks leaching, storm-water outfalls, and the Oyster Bay Sewer Treatment facility. The shipyard was closed and has undergone remediation, and it is no longer considered a PCB source. The residual levels of PCBs found in the bay sediment are believed to be from sediment sinks, sewage treatment and runoff from land sources.

A number of pesticides are used for the control of vector borne mosquitoes. The primary approach is to use larvacides as opposed to adulticides. The larvacides used are bti, bs and methoprene. Mosquito larval treatments include VectobacTM (bti), VectotexTM (bs) and Altosid (methoprene). The adult mosquito control agents that are used include ScourgeTM (resmethrin) 1995-, AnvilTM (Sumithrin - chrysanthemums derivative) 1999 and FyfanonTM (malathion-organophosphate) that has been used for over 20 years. The method of application is by truck and/or airplane application, and occurs from May until September. Because of the application times for these agents they will overlap with the most active time for summer breeding in invertebrate, lower vertebrates and some higher vertebrates. Abbene et al. (2005) reported that of a total of 72 surface water samples collected from 27 sites and analyzed for six commonly used pesticides for mosquito control (malathion, methoprene, methoprene acid, piperonyl butoxide [PBO], resmethrin and sumithrin) in Suffolk County, that PBO was the most frequently detected (33.3%). Table 1 summarizes the results from the Suffolk County study in which grab samples were collected within 60 minutes after application.

Malathion is a broad-spectrum organophosphate insecticide that is widely used both for crop protection and control of large adult populations of mosquitoes carrying either West Nile Virus or EEE. The general application rate is 0.2 to 4.3 kg/ha and this translates into a potential concentration of 0.1 to 0.6 mg/L in a 30 cm deep pool. The half-life is dependent on pH with values of eight and six resulting in two and 26 days, respectively. This compound is approved for use, but would be used only in true public health emergencies (Suffolk County Mosquito Control, personal communication, March 2006). Aerial application over estuaries and freshwater ponds should be avoided due to its extreme broad spectrum toxicity.

The Oyster Bay Sewer Facility discharges into Oyster Bay and has an average flow of 3,697 m³/day, and flow design capacity of 6,804 m³/day. The district encompasses 3.95 km², and serves approximately 8,500 people. There are no hospitals that discharge into the facility. The primary sources of waste are from households with little or no large industrial input. The discharge would contain personal care products, surfactants, prescription drugs (estrogen), and other compounds that are considered COCs (IUPAC 2003). The plant was originally constructed in 1929 and had significant upgrades in 1965 and 1992. The type of treatment is secondary treatment with a trickle filter. The plant has been recognized for its excellence in wastewater treatment and management for a secondary treatment facility. The plant produces approximately 28.6 metric tons of sludge per year, which is trucked offsite for disposal. The input from this plant into the system would be consistent with other sewage treatment plants of its design and size. However, during heavy rains the system can be overwhelmed releasing large volumes of untreated sewage that contains high total organic carbon, which would contain low levels of inorganic and organic compounds. This facility would be considered a point source into Oyster Bay and it is unlikely to have a direct major impact on the national park beach and salt marsh, but it contributes to the contaminant loads observed in the sediments in the surrounding waters (Tables 2, 3 and 4).

There are at least three large marinas that are located on the West Neck area in Cold Spring Harbor, Centre Island and Oyster Bay. Sediments within these marinas may contain elevated metals (TBT, lead and copper) and petroleum products. Because of the distance between these marinas and the park's lands it is unlikely that they would have an impact. As with the sewage treatment plant they would contribute to metal and petroleum products entering the nearby Oyster Bay/Cold Spring Harbor Estuary.

The amount of boat traffic in the area offshore of the park contributes to gasoline and oil sheens being observed on the beach at the park (S. Gurney, personal communication, January 2006). For a detailed discussion of chemical components in oil and gasoline refer to the "Onsite Inputs" discussion above.

Terrestrial Sources

According to the USEPA regulated toxic reporting inventory (TRI) list, only two facilities were considered potential sources for COCs: Commander Terminal Oil Company and Mill Max Manufacturing Corporation. All other reporting industries were small businesses such as laundries, dry cleaning establishments, and restaurants (Figure 4). The principal industry that could impact the park is the Commander Terminal Oil Company. The Commander Terminal Oil Company primarily releases mono-aromatic solvents like benzene and toluene, which are very volatile and hence probably not a problem unless released in very large quantities. In discussions

with “Friends of the Bay” we found that there have been no spills from this facility for a number of years. Its location is along the north shore of Cold Spring Harbor near the mouth of the bay. A large release of gasoline or fuel oils would likely impact the beach and salt marsh area of the park even though it is on the opposite shoreline.

Mill Max Manufacturing Corporation has minimal air releases and is located quite a distance from the park. Due to both the distance and the nature of the releases (volatile aromatic compounds) this facility is unlikely to pose a threat to the park flora and or fauna.

The closest landfill near SAHI is approximately 7.5 miles from the park. The Syosset Landfill is a 32 acre site in the town of Oyster Bay and is on the USEPA National Priorities List. Refuse disposal reportedly began in 1933 and continued until 1975. Until 1967, there were no restrictions on the type of wastes received at the site. Materials disposed of during that period included residential, commercial, industrial and demolition wastes, sludge, and incinerator ash. After 1967, only industrial wastes and sludge were accepted until the site's closure in 1975. This landfill generates, on an annual basis, an estimated 185.6 million liters of leachate, which prior to remediation would have been affecting the groundwater in the vicinity of the site. ERM-Northeast installed seven monitoring wells onsite in 1982 and sampled them for priority pollutants. They found concentrations of heavy metals and PCBs (0.1-0.2 ppm) in several wells, and chloroethyl ether (47 ppm) in one well. The Remedial Investigation/Feasibility Study (RI/FS) for operable unit 1 (source characterization and remediation), was completed with a Record of Decision (ROD) dated September, 1990. It calls for a municipal landfill final cover and gas migration control, which are under design. The offsite plume was addressed under operable unit 2 (OU-2) in a Remedial Investigation. Only iron and sodium in the offsite groundwater exceed Part 703 Groundwater Standards. The proposed remedy for OU-2 is "no action" with continued monitoring of offsite groundwater. Final cap construction began in August 1996 and was completed in November 1997. Flaring of gas from the site minimizes atmospheric contamination. Because the remediation action is completed and monitoring of the groundwater revealed only iron and sodium exceeding standards, there appears to be no threat to the park from this source (Figure 4).

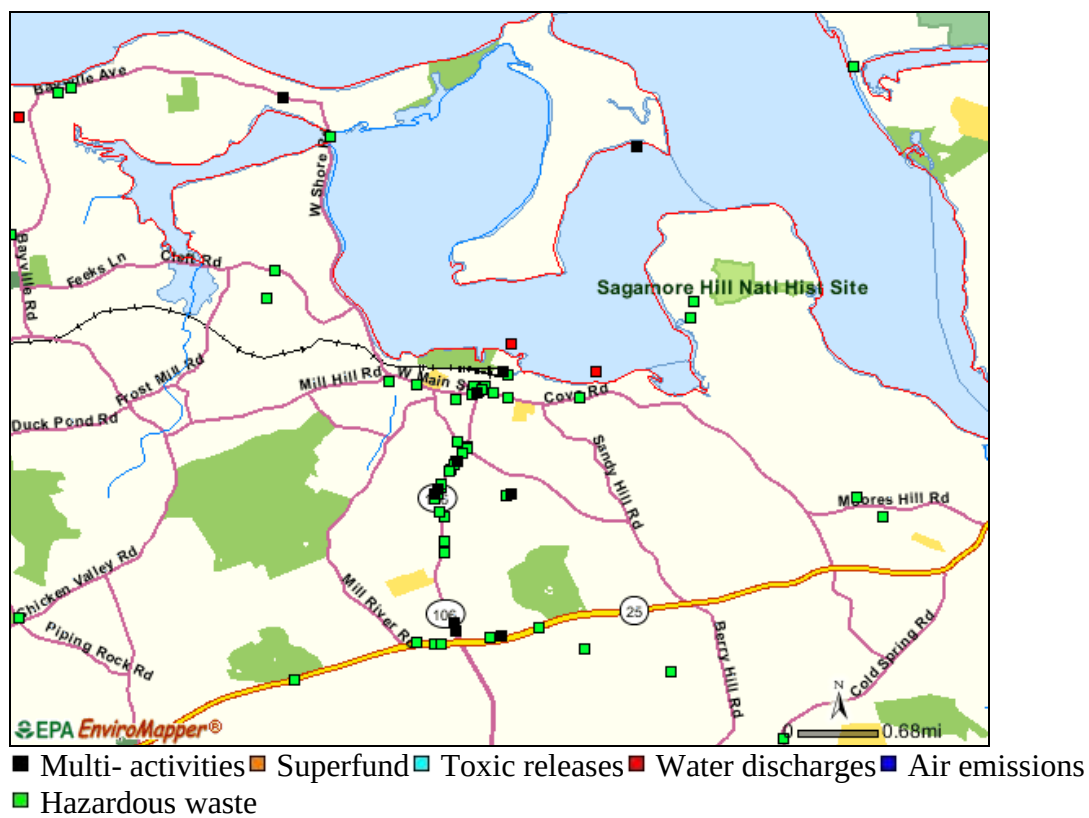


Figure 4. Hazardous Waste Sites near SAHI.

Chemicals of Concern in Different Matrixes

In this section the concentrations of chemicals that are reported from measurements of metal and organic compounds are surface water and sediment samples. There were no direct chemical measurements on the park grounds. Toxicology related information on each of the metals listed within Table 3 and organic compounds in Table 4 are provided in Appendix 1. The information provided in Appendix 1 also identifies background levels, sources, mechanism of action, and associated toxicity.

Surface Water Analysis

The Water Resources Division and National Park Service carried out an inventory and monitoring program to establish a baseline water quality. The data for this analysis were from 1964 to 1993, but none of the data were within the park boundary itself. These data are from surrounding stations: Mill Neck Creek at Mill Neck, NY; Oyster Bay Harbor, Oyster Bay; and other surrounding areas. Table 2 summarizes the number of observations along with the number and percentage of values exceeding the standard. In general, the values above the standard values were infrequent (low percentages). It was reported that dissolved O₂, pH (14%), chloride (1%) and copper (11%) exceeded USEPA criteria for protection of freshwater aquatic life. For the marine aquatic life there were values that were outside acceptable ranges for pH (5%), copper (100%), silver (100%), and zinc (4-7%). Based on this data set from the water column, it would appear that for freshwater areas copper was the only COC. For the marine area copper and silver were COCs.

Nassau County has carried out a series of studies in collaboration with Friends of the Bay, which has supplied a great deal of data on surface water quality from the surrounding Oyster Bay/Cold Spring Harbor System. The action levels currently being used by the county are in agreement with USEPA (1986) or state standards (ammonia > 0.3 ppm, total suspended solids > 20mg/L, total volatile organics 10-50 ppb). In 2005, MTBE was detected in only one sample (2 ppb). This is attributed to the banning of MTBE for use in New York in 2004. Enterococci sampling indicated a wide range of sources for the elevated fecal coliform ranging from humans, dogs, gulls, swans, muskrat, horse, cormorant, Canadian goose, and fox. The results of 2005 were consistent with values obtained in 2003 and 2004 with improvement in several areas for the region. Total VOCs have remained consistent; the mean ammonia levels have decreased as well as the mean levels of enterococci. The most likely reason for VOCs remaining somewhat constant is likely due to their release from groundwater sources that are acting as a reservoir for historical contamination. It is also likely that areas with greater numbers of septic tanks will continue to release these chemicals because they are present in our everyday household products.

Oyster Bay and Cold Spring Harbor Sediment Toxicity and COCs

A survey of sediment toxicity was carried out in 1991 by NOAA's National Status and Trends Program in the coastal bays that surround Long Island Sound in New York and Connecticut (Figure 5). Located adjacent to SAHI, Oyster Bay (40° 53.02 N 73° 30.65 W, 40° 53.50 N 73° 30.65 W, 40° 54.50 N 73° 29.60 W) and Cold Spring Harbor (40° 52.47 N 73° 28.25 W, 40° 53.70 N 73° 29.30 W, 40° 54.50 N 73° 29.60 W) were the two bays evaluated. The sediment toxicity tests conducted indicated that a number of the sediments were acutely toxic to benthic invertebrates (*Ampelisca abdeta* and *Mulinia lateralis* or inhibited fluorescence in the microtox test) (www.ccma.nos.noaa.gov/publications/tm80.pdf).

Table 2. EPA Water Quality Criteria Analysis for Entire SAHI Study Area.

Parameter	Std. Type	Std.Value	Total Observation	Exceed Standard	Proportion Exceeding
pH field	Fresh Chronic	9.0	178	10	0.06
	Other Lo- lim	6.5	244	19	0.08
	Marine Chronic	8.5	66	3	0.05
pH Lab	Fresh Chronic	9.0	46	2	0.04
Nitrate Nitrogen, Total as N	Drinking Water	10	80	2	0.03
Chloride Total in Water	Fresh Acute	860	179	1	0.01
	Drinking Water	250	179	2	0.01
Sulfate Total	Drinking Water	260	167	1	0.01
Copper Dissolved	Marine Acute	2.9	14	10	0.71
Copper Total	Fresh Acute	18	9	1	0.11
	Marine Acute	2.9	26	26	1.00
Silver Total	Marine Acute	0.12	13	13	1.00
Zinc Dissolved	Marine Acute	95	14	1	0.07
Zinc Total	Marine Acute	95	26	1	0.04
Fecal Coliform, MPN	Other Hi-Lim	200	69	4	0.06

*These are only compounds that have exceeded Std values.

The specific data for the two nearest bays to SAHI for inorganic compounds are shown in Table 3. It must be recognized that many of these metals occur naturally in the earth's crust and therefore there would be a naturally occurring background level based solely on the geological nature of the regional soils and sediments (Mason 1966). The bioavailability of many metals are determined by their ionic form that is dramatically modified based on pH, alkalinity and oxidative/reduction state of the matrix in which they are found. For example, aluminum is a crustal element with an average of 81,330 ppm and the SAHI sediments would be in line with those values (Mason 1966). The threshold effects level (TEL) indicates the concentration at which there would be expected no observed adverse effect. The effect range low (ERL) value is where low toxicity would be expected to be observed in sensitive organisms. The effects range medium (ERM) is where toxicity would be observed from sediment exposure (Buchman 1999). Silver, arsenic, cadmium, chromium, copper, nickel, lead, and zinc were above the ERL values. Based on these results these sediments would be expected to produce low level toxicity. Because a number of these metals act through similar toxic pathways there could be at least additive toxicity. This would support the biological findings reported above. There is no way to identify the source of the observed metals, but this does demonstrate how environmental samples are contaminated with complex mixtures of organic and inorganic compounds. The metals that did not have ERM or ERL levels have been listed as their reported background levels. In all cases where the reported values are below these levels it is assumed not to be from an anthropogenic source. Therefore, they are listed as background in Table 3.

The same is true for the organic compounds that were present at these locations. There are a number of detected chemicals where there is no ERL or ERM (Table 4). It must be appreciated that estuarine bays are the receiving basins for chemicals being transported off the land or from freshwater streams to a sub-watershed or to an entire watershed. A number of organic compounds primarily PAHs frequently exceeded their ERM value (Table 4). In addition, several pesticides (DDT/DDE, chlordane, and dieldrin) were reported above ERM values. The NOAA report asserts that the organic compounds were mostly responsible for the observed biological toxicity. It must be realized that because of improved analytical capabilities, many more chemicals are being detected, but that does not mean that either individually or in combination they will result in a deleterious effect. The classes of compounds that are shown in the table represent the different PCB congeners (CL#), various pesticides and their metabolites, and mono and polycyclic aromatic compounds generally associated with petroleum products. The PCBs present in this sample are in the low ng/g range and at these levels pose little or no threat to wildlife (NAS 2003). The PCB congeners that have dioxin like activities are PCB 77, 105, 118, 126, 170, 180, and they were either not detected or at very low concentrations. The other congeners are also at very low concentrations. The PCB concentrations would not pose acute, chronic, or bioaccumulation at these levels. The PCBs, although present, would not appear to pose a hazard or be considered a class of chemicals that would pose a risk to wildlife at the park or the surrounding waters.

In the case of DDT and its metabolites, a number were detected in the sediments, which is not unexpected due to the long half-life of these compounds (Smith 1987). This would also be consistent for the area and the historical use of these pesticides. Chlordane (ERL HQ>1), dieldrin (ERL HQ>1) and PPDDE (ERL HQ>1) were detected (National Pesticide use Database, www.ncfap.org/data-base/default.htm).

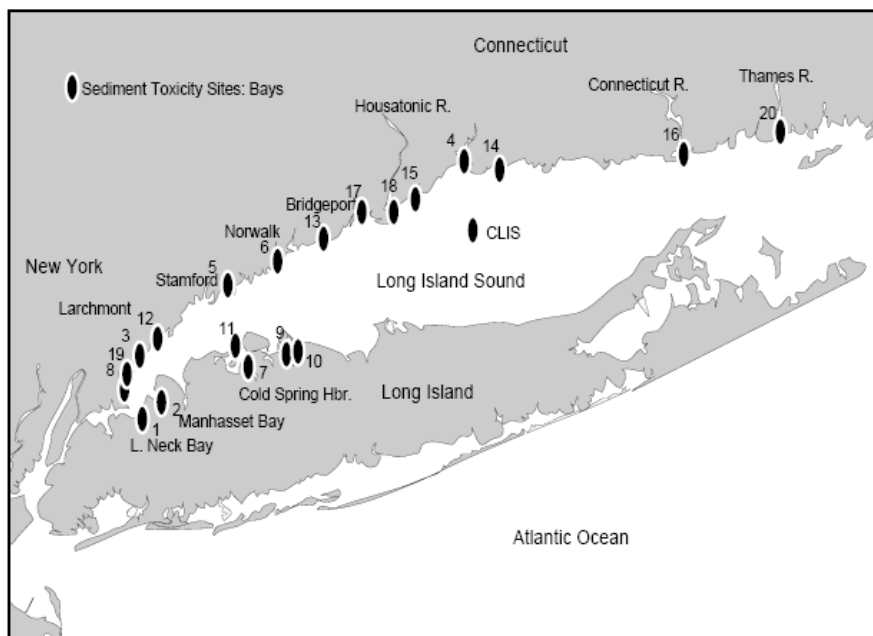


Figure 5. Sampling Locations in Oyster Bay (#11) and Cold Spring Harbor (#7).

There were a number of polyaromatic compounds associated with fossil fuels and the burning of fossil fuels that were present. However, none were above the ERL values ($HQ < 1$). The presence of these could be from atmospheric sources, automobile/motorboat activities, or from terrestrial sources. Several of the hydrocarbons were above the TEL, but were below the ERL. Based on these sediment values it would be concluded that the report levels are at the threshold values for observing toxicity.

Examination of blue mussel (*Mytilus edulis*) tissue samples (NOAA Mussel Watch) from Huntington Harbor (the next bay over to the east on the Long Island Sound) that have been collected since 1986 show that the metals have either remained relatively constant (As, Cd, Cu, and Zn) since the early 1990s or increased (Cr, Hg and Ni). Both silver and mercury show elevated levels in the mussel tissues in the late 1990s and 2000s. Dieldrin, chlordane, and DDT/DDE have decreased in tissue concentrations. PCBs have decreased by a little over a third (from 400 to 250 ng/g). The petroleum derived hydrocarbons have remained relatively constant. If the assumption is made that bivalves in the Oyster Bay/ Cold Spring Harbor complex have similar patterns, then the major COCs would be metals and petroleum hydrocarbons. The PCBs were low in the NOAA sediment samples from the Oyster Bay/ Cold Spring Harbor complex.

Groundwater

Volatile organics and elevated nitrates are common groundwater contaminants on Long Island (Eric Vowinkel, USGS, personal communication, February 2006). Groundwater in the area continues to have VOCs in the <10 ppb range and is attributable to groundwater contamination entering the surface waters.

Table 3. NOAA Sediment Data for Metals in Sites near SAHI.

Contaminant	Cold Spring Harbor	Oyster Bay	ERM ug/g dry weight	ERL (TEL) ug/g dry weight	Crustal Occurrence	RANGE THQ (MHQ)
Al (ug/g) Aluminum	53300 – 68600	38800 – 60700			81,300 (8.1%)	BG
Ag (µg/g) Silver	0.98- 1.38	0.65 – 1.51	3.7	1.0¹ (0.73)	0.07	0.98-1.5 (0.9-2.1)
As (µg/g) Arsenic	8.5 – 10.2	4.9 – 9.0	70	8.2 (7.24)	1.8	0.60-1.2 (0.68-1.4)
Cd (µg/g) Cadmium	1.16 – 1.42	0.43 – 1.3	9.6	1.2 (0.676)	0.2	0.36-1.2
Cr (µg/g) Chromium	96-99	62 – 106	370	81 (52.3)	100	0.76-1.3
Cu (µg/g) Copper	96.2– 112.2	55.2– 109.8	270	34 (18.7)	55	1.6-3.3 (2.9-5.9)
Fe (ug/g) Iron	33400-37700	19900- 34000			38,000 (5%)	BG
Hg (µg/g) Mercury	0.304 – 0.397	0.177- 0.328	0.71	0.15 (0.13)	0.08	1.2-2.6 (1.4-3.1)
Mn (µg/g) Manganese	517 – 807	668-1371			600-6000 (2.1%)	BG
Ni (µg/g) Nickel	33.2 – 33.4	17.5- 35.7	51.6	20.9 (15.9)	(0.0075%)	0.8-1.7 (1.1-2.2)
Pb (µg/g) Lead	1.6-81.9	47.2-90.2	218	48.7 (30.24)	13	0.03-1.9 (0.05-3.0)
Sb (µg/g) Antimony	0.49- 0.59	0.33-0.68	25	2.0	0.2	BG
Se (µg/g) Selenium	0.29- 0.87	0.29-0.58			0.05-0.07	BG
Si % dry wt. Silacon	243000-248000	239000-245000			330,000	BG
Sn (µg/g) Tin	9.2-11	5.45-9.81			10.0	BG
Zn (µg/g) Zinc	226-239	144.3 -245	410	150 (124.0)	50	0.96-1.6 (1.2-2.0)

¹ Values in bold indicate the sample was above the ERL. The ERM, ERL and TEL values are derived from two sources Long et al. (1994) or Morgan and Long (1990). The Crustal values are from Jorgensen et al. 1991 and values at or below crustal occurrence are background (BG).

Table 4. NOAA Sediment Data for Organic Chemicals.

Contaminant	Cold Spring Harbor	Oyster Bay	ERM ¹ ng/g dry weight	ERL ¹ ng/g dry weight	TEL ¹	LEL ² NJ ug/g ²	HQ (THQ) ³
CL2(08) (ng/g)	0 – 7.045	2.274 – 8.167					
HCB (ng/g)	0 – 15.45	0 – 50.132				20	0-2.3
Lindane (ng/g)	0 – 0.969	0			0.32	3	0-03 (0-3.0)
CL3(18) (ng/g)	0 – 0.247	0					
CL3(28) (ng/g)	0 – 1.112	0.159-0.733					
Heptachlor(ng/g)	0 – 0.632	0 – 0.432				5	0-0.13
CL4(52) (ng/g)	0 – 1.629	0.015-0.664					
Aldrin (ng/g)	0	0				2	ND ³
CL4(44) (ng/g)	0 – 0.588	0 – 0.35					
Heptachlorepoxyde (ng/g)	0	0			0.6	5	ND
CL4(66) (ng/g)	0.451 – 1.945	1.05 – 1.595					
O,P DDE (ng/g)	0 – 0.488	0.371-0.889				8	0-0.1
CL5(101) (ng/g)	3.817 – 5.491	2.191-3.564					
A Chlordane (ng/g)	0.887 - 1.616	0.906-1.373	6	0.5	2.8		1.8-3.2 (0.3-0.6)
Transnonachlor(ng/g)	0.987 – 1.748	0.527-0.97					
Dieldrin (ng/g)	1.181 – 1.867	0.665-1.48	8	0.02	0.715		33.3-93.4 (0.93-2.61)
PPDDE(ng/g)	3.737 – 4.769	2.539-4.22	27	2.2	2.07		1.2-2.2 (1.2-2.3)
CL4(77) (ng/g)	0 – 2.607	0					
OPDDD(ng/g)	0 – 0.227	0 – 0.042					
Endrin(ng/g)	0	0				3	ND

Table 4. NOAA Sediment Data for Organic Chemicals (continued).

Contaminant	Cold Spring Harbor	Oyster Bay	ERM ¹ ng/g dry weight	ERL ¹ ng/g dry weight	TEL ¹	LEL ² NJ ug/g ²	HQ (THQ) ³
CL5(118) (ng/g)	1.208 – 2.865	1.627-2.854					
PPDDD(ng/g)	2.17 – 2.908	2.005-3.033	20	2	1.22	8	1.0-1.5 (1.6-2.5)
OPDDT(ng/g)	0	0					ND
CL6(153) (ng/g)	2.271 – 7.326	4.959-7.831					
CL5(105) (ng/g)	0 – 0.603	0.258-0.604					
PPDDT(ng/g)	0.996 – 1.811	0 – 1.195	7	1	1.19		0-1.8 (0-1.5)
CL6(138) (ng/g)	0.852 – 3.937	0 – 2.996					
CL5(126) (ng/g)	0	0					ND
CL7(187) (ng/g)	0 – 1.355	0.683 – 1.18					
CL6(128) (ng/g)	0 – 3.923	2.11-4.504					
CL7(180) (ng/g)	0 – 1.514	0.96-1.128					
Mirex (ng/g)	0	0				7	ND
CL7 (170) (ng/g)	0 – 6.494	0.338-0.849					
CL8(195) (ng/g)	0 – 0.016	0					
CL9(206) (ng/g)	0	0					ND
CL10(209)	0	0					ND
Naphthalene(ng/g)	43.5 – 50.79	43.31-52.46	2100	160	34.57	160	0.3-0.33 (1.3-1.5)
2Methyl Naphthalene (ng/g)	34.43 – 40.48	33.84-44.52	670	70	20.21	70	0.5-0.6 (1.7-2.2)
1Methyl Naphthalene (ng/g) (same as 2-methyl)	15.9 – 18.42	19.3-20.39	670*	70*	20.21*		0.2-0.3 (0.8-1.0)
Biphenyl (ng/g)	11.62 – 12.53	10.83-14.36					
2,6 Dimethyl Naphthalene (ng/g)	23.33 – 28.55	25.14-37.36					
Ace Naphthylene(ng/g)	50.18 – 56.02	23.52-54.28	640	44	5.87	44	0.5-1.3 (3.5-8,3)
Ace naphalene(ng/g)	8.73 – 12.9	8.91-25.71	500	16	6.71		0.5-1.6 (1.3-3.8)

Table 4. NOAA Sediment Data for Organic Chemicals (continued).

Contaminant	Cold Spring Harbor	Oyster Bay	ERM ¹ ng/g dry weight	ERL ¹ ng/g dry weight	TEL ¹	LEL2 NJ ug/g2	HQ (THQ) ³
2,3,5 trimethyl naphthalene (ng/g)	4.91 – 7.23	5.44- 6.9					
Fluorene(ng/g)	15.61 – 23.11	17.14- 34.9	540	19	21.17	19	0.8-1.8 (0.7-1.6)
Phenanthrene (ng/g)	121.15 - 182.6	137.84- 269.36	1500	240	86.68		0.5-1.1 (1.4-3.1)
Anthracene(ng/g)	41.87 – 58.62	39.62- 76.7	1100	85.3	46.85	85	0.5-0.9 (0.9-1.6)
1Methylphenanthrene(ng/g)	22.46 – 29.00	24.68- 30.85					
Fluoranthene(ng/g)	280.94 - 431.8	337.39- 418.66	5100	600	112.8 2	600	0.5-0.7 (2.5-3.7)
Pyrene(ng/g)	271.18- 402.08	324.47- 381.78	2600	665	152.6 6	665	0.4-0.6 (1.8-2.6)
Benz[a]anthracene(ng/g)	128.31- 195.16	161.53- 204.9	1600	261	74.83	261	0.5-0.8 (1.7-2.7)
Chrysene (ng/g)	183.42- 241.3	228.64- 250.21	2800	384	107.7 7	384	0.5-0.7 (1.7-2.3)
Benzo[b]fluoranthene(ng/g)	193.25- 252.15	180.75- 217.06				240	
Benzo[k]fluoranthene(ng/g)	144.87- 188.85	135.82- 181.81				240	(0.08- 0.1)
Benzo[e]pyrene (ng/g)	146.71 – 79.43	129.05- 165.39					
Benzo[a]pyrene (ng/g)	169.45- 213.57	170.32- 193.18	1600	430	88.81	430	0.4-0.5 (1.9-2.4)
Perylene (ng/g)	49.94 – 66.19	47.97- 57.92					
Indeno[1,2,3-c,d]pyrene (ng/g)	155.02- 194.29	138.1- 184.54				200	0.7-0.97
Dibenz[a,h]anthracene(ng/g)	21.67- 26.81	22.45- 29.15	260	63.4		63	0.3-0.5
Benzo[g,h,i]perylene(ng/g)	141.52- 183.45	133.24- 184.21				170	0.8-1.1

¹Long et al (1994) or Morgan and Long (1990). Treshold Effects Level (TEL), Effects Range Low (ERL), Effects Range Medium (ERM).

²Lowest Effect Level for observing any effect NJDEP sediment values.

³ND = compound not detected. Values in parenthesis are denominator threshold values, (THQ). HQ = denominator ERL/ERM or LEL NJ value.

Monitoring Recommendations Based on Risk Evaluations

Because of the lack of data within the park boundaries, a minimum preliminary sampling needs to be conducted. This sampling will strengthen any actions that need to be implemented. It will also allow for a baseline to be established from data collected specifically addressing COCs within the park. Table 4 summarizes the recommended samples and their collection locations. In addition, there are a series of management recommendations concerning the actions that can be implemented at the park.

The sediments from both Heron and Woodpile pond should be analyzed for the full suite of metals and organic compounds. This should be done in the first sample and then if specific compounds appear to be above threshold level values then they should be selected as the COCs. This sample can be collected as a composite using a ponar grab sampler or an appropriate alternative (USEPA ERT SOP #2016). A composite sample is comprised of five sub-samples mixed to make up a single composite sample.

The sediment sample under the walkway should be analyzed for the presence of copper, chromium, and arsenic. This sample can be collected as a composite using a ponar grab sampler or an appropriate alternative (Sediment Sampling USEPA ERT SOP #2016). This would be a one-time sample.

The sediments to be collected in the marsh and along the beach should be collected below the high-water mark and should be collected from the north, middle and southern ends of the marsh and beach. Finer sediment depositional areas should be selected for sampling if possible.

The biota to be collected at the marsh area should be taken from the same areas as the sediment samples collected above. This sampling can be carried out once to assess the accumulation of the compounds into these different biota. This assessment will allow for determination of food exposure routes to other wildlife (Sample et al. 1996).

The soil sample to be collected at the septic field drainage area should be collected annually. This sample will examine the suite of contaminants in the first sampling and then the sample site can be targeted in future years. The method for collection could be a core sample or an appropriate method (Soil Sampling USEPA ERT SOP #2012)

The one time soil sampling is being carried out to look for specific contaminants associated either with current or historic chemical usage. The orchard area should be sampled for arsenic and other pesticides that may be present in the soil. The maintenance area should be sampled for PAHs and for VOCs that would be used for cleaning and repair of equipment. The samples near the foundations of wooden buildings that were painted prior to 1978—when lead was banned from use in paints—should be sampled. A onetime sample should be collected in the drainage area of the parking area. This would be on the downward slope furthest away from the visitor center.

The one-time sampling of the biota on the grounds of the park include grass and earthworm samples from these same areas. These samples should be collected near the areas where samples are collected for the soil composites described above. This information will allow for extrapolation to the American robin (*Turdus migratorius*) as a pathway to terrestrial birds. The grass sample will also allow for extrapolation to wildlife that consumes plant material in their diets (Sample et al. 1996).

Management Recommendations

1. Routinely monitor the water in the ponds for pH, phosphorus, nitrogen, and other components.
2. Design catchments to prevent surface water runoff from parking surfaces to reduce inputs into ponds and marsh areas on the down slope.
3. Continue remediation of the buildings to remove remaining lead.
4. Implement an IPM program if it does not already exist both for buildings and grounds. Do not use RoundupTM or 2,4-D as herbicides due to toxicity to tadpoles and other aquatic life.
5. Try and prevent the use of pesticides for control of mosquito larvae on park premises. If malathion is applied to control adult mosquitoes due, insist that it not be applied in sensitive areas, due to human health risks.
6. The implementation of conservation and moving to a “green purchasing” approach to chemical use will continue to reduce chemical impacts on wildlife in the park. To further reduce the use of traditional VOC cleaners and petroleum-based solvents, the park purchasing officer should pursue alternatives.
7. Conduct a chemical audit every three to five years to see how much and what types of compounds are being used onsite.

Table 5. Recommendations for Sampling to Examine COCs in Different Matrix in SAHI.

Matrix	Analyte (1)		Number of Samples/Type		Frequency/Method	Location Onsite
	(Method#)					
Sediment	Heavy Metals	(7000, 7010, 6010B, 6020A)	3	Composite	1-3/ Ponar Grab	Heron Pond
	Imw PAHs	(8100, 8275A)				
	Hmw PAHs	(8100, 8275A)				
	VOCs	(8240)				
	Pesticides	(8270D)				
Sediment	Heavy Metals	(7000, 7010, 6010B, 6020A)	3	Composite	1-3/ Ponar Grab	Woodpile Pond
	Imw PAHs	(8100, 8275A)				
	Hmw PAHs	(8100, 8275A)				
	VOCs	(8240)				
	Pesticides	(8270D)				
Sediment	Copper, Chromium, Arsenic	(6010B, 6020A)	3	Composite	1 / ponar or surface sample	Under Walkway
Sediment	Heavy Metals	(7000, 7010, 6010B, 6020A)	3	Composite	1-3/Ponar Grab	Marsh Area
	Imw PAHs	(8100, 8275A)				
	Hmw PAHs	(8100, 8275A)				
		(8240)				
	Pesticides	(8270D)				
Sediment	Heavy Metals	(7000, 7010, 6010B, 6020A)	3	Composite	1-3/Ponar	Beach Area
	Imw PAHs	(8100, 8275A)				
	Hmw PAHs	(8100, 8275A)				
	Pesticides	(8270D)				
Soil	Metals	(7000, 7010, 6010B, 6020A)	3	Composite	Annually/Core Sampler (Top 5cm)	Septic Field
	Organics Compounds	(8260B, 8021B,)				Visitor Center
	VOCs	(8270D)				

Table 5. Recommendations for Sampling to Examine COCs in Different Matrix in SAHI (continued).

Matrix	Analyte (1)		Number of Samples/Type		Frequency/Method	Location Onsite
	(Method#)					
Soil	Arsenic	(7060,7062)				
	Pesticides	(8270D)	3	Composite	Once / Core Sampler (Top 5cm)	Orchard Area
Soil	Total PAHs	(8015B)	3	Composite	Once / Core Sampler (Top 5cm)	Maintenance area
	VOCs	(8270D)				
Soil	Lead	(7040,7421)	3	Composite	Once Core Sampler (Top 5cm)	Adjacent to Wood building foundation
Soil	Total PAHs	(8015B)	3	Composite	Once Core Sampler (Top 5cm)	Main Parking Area on downward slope
	Lead	(7040,7421)				
Biota	Metals	(7000, 7010)	3	Composites Earthworms	Once	Septic Field
	Organic Compounds	(8260, 8270)		grass		Open Field
						Orchard Area
Biota	Metals	(7000,7010)	1	Composite	Once	Marsh Area
	Organic Compounds	(8260,8270)		of each Class		
			1	Bivalve Mollusk (M.edulis)		
			1	Crustacea (Fiddler Crab)		
			1	Teleost (Mummichog)		
			1	Annelid (Sandworm)		
	(1) All method numbers refer to EPA SW-846					
	(2) 1-3 Means sample in the first year then at 3 yr intervals					

Conclusion

This report deals with the COCs for SAHI and its surrounding waters and makes specific recommendations for sampling locations and specific compounds. Telephone and survey interviews, along with site visits, were conducted with NPS staff, and, where appropriate, with county and regional USGS officials. Contaminant data have been reviewed by state, county, USEPA, NPS, and National Oceanographic and Atmospheric Administration (NOAA) to prepare the data synthesis for this park.

After a thorough assessment of exposure pathways, we determined that the onsite threats at the park include: contamination from septic tanks (metals and VOCs); contamination from parking lot runoff (petroleum derived hydrocarbons and fuel additives); herbicide and pesticide use; and chromium copper and arsenic (CCA) treated walkways to the beach. The primary offsite threats to the park come from motorboat activities near shore (petroleum products), metal contamination from multiple sources into the general watershed sediments, pesticide use for mosquito control (West Nile or EEE threat), and the potential threat of a larger petroleum spill from the Commander Terminal Oil facility.

Based on the NOAA Status and Trends sediment data from the Oyster Bay/Cold Spring Harbor complex, silver, arsenic, cadmium, chromium, copper, mercury, nickel, and zinc had HQ and threshold toxicity hazard quotients (THQ) values above one. Dieldrin, chlordane, DDT/DDE, and lindane present in sediments had $HQ > 1$. Petroleum derived hydrocarbons were detected in sediments at levels above threshold levels for toxicity ($HQ > 1$). Surface water collected by USEPA showed that silver and copper were at levels above water quality criteria for aquatic species.

Groundwater on Long Island contains VOCs from current and historical use of cleaning solvents and other industrial activities (USGS). The groundwater also poses as a chronic exposure scenario to wildlife through surface water.

Literature Cited

- Abbene, I.J., Fisher, S.C., and Terracciano, S.A. 2005. Concentrations of Insecticides in Selected Surface Water Bodies in Suffolk County, New York, Before and After Mosquito Spraying, 2002-2004: U.S. Geological Survey Open-File Report 2005-1384, 14.
- A Compendium of Superfund Field Operations Methods, EPA 540/p-87/001. Engineering Support Branch Standard Operating Procedures and Quality Assurance Manual, USEPA Region IV, April 1, 1986.
- Agency for Toxic Substances and Disease Registry (ATSDR). 1990. Toxicological Profile for Copper, ATSDR/TP-90/08. ATSDR, Atlanta, GA.
- Agency for Toxic Substances and Disease Registry (ATSDR). 1992. Toxicological Profile for Mercury (update - draft for public comment). ATSDR, Atlanta, GA.
- Agency for Toxic Substances and Disease Registry (ATSDR). 1993a. Toxicological Profile for Chromium. TP-92/08. ATSDR, Atlanta, GA.
- Agency for Toxic Substances and Disease Registry (ATSDR). 1993b. Toxicological Profile for Lead (update). TP-92/12. ATSDR, Atlanta, GA.
- Agency for Toxic Substances and Disease Registry (ATSDR). 1994. Toxicological Profile for Selenium (update). ATSDR, Atlanta, GA.
- Agency for Toxic Substances and Disease Registry (ATSDR). 1995a. Toxicological Profile for Polycyclic Aromatic Hydrocarbons (PAHs) (update). ATSDR, Atlanta, GA..
- Agency for Toxic Substances and Disease Registry (ATSDR). 1995b. Toxicological Profile for Methyl T-Butyl Ether (draft). ATSDR, Atlanta, GA.
- Agency for Toxic Substances and Disease Registry (ATSDR). 1995c. Toxicological Profile for Automotive Gasoline. Atlanta, GA: U.S. Department of Health and Human Services, Public Health Service.
- ASTM D 1586-98, ASTM Committee on Standards. Philadelphia, PA.
- Atlas, R.M. and Bartha, R. 1973. Stimulated Biodegradation of Oil Slicks Using Leophilic Fertilizers. *Environmental Science and Technology*, 7:538-541.
- Baes, C.F., et al. 1984. A Review and Analysis of Parameters for Assessing Transport of Environmentally Released Radionuclides Through Agriculture. Oak Ridge, TN: Oak Ridge National Laboratory, ORNL-5786.
- Barcelona, M.J., et al. 1984. A Laboratory Evaluation of Groundwater Sampling Mechanisms. *Groundwater Monitoring Review*, pp. 32-41.

- Barcelona, M.J., Helfrich, J.A., and Garske, E.E. 1985. Sampling Tubing Effects on Groundwater Samples. *Analytical Chemistry*, 57: 460-463.
- Barth, D.S. and B.J. Mason. 1984. Soil Sampling Quality Assurance User's Guide. EPA-600/4-84-043.
- Birak, P., et al. 2001. Travis and Arms Revisited: A Second Look at a Widely Used Bioconcentration Algorithm. *Toxicology and Industrial Health*, 17:163-175.
- Bossert, I and Bartha, R. 1984. The Fate of Petroleum in Soil Ecosystems. In Atlas, R.M. ed. *Petroleum Microbiology*, New York, NY: MacMillan publishing Company, 435-473.
- Buchman, M.F. 1999. NOAA Screening Quick Reference Tables, NOAA HAZMAT Report 99-1. Seattle, WA: Coastal Protection and Restoration Division, National Oceanic and Atmospheric Administration.
- Burger, J. 1994. Immediate Effects of Oil Spills on Organisms in the Arthur Kill. In: *Before and After an Oil Spill*. Ed. J. Burger. Rutgers University Press. New Brunswick, N.J.
- Calabrese, E.J., Kostecki, P.T. 1991. *Hydrocarbon Contaminated Soils*. Lewis Publishers.
- California EPA. 2000. *Guidelines for Assessing Ecological Risks Posed by Chemicals*.
- Casarett, L.J. and Doull, J. 1991. *Toxicology: The Basic Science of Poisons*. Fourth Edition. M.O. Amdur, J. Doull, and C.D. Klaassen, eds. McGraw-Hill Inc. Health Profession Division.
- Casarett, L.J. and Doull, J. 1996. *Toxicology: The Basic Science of Poisons*. Fifth Edition. M.O. Amdur, J. Doull, and C.D. Klaassen, eds. McGraw-Hill Inc. Health Profession Division.
- Connell, D.W. and Markwell, R.D. 1990. Bioaccumulation in the Soil to Earthworm System. *Chemosphere*, 20:91-100.
- Crane, M. and Newman, M.C. 2000. What Level of Effect Is a No Observed Effect? *Environmental Toxicology and Chemistry*, 19:516-519.
- de Vera, E.R., et al. 1980. Samplers and Sampling Procedures for Hazardous Waste Streams. EPA-600/2-80-018.
- DiToro, D.M., et al. 1990. Toxicity of Cadmium in Sediments: The Role of Acid Volatile Sulfide. *Environmental Toxicology and Chemistry*, 9: 98-101.
- Driscoll, F.G. 1986. *Groundwater and Wells*. Second Edition. Johnson Division, UOP Inc. St. Paul, MN:
- Efroymson, R.A., et al. 1997. *Toxicological Benchmarks for Screening Contaminants of Potential Concern for Effects on Terrestrial Plants*. Oak Ridge, TN: Oak Ridge National Laboratory, 128 pp. ES/ER/TM-85/R3.

- Eisler, R. 1988. Arsenic Hazards to Fish, Wildlife and Invertebrates: A Synoptic Review. Biological Report 88(1.12). U.S. Fish and Wildlife Service. US Department of the Interior.
- Gibb, J.P., Schuller, R.M., and Griffin, R.A. 1980. Monitoring Well Sampling and Preservation Techniques, EPA-600/9-80-010.
- Guidelines for the Selection of Chemical Protective Clothing, Volume 1. Third Edition. 1987. American Conference of Governmental Industrial Hygienists, Inc., Occupational Safety and Health Guidance Manual for Hazardous Waste Site Activities, NIOSH/OSHA/USCG/EPA, 1985.
- Gustavsson, N., et al. 2001. Geochemical Landscapes of the Conterminous United States - New Map Presentations for 22 Elements. U.S. Geological Survey Professional Paper 1648. Retrieved November 7, 2006. Available on-line at: <http://geology.crusgs.gov/pub/ppapers/p1648/>.
- Heath, J.S., et al. 1993. Risk Assessment for Total Petroleum Hydrocarbons. In: Hydrocarbon Contaminated Soils. Eds. E.J. Calabrese and P.T. Kostecki. Lewis Publishers, an imprint of CRC Press, Boca Raton, FL. Volume Three, pp. 267-302.
- Huckins, J.N., Tubergen, M.W., and Manuweera, G.K. 1990. Semipermeable Membrane Devices Containing Model Lipid: a New Approach to Monitoring Bioavailability of Lipophilic Pollutants and Estimating Their Bioconcentration Factor.
- Instrument Specialties Company. 1980. Instruction Manual, Model 2100 Wastewater Sampler, Lincoln, NB.
- International Agency for Research on Cancer (IARC). 1989. IARC Monographs on the Evaluation of Carcinogenic Risks to Humans. Vol. 45: Occupational Exposures in Petroleum Refining, Crude Oil, and Major Petroleum Fuels. Lyon, France: World Health Organization, International Agency for Research and Cancer, 159-201.
- International Union of Pure and Applied Chemistry (IUPAC). 2003. Implications of Endocrine Active Substances for Humans and Wildlife—A SCOPE/IUPAC Project. Pure and Applied Chemistry 75, 1617-2615.
- Jager, T. 1998. Mechanistic Approach for Estimating Bioconcentration of Organic Chemicals in Earthworms (Oligochaeta). Environmental Toxicology and Chemistry, 17:2080-2090.
- Jorgensen, S.E., Nielson, N.S., and Jorgensen, L.A. 1991. Handbook of Ecological Parameters and Ecotoxicology. Amsterdam: Pergamon Press. Elsevier.
- Kannan, K., et al. 2007. Trace Element Concentrations in Livers of Polar Bears from Two Populations in Northern and Western Alaska. Archives of Environmental Contamination and Toxicology, 53:473-482.
- Keely, J.F. and Boateng, K. 1987. Monitoring Well Installation, Purging and Sampling Techniques – Part I: Conceptualizations, Groundwater, 25: 300-313.

- Keith, L. H. 1988. Principles of Environmental Sampling, American Chemical Society.
- Klaassen, C.D. and Rozman, K. 1991. Chapter 3: Absorption, Distribution and Excretion of Toxicants. In: Casarett and Doull's Toxicology, The Basis Science of Poisons. Fourth Edition. M.O. Amdur, J. Doull, and C.D. Klaassen, eds. McGraw-Hill, Inc. Health Professions Division.
- Korte, N. and Ealey, D. 1983. Procedures for Field Chemical Analyses of Water Samples. U.S. Department of Energy, GJ/TMC-07, Technical Measurements Center, Grand Junction Project Office.
- Korte, N. and Kearl, P. 1985. Procedures for the Collection and Preservation of Groundwater and Surface Water Samples and for the Installation of Monitoring Wells: Second Edition, U.S. Department of Energy, GJ/TMC-08, Technical Measurements Center, Grand Junction Projects Office.
- Kramer, W.H. 1982. Groundwater Pollution from Gasoline. Groundwater Monitoring Review, 2:18-22.
- Kramer, W.H. 1989. Benzene Exposure Assessment of Underground Storage Tanks Contractors. Applied Industrial Hygiene, 4:269-272.
- Long, E.R., Sloane, et al. 1994. Sediment Toxicity in Boston Harbor: Magnitude, Extent, and Relationships With Chemical Toxicants. NOAA Technical Memorandum NOS ORCA 96. National Oceanic and Atmospheric Administration, Silver Spring, MD.
- Loganathan, B.G. and Kannan, K. 1994. Global Organochlorine Contamination Trends: An Overview. Ambio, 23:187-191.
- Lyman, W.J., Reehl, W.F., and Rosenblatt, D.H. 1982. Handbook of Chemical Property Estimation Methods: Environmental Behavior of Organic Compounds. New York, NY: McGraw-Hill Book Company.
- MacDonald, D.D., Ingersoll, C.G. and Berger, T.A. 2000. Development and Evaluation of Conservation Based Sediment Quality Guidelines for Freshwater Ecosystems. Archives of Environmental Contamination and Toxicology, 39:20-31.
- Mason, B.J. Preparation of Soil Sampling Protocol: Technique and Strategies. 1983 EPA-600/4-83-020.
- Mason, B. 1966. Principles of Geochemistry: Third Edition. John Wiley & Sons, Inc.
- May, M. 2004. Sensitive Indicator Species. Mosquito Control Plan. 2006. Nassau and Suffolk County Plans, 3pp.
- Menzie, C.A., Potocki, B.B., and Santodonato, J. 1992. Exposure to Carcinogenic PAHs in the Environment. Environmental Science and Technology, 26:1278-1284.

- Nagy, K.A. 1987. Field Metabolic Rate and Food Requirement Scaling in Mammals and Birds. *Ecological Monographs*, 57:111-128.
- Nassau Board of Health. 2006. Local Water Quality Information: Pollution of Concern.
- Nassau County: Storm Water Program implementation 2006. Nassau County website. 28 pp.
- National Academy of Sciences (NAS). 2003. Dioxin and Dioxin-Like Compounds in the Food Supply: Strategies to Decrease Exposure.
- National Council of the Paper Industry for Air and Stream Improvement, Inc. 1982. A Guide to Groundwater Sampling. Madison, NY: Technical Bulletin No. 362.
- National Library of Medicine (NLM). 1996. Hazardous Substances Data Bank (HSDB). Public domain information available from the government. Additional commercially available copies of this public domain information have included (but may not be limited to, no government endorsement implied): the Tokes Plus (TM) CD-ROM data base, Micromedex Inc., Denver, CO.
- National Oceanic Atmospheric Association (NOAA). 1994. NOAA Technical Memorandum NOS OPCA 80, NS&T Program for Marine Environmental Quality. Biological Effects of Toxic Contaminants in Sediment from Long Island Sound and Environs, 117 pp.
- National Research Council Canada (NRCC). 1978. Effects of Lead in the Canadian Envir. NRCC No.0316-0114, 76 pp.
- National Research Council (NRC). 1993. Issues in Risk Assessment. Washington DC: National Academy Press, 191 pp.
- National Research Council (NRC). 1994. Science and Judgement in Risk Assessment, Washington, DC National Academy of Sciences, 652 pp.
- New Jersey Department of Environmental Protection. 1988. Field Sampling Procedures Manual.
- New Jersey Department of Environmental Protection (NJDEP). 2006. SERP Guidelines for Marine and Freshwater Sediments. Available on-line at: http://www.state.nj.us/dep/srp/regs/sediment/table_03.htm.
- New Jersey Department of Environmental Protection (NJDEP). 2008. Updated February 15, 2008. Available on-line at: <http://www.nj.gov/dep>.
- Newman, M.C. and Unger, M.A. 2003. Fundamentals of Ecotoxicology. Second Edition. Boca Raton, FL: CRC/Lewis Press.
- Nielsen, D. M. and Yeates, G. L. 1985. A Comparison of Sampling Mechanisms Available for Small-Diameter Groundwater Monitoring Wells. *Groundwater Monitoring Review*, pp. 83-99.

- Peterson, J.A. and Nebeker, A.V. 1992. Estimation of Waterborne Selenium Concentrations That Are Toxicity Thresholds for Wildlife. *Archives of Environmental Contamination and Toxicology*, 23:154-162.
- Petty, J.D, et al. 2000. Considerations Involved with the Use of Semipermeable Membrane Devices for Monitoring Environmental Pollutants. *Journal of Chromatography A*, 879:83-95.
- Rand, G.M. and Petrocelli, S.R, eds. 1985. *Fundamentals of Aquatic Toxicology.*, Chapter 1. Introduction. Hemisphere Publishing Corporation, Washington, New York, and London.
- Ratte H.T. 1999. Bioaccumulation and Toxicity of Ag Compounds a Review. *Environmental Toxicology and Chemistry*. 18:89-108.
- Reese, E. and Kimbrough, R.D. 1993. Acute Toxicity of Gasoline and Some Additives. *Environmental Health Perspectives*. 101:115–118.
- Sagamore Hill Environmental Management Plan. 2006. National Park Service, U.S. Department of Interior, 44 pp.
- Sample, B.E. and Suter II, G.W. 1994. Estimating Exposure of Terrestrial Wildlife to Contaminants. Oak Ridge, TN: Oak Ridge National Laboratory, ES/ER/TM-125
- Sample, B.E., Opresko, D.M. and Suter II, G.W. 1996. Toxicological Benchmarks for Screening Contaminants for Wildlife. Oak Ridge, TN: Oak Ridge National Laboratory, ES/ER/TM-86/R3, 227pp.
- Sample, B.E., et al. 1997. Literature-Derived Bioaccumulation Models for Earthworms: Development and Validation. *Environmental Toxicology and Chemistry*, 18:2110-2120.
- Sanders, P.F. 2003. Ambient Levels of Metals in New Jersey Soils. Research Project Summary: Environmental Assessment and Risk Analysis Element. New Jersey Department of Environmental Protection, Division of Science, Research, and Technology. 5pp.
- Scalf, M.J., et al. 1980 *Manual for Groundwater Sampling Procedures*. Ada, OK: R.S. Kerr Environmental Research Laboratory, Office of Research and Development.
- Schiffer, D.M. 1989. Effects of Highway Runoff on the Quality of Water and Bed Sediments of Two Wetlands in Central Florida. USGS Water-Resources Investigations Report 88-4200. Department of the Interior, U.S. Geological Survey, Tallahassee, FL, 63 pp.
- Schmitt, C.J., et al. 1987. Bioavailability of Lead and Cadmium from Mine Tailings to the Pocketbook Mussel. Proceedings, Workshop on Die-Offs of Freshwater Mussels in the U.S., Richard J. Neves, ed., U.S. Fish and Wildlife Service, Columbia, MO.
- Schwarzenbach, R.P., Gschwend, P.M., and Imboden, D.M. 2003. Chapter 10: Partitioning to Living Media-Bioaccumulation and Baseline Toxicity. In: *Environmental Organic Chemistry*, Second Edition. Hoboken, NJ: Wiley-Interscience.

- Seiler, H.G., Sigel, H., and Sigel, A. (eds.). 1988. Handbook on the Toxicity of Inorganic Compounds. New York, NY: Marcel Dekker, Inc.
- Shacklette, H.T. and Boerngen, J.G. 1984. Element Concentrations in Soils and Other Surficial Materials of the Conterminous United States. U.S. Geological Survey Professional Paper 1270, 105pp.
- Sheppard, S., et al. 1997. Advances in Earthworm Ecotoxicology. A Technical Publication of SETAC. SETAC Press, 413 pp.
- Sisk, S.W. 1981. NEIC Manual for Ground/Surface Investigations at Hazardous Waste Sites, EPA-330/9-81-002.
- Society of Environmental Toxicology and Chemistry (SETAC) Press. 1997. Advances in Earthworm Ecotoxicology. Editors; S. Sheppard, J. Bernbridge, M. Holmstrup, L. Postuma. SETAC Press. Proceedings from the Second International workshop on Earthworm Ecotoxicology.
- Sorensen, E.M. 1991. Metal Poisoning in Fish. Lewis Publishers, an Imprint of CRC Press, Boca Raton, FL. Reprinted by permission CRC Press, 374pp.
- Spacie, A. and Hamelink, J.L. 1985. Chapter 17. Bioaccumulation. In: Fundamentals of Aquatic Toxicology. G.M. Rand and Petrocelli, eds. Hemisphere Publishing Corporation, Washington, New York, and London.
- Sprague, J.B. 1985. Chapter 6: Factors that Modify Toxicity. In: Fundamentals of Aquatic Toxicology. G.M. Rand and Petrocelli, eds. Hemisphere Publishing Corporation, Washington, New York, and London.
- Stubblefield, W.A., et al. 1997. Effects of Water Hardness on the Toxicity of Manganese to Developing Brown (SALMO TRUTTA). Environmental Toxicology and Chemistry, 16:2082–2089.
- Sun, H., et al. 2008. Semipermeable Membrane Device-Assisted Desorption of Pyrene from Soils and Its Relationship to Bioavailability. Environmental Toxicology and Chemistry, 27:103-111.
- Suter, G.W. 1993. Ecological Risk Assessment. Boca Raton, FL: Lewis Publishers, 538 pp.
- Suter, G.W. II and Mabrey, G.W. 1994. Toxicological Benchmarks for Screening of Potential Contaminants of Concern for Effects on Aquatic Biota on Oak Ridge Reservation, Oak Ridge, Tennessee: 1994 Revision. Publication Number ES/ER/TM- 96/R1. Oak Ridge National Laboratory, Oak Ridge, TN.
- Totten, L. A., et al. 2004. Atmospheric Concentrations and Deposition of PCBs to the Hudson River Estuary. Environmental Science and Technology, In press.

- Travis, C.C. and Arms, A.D. 1988. Bioconcentration of Organics in Beef, Milk and Vegetation. *Environmental Science and Technology*, 22:271-274.
- U.S. Code of Federal Regulations, 49 CFR Parts 100 to 177, Transportation revised November 1, 1985.
- U.S. Department of the Interior, National Handbook of Recommended Methods for Water-Data Acquisition, Reston, Virginia.
- U.S. Department of Interior, Fish and Wildlife Service. 1980. Handbook of Acute Toxicity of Chemicals to Fish and Aquatic Invertebrates. Resource Publication 137. Washington, DC
- U.S. Environmental Protection Agency. 1977. Procedures Manual for Groundwater Monitoring at Solid Waste Disposal Facilities. EPA-530/SW-611.
- U.S. Environmental Protection Agency (USEPA). 1980a. Ambient Water Quality Criteria for Mercury. EPA Report 440/5-80-058. National Technical Information Service, Springfield, VA.
- U.S. Environmental Protection Agency (USEPA). 1980b. Ambient Water Quality Criteria for Copper. EPA Report 440/5-80-036. National Technical Information Service, Springfield, VA. Also available as a January 1985 revision (NTIS PB0227023).
- U.S. Environmental Protection Agency (USEPA). 1980c. Ambient Water Quality Criteria for Zinc. EPA Report 440/5-80-079. National Technical Information Service (NTIS), Springfield, VA. USEPA 1980. Ambient Water Quality Criteria Doc: Silver p.C-1, 1980, EPA 440/5-80-071.
- U.S. Environmental Protection Agency. 1982. Handbook for Chemical and Sample Preservation of Water and Wastewater. EPA-600/4-82-029.
- U.S. Environmental Protection Agency. 1983a. Methods for Chemical Analysis of Water and Waste, August, 1977. EPA-600/4-79-020.
- U.S. Environmental Protection Agency (USEPA). 1983b. Process Design Manual for Land Concentration of Municipal Sludge. EPA, Cincinnati, OH.
- U.S. Environmental Protection Agency, 1984a. Test Methods for Evaluation of Solid Waste. EPA-SW-846, Second Edition. EPA-600/2-81-160.
- U.S. Environmental Protection Agency. 1984b. Characterization of Hazardous Waste Sites – A Methods Manual: Volume II. Available Sampling Methods, Second Edition. EPA/600/4-84-076.
- U.S. Environmental Protection Agency (USEPA) 1984c. Ambient Water Quality Criteria Doc: Mercury p.10 (1984) EPA 440/5-84-026.

- U.S. Environmental Protection Agency. 1985. Practical Guide for Groundwater Sampling, EPA-600/2-85/104.
- U.S. Environmental Protection Agency. 1986. RCRA Groundwater Monitoring Technical Enforcement Guidance Document, OSWER-9950-1.
- U.S. Environmental Protection Agency. 1992a. Framework for Ecological Risk Assessment. EPA/630/R-92/001.
- U.S. Environmental Protection Agency (USEPA). 1992b. Pesticide Tolerance for Glyphosphate. Federal Register 57:8739 40, 10-98.
- U.S. Environmental Protection Agency (USEPA). 1993a. Interim Report on Data and Methods for Assessment of 2,3,7,8-Tetrachlorodibenzo-p-dioxin Risks to Aquatic Life and Associated Wildlife. EPA/600/R-93/055.
- U.S. Environmental Protection Agency (USEPA). 1993b. Oil and Hazardous Materials/Technical Assistance Data System (OHM/TADS). Public domain information available from the government. Additional commercially available copies of this public domain information have included (but may not be limited to, no government endorsement implied): The Toms Plus (TM) CD-ROM data base Vol. 17, Micromedex Inc., Denver, CO. (NOTE: OHM/TADS Data System has reviews of over 1,200 petroleum products and hazardous chemicals.).
- U.S. Environmental Protection Agency. 1993c. Wildlife Exposure Factors Handbook. Volume 1. EPA/600/R-93/187a.
- U.S. Environmental Protection Agency. 1995. Great Lakes Water Quality Initiative Criteria Documents for the Protection of Wildlife. EPA-820-B-95-008.
- U.S. Environmental Protection Agency (USEPA). 1996. EPA Integrated Risk Information System (IRIS) Electronic Database. Public domain information available from the government. EPA Criteria and Assessment Office, Cincinnati, OH. Also available from various commercial sources, but information in this document was copied directly from EPA government source rather than from commercial re-publishers.
- U.S. Environmental Protection Agency. 1997a. Ecological Risk Assessment Guidance for Superfund: Process for Designing and Conducting Ecological Risk Assessments, Interim Final. EPA 540-R-97-006.
- U.S. Environmental Protection Agency. 1997b. Mercury Study Report to Congress, Vol VII: Characterization of Human Health and Wildlife Risks from Mercury Exposure in the United States. EPA-452/R-97-009.
- U.S. Environmental Protection Agency. 1998. Guidelines for Ecological Risk Assessment. EPA/630/R095/002F.

- U.S. Environmental Protection Agency (USEPA). 2000. Chapter 3. Establishing Treatment System Performance Requirements. National Risk Management Research Laboratory. EPA 625/R-00/008- Ch.3.
- U.S. Environmental Protection Agency. 2002. Guidance on Choosing a Sampling Design for Environmental Data Collection; For Use in Developing a Quality Assurance Project Plan. EPA QA/G-5S. EPA/24D/R-02/005.
- U.S. Environmental Protection Agency. 2003. Guidance for the Development of Ecological Soil Screening Levels. Washington, DC: Office of Solid Waste and Emergency Response. OSWER Directive 92857-55.
- U.S. Environmental Protection Agency. 2006. Emergency Response Team. Retrieved July 22, 2006. Available on-line at: <http://www.ert.org>.
- U.S. Environmental Protection Agency. 2007. Framework for Metals Risk Assessment. Retrieved August 3, 2006. Available on-line at: <http://www.epa.gov/osa/metalsframework>.
- U.S. Geological Survey (USGS). 1977. National Handbook or Recommended Methods for Water Data Acquisition. Office of Water Data Coordination Reston, Virginia. (Chapter Updates available).
- U.S. Geological Survey (USGS). 1996. Summary Document for the USGS Workshop on Mercury Cycling in the Environment, Golden, Colorado, July 7-9, 1996. U.S. Geological Survey, Water Resources Division, Office of Water Quality. Reston, VA.
- Van den Berg, M. et al. 2006. The 2005 World Health Organization Reevaluation of Human and Mammalian Toxic Equivalency Factors for Dioxins and Dioxin-Like Compounds. Toxicological Sciences, 93: 223-241.
- Walsh, D.F., Berger, B.L., and J.R. Bean. 1977. Mercury, Arsenic, Lead, Cadmium, and Selenium Residues in Fish. 1971-1973-National Pesticide Monitoring Program. Pesticide Monitoring Journal, 11:5-34.
- Weston, 1987. Standard Operations Procedures for Monitor Well Installation. MOUND IGMP/RIP.
- Wiener, J.G. and Stokes, P.M. 1990. Enhanced Bioaccumulation of Mercury, Cadmium, and Lead in Low - Alkalinity Waters; An Emerging Regional Environmental Problem. Reprinted with permission from Environmental Toxicology and Chemistry, 9:821-823. Copyright 1990 SETAC.

- Wiener, J.G. 1996. Mercury in Fish and Aquatic Food Webs. Paper presented at a July 9, 1996, USGS Meeting "Mercury Cycling in the Environment." U.S. Geology Survey, Office of Water Quality, Denver, CO. Abstract available from USGS, Denver, CO, or from Jim Wiener, NBS, LaCrosse, WI. Highlights available in: Summary Document for the USGS Workshop on Mercury Cycling in the Environment Golden, Colorado, July 7-9, 1996 U.S. Geological Survey, Water Resources Division Office of Water Quality. Reston, Virginia October, 1996.
- Will, M.E. and Suter, G.W. 1994. Toxicological Benchmarks for Screening Potential Contaminants of Concern for Effects on Terrestrial Plants: 1994 Revision. Publication Number ES/ER/TM-85/R1. Oak Ridge National Laboratory, Oak Ridge, TN.
- Wong, C.K., Chu, K.H., and Shum, F.F. 1995. Acute and Chronic Toxicity of Malathion to Fresh-Water Cladoceran *Moina macrocarpa*. Water Air Soil Pollution, 84:399-405.
- Wong, N.C., et al. 2006. Dependency of Copper Toxicity to Polychaet Larvae on Algal Concentration. Aquatic Toxicology, 77:117-125.
- World Health Organization (WHO). 1989. International Agency for Research on Cancer (IARC) Monographs on the Evaluation of Carcinogenic Risks to Humans: Occupational Exposures in Petroleum Refining; Crude Oil and Major Petroleum Fuels. Volume 45. IARC, Printed in the UK.
- Zulkosky, A.M., et al. 2005. Acute Toxicity of Resmethrin, Malathion and Methoprene to Larval and Juvenile American Lobsters (*Homarus americanus*) and Analysis of Pesticide Levels in Surface Water after ScourgeTM, AnvilTM, and AltosidTM Application. Journal of Shellfish Research, 24(3):795-804.

Appendix 1: Hazard Quotient Approaches and Sampling Protocols for Screening Level Evaluations for Chemicals of Concern at National Parks

Contents

	Page
Tables	40
Figures	41
1.0 Introduction	42
2.0 Routes of Entry of Pollutants into Ecosystems	43
2.1 Fate and Transport	44
2.1.1 Atmospheric	48
2.1.2 Soil	48
2.1.3 Surface Water	50
2.1.4 Sediment	51
2.1.5 Groundwater	51
3.0 Ecological Risk Assessment	52
3.1 Screening Level for Ecological Risk Assessment	52
3.2 Hazard Quotient Approach (HQ)	55
3.3 Estimating Body Burdens for Comparison to NOAELs for Wildlife	56
4.0 Trophic Level Evaluation	57
4.1 Estimating Aquatic Organisms' Body Burdens	57
4.2 Aquatic Food Chain Multiplier (FCM)	58
4.3 Terrestrial Organisms (Wildlife and Plants)	61
4.4 Terrestrial Plant Contamination	66
5.0 Sample Collection and Analytical Techniques	67
5.1 Sampling Design	67
5.2 Discrete or Composite Samples	68
6.0 Conclusion	72

Tables

	Page
Table 1. Levels Reported in the Earth's Crust (ppm).	49
Table 2. Aquatic Food Chain Multipliers.	59
Table 3. Selected Compounds for Determining Trophic Level BAFs.	62
Table 4. Reference Values for Representative Terrestrial Mammalian Species.	62
Table 5. Estimated Water Content for Various Types of Food	64
Table 6. Diet Composition of Representative Terrestrial Mammals Likely to be Encountered at Park Locations.	64
Table 7. Avian Species That Are Recommended for Estimating Exposure Concentrations.	65
Table 8. Diet Composition of Representative Avian Species Likely to be Encountered at Park Locations.	65
Table 9. Recommended Analytical Methods by Matrix Being Analyzed.	70
Table 10. Summary of Collection and Holding Requirements Based on Analyte and Specimen.	71

Figures

	Page
Figure 1. Pathways for Contaminant Movement (Arrows) Between the Different Matrixes Comprising the Ecosystem.	45
Figure 2. Conceptual Diagram for Evaluating Bioavailability to Organisms from a Compound (Stars) Present in the Environment in a Bound (NOT BIOAVAILABLE) and Free State (BIOAVAILABLE) for Exposure, Uptake across the Biological Membrane Resulting in Bioaccumulation within the Organism, and Subsequent Internal Transport and Distribution.	46
Figure 3. Proposed Guidelines for Ecological Risk Assessment.	53

1.0 Introduction

Appendix 1 gives a brief overview of ecological risk assessment approaches and standard sample collection methods that can be employed at the National Parks for various matrixes and compounds. It is not our intention to recreate the wheel, but to incorporate methods that are generally accepted by the scientific community. Many of the sampling protocols cited are from a number of different agencies (USEPA Emergency Response Team website, NOAA Status and Trends, and the New Jersey Department of Environmental Protection). The methods described in these documents are standard methods and would be appropriate for use by the National Park Service. The standard operating procedures (SOPs) are slightly different for each agency, but the basic approaches and quality assurance and quality controls (QA/QC) are comparable. Appendix 1 is not exhaustive, but attempts to bring together in a single location, SOPs that can be used by park personnel involved in chemical of concern (COC) evaluations. In some instances, the recommendation of one protocol over another is based on our own experience or bias, and is only a recommendation. The detailed protocols are presented in Appendix 2.

The National Park Service (NPS) has a website wherein a number of commonly occurring compounds are discussed, from a broad basis incorporating human and rodent information, and where available, wildlife and plant toxicity data (Environmental Contaminants Encyclopedia, Ed. Roy Irwin (www.nature.nps.gov/hazardssafety/toxic/). The general mechanism of toxicity is also presented and can be applied to a wide variety of wildlife. In many instances the mechanism of action of a COC will result in similar effects across a wide variety of flora and fauna due to similar biochemical pathways. The ECOTOX database (<http://cfpub.epa.gov/ecotox/>) released in 2000 by the USEPA and managed by the USEPA Duluth Laboratory has extensive ecological data both for terrestrial and aquatic species, as well as greater detail than what is described in this appendix. For chemical, physical, and fate data on specific compound the CHEMFATE database (<http://www.syrres.com/eSc/chemfate.htm>), maintained by Syracuse Research Corporation, is also a reference source. Another valuable resource for using screening benchmarks is available from Oak Ridge National Laboratory, which describes ecological risk analysis including guidance, tools, and applications (www.esd.ornl.gov/programs/ecorisk/ecorisk.html). The Agency for Toxic Substances and Disease Registry provides individual chemical Toxicological Profiles (www.atsdr.cdc.gov/). The USEPA ECOTOX Database provides toxicology data on individual compounds for aquatic and terrestrial life (www.epa.gov/med/Prods_Pubs/ecotox.htm).

2.0 Routes of Entry of Pollutants into Ecosystems

This is a simple overview of the fate and transport of COCs (Suter 1993). It is important for any ecological based assessments to realize that COCs can enter an ecosystem by many routes (transport through air, water, or soil/sediments) from point and non-point sources. The fate of the COC can be impacted by a number of physical parameters of the receiving area. Any park, whether small or large, is part of a larger watershed and airshed, with many different inputs. Therefore, it is essential that the park lands properties be examined in relationship to their surrounding environs. Establishing a baseline level of chemicals present on the park lands and waters is important to be able to determine increases or decreases in a particular chemical. Because a number of chemicals occur naturally, it is important to understand the naturally occurring levels. The plants and animals that are present at the parks and surrounding areas are important in assessing the potential impact of specific COCs on the organisms. Because of the diversity of the plant and animals (ecological receptors), it is impossible to assess each species independently. It is vital, therefore, to identify representative or surrogate species that can be used to assess potential impacts on larger groups of organisms. This is one of the underlying principles for historical and continued collection of Mussel Watch Data (oysters, mussels, and clams). The use of a surrogate species may not always be the most sensitive organisms, but they do allow for evaluation of a single species over multiple years as an indicator of improvement, constancy, or deterioration of the organisms' exposure and possible health. If such a species is identified, it should be used as an indicator species for that park. For example, there are specific plant species that are very sensitive to ozone, while other plants show no toxicity at much higher atmospheric concentrations. In that particular case, the most sensitive species would become the plant species that sets the lowest observable adverse effects level (LOAEL) in the atmosphere. If this sensitive species approach is taken then it will protect other more resistant species in the park. The natural resource surveys and inventories at the park can give information on population level changes and the trends can be compared with chemical level exposures.

In the above paragraph, COCs were discussed, but it also must be realized that individual species can be impacted by non-chemical stressors that can have deleterious effects. Physical parameters such as pH, alkalinity, salinity, dissolved oxygen, water transparency, and temperature can result in the loss of species and be important stressors affecting an organisms response. It should be recognized that physical parameters often limit distributions of organisms. Therefore, plants and animals living in an ecosystem can be impacted both by physical parameters, as well as COCs. Because of this fact, the USEPA's (1992) Framework for Ecological Risk Assessment includes "stressor response" which would include physical parameters as do later EPA documents (USEPA 1993, 1997a, 1998). A classic example is the effect of pH in freshwater systems and the loss of species dependent on pH tolerances. These physical parameters are easily measured and should be incorporated into any monitoring plan since they have profound effects on bioavailability and uptake (Rand and Petrocelli 1985; Schwarzenbach et al. 2003).

The selection of the animals and plants to be used in the risk assessment will be in some cases site specific because of the unique species present at the park or the surrounding area. Generally, there will be both terrestrial and aquatic species and associated toxicity data used for determining which if any COCs pose a hazard. The selected species may also be used as indicator species that

can be collected and analyzed for COCs. The sampling may be done to determine if COCs are reaching elevated levels. This will also allow for COC trends to be developed. Samples of water, soil, sediment and air may be conducted in concert or as independent samples to establish reference or baseline levels. In many parks, there is no plan in place. High volume air samples and semi-permeable membrane water and soil samples could be added if grab samples would not be able to detect COCs (Huckins et. al. 1990; Petty et. al. 2000; Sun et al. 2008).

2.1 Fate and Transport

Pollutants can enter an ecosystem through both human activities, and naturally occurring processes (weathering of rocks, volcanic activity, and others). While knowledge of sources will give you important information on the type of contaminants your environment might be exposed to, the concentration or dose of a compound will dictate the response observed in the wild. As all toxicologists know “the dose makes the poison,” and once this level has been exceeded, toxicity may be observed. In all of the different matrices (surface and groundwater, sediments, and terrestrial soil), there are both point and non-point sources of contamination. Ecosystems are impacted from contamination contributed from atmospheric, terrestrial and aquatic sources. Below is a brief description of sources of contaminants entering into the different media, also shown in Figure 1.

The conceptual diagram shown in Figure 2 illustrates the requirement that the chemical can be bound or in a free state during exposure. Generally, if the compound is sequestered in a particle it is not available to be taken up by an organism since the compound must be free to be able to be transported across a biological membrane. A number of factors, such as charge and size, can determine whether a compound will be taken up by an organism. Once inside the cell, the compound can be metabolized, stored or excreted. If the compound reaches a target tissue where it causes toxicity at sufficient concentration then sublethal or lethal effects may be observed (Klassen and Rozman 1991). The physical chemical environments in which they exist can dramatically alter the chemical species that is available for accumulation (Spacie and Hamelink 1985). These general principles apply to organic compounds as well as metallic compounds.

Atmospheric contamination can enter the terrestrial soil and surface waters through precipitation (wet deposition) or from suspended particulates (dry deposition). There can be a contribution from both the terrestrial soil compartment and the surface water compartment into the atmosphere via particle suspension and volatilization processes. The contamination of the terrestrial soil from atmospheric deposition or from crustal compounds (background) can flow into the surface waters and end up in suspension or depositing on the bottom as sediment. Groundwater can become contaminated from compounds leaching into the groundwater. Surface waters can also contaminate groundwater when they are in direct contact (e.g., saltwater intrusion) or as the groundwater is being recharged. Groundwater contamination can reach surface waters in the basal flow of rivers and through seeps. The ability of a compound to move between these different compartments is determined by the physical chemical properties of the individual compound. Biotic factors can result in modifying the amount of a COC that could be released from any of these compartments. Regional point sources of contamination can result in contamination spreading into several of these compartments.

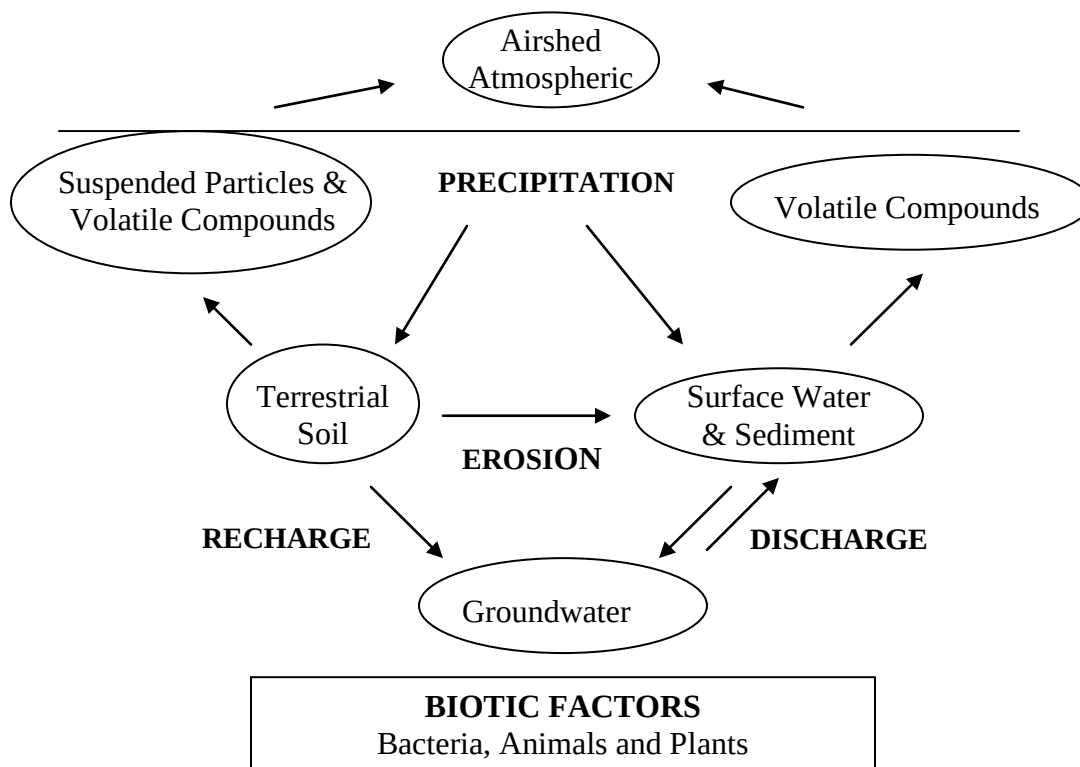


Figure 1. Pathways for Contaminant Movement (Arrows) Between the Different Matrixes Comprising the Ecosystem. Biotic factors can modify fate and transport of contaminants within an ecosystem by increasing or decreasing bioavailability.

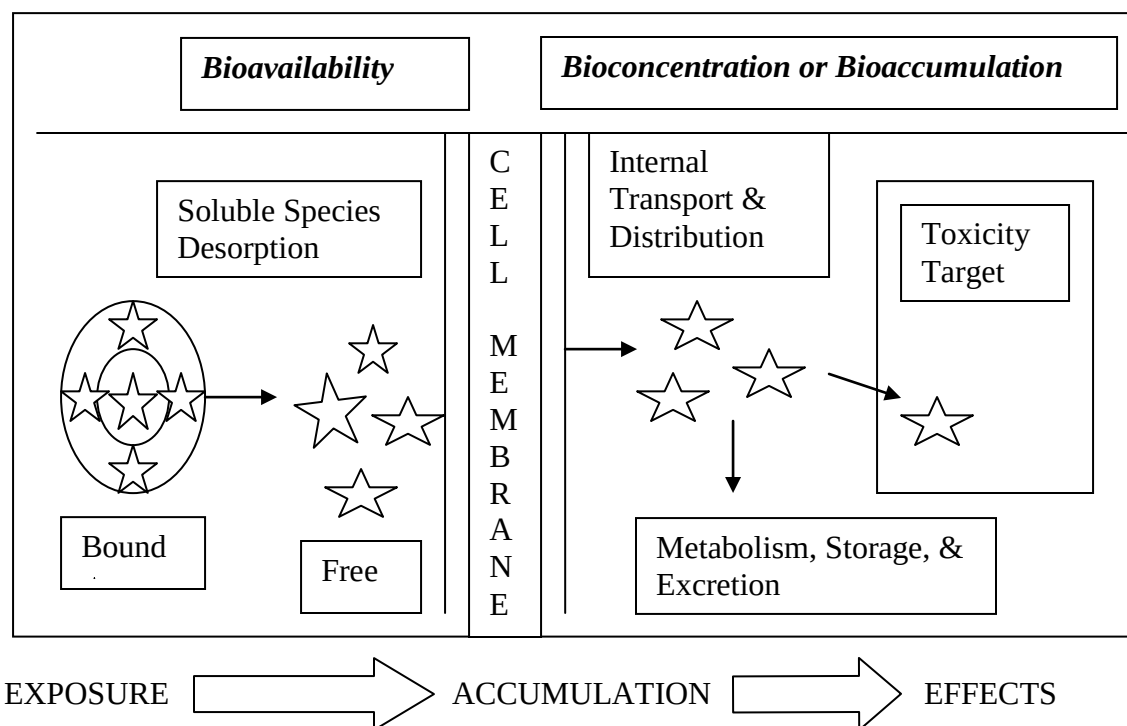


Figure 2. Conceptual Diagram for Evaluating Bioavailability to Organisms from a Compound (Stars) Present in the Environment in a Bound (NOT BIOAVAILABLE) and Free State (BIOAVAILABLE) for Exposure, Uptake across the Biological Membrane Resulting in Bioaccumulation within the Organism, and Subsequent Internal Transport and Distribution. The compound can undergo metabolism, storage and excretion. A metabolite or the parent compound could interact at the toxicity target site resulting in sublethal or lethal effects.

The movement of contaminants through the different matrices and ultimately into plants and animals (environmental fate) is determined by the physical characteristics of the compound and the environmental compartment it is entering (Figure 2). Bioavailability is an important concept that determines what levels of specific compounds will be present in the biota inhabiting contaminated and non-contaminated environments. Bioavailability is determined by many factors that determine how much of the compound or metal is in a free state that can be taken up by an organism or plant. Physical-chemical properties of the matrix into which a compound is associated and the properties of the surrounding medium will affect the level of compound that is free to be taken up by the organism. Factors such as pH, total organic carbon, and acid volatile sulfides can dramatically affect the uptake of a compound. A full discussion of release from a specific matrix and the uptake mechanisms based on characteristics of a metal or organic compound are too complicated for this appendix (Casarett and Doull 1991, 1996, 2008; Jorgensen et al. 1991; Schwarzenbach et al. 2003).

A critical physical characteristic of a compound is polarity, which will determine the compound's affinity for polar (water) and non-polar (lipids and non-polar materials) matrixes. In the case of water, oxygen draws electrons away from the two hydrogen atoms, which creates a partial negative charge on the oxygen and a partial positive charge on the hydrogen atoms. Because of the polar nature of water, cations and anions (i.e., positively and negatively charged compounds) are attracted to water and are soluble. These include inorganic salts (alkali earth metals) and polar organic compounds containing polar groups (e.g., alcohols, acids, and amines). Compounds that are not polar generally will partition into non-polar compartments that contain lipids (such as living organisms) and organic carbon (organic enriched particles). An important property of chemicals, which is used in estimating the potential to accumulate into living organisms is the octanol/water partitioning coefficient (K_{ow}). As the name implies, it is the concentration of a compound in octanol divided by the concentration of the compound in the water phase at equilibrium. This is a measure of the hydrophobicity of the compound. This value can be used to estimate the bioconcentration of compounds into organisms. In a similar fashion, compounds will partition between the different compartments described in Figure 1 based on physical chemical properties of the compound (e.g., Henry's constant relating distribution of volatile compounds between air and water and soil).

The residence time of the parent compound and its metabolites are determined by the compound's molecular stability. There are many methods by which a compound can be broken down in the environment (e.g., hydrolysis, auto-oxidation, photolysis, and enzymatic biotransformation). The rate of breakdown of a compound will determine the half-life in any particular medium. Persistent organic pollutants are generally recalcitrant to physical, chemical, and biochemical transformation (e.g., DDT/DDE, PCBs, and dioxins). However, in some instances metabolism (e.g., Benzo(a)pyrene, dieldrin) and photolysis (e.g., petroleum hydrocarbons) can result in activation of a compound to reactive chemical species that can result in cellular transformation leading to cancer, developmental effect, or acute toxicity.

Metals are non-biodegradable and do not breakdown in a similar fashion to organic compounds in the environment. Metals can exist as multiple converting species that are determined by the environmental chemistry of the medium they are located in. In the case of metal contaminants, they also are persistent and their ionization state will affect their residence time and transport

within the environment (USEPA 2007). USEPA's Framework for Metal Risk Assessment (<http://www.epa.gov/osa/metalsframework>) is a document that discusses in great detail each of these issues, and should be referred to when dealing with metal risk assessments (USEPA 2007). In the case of mercury, the metabolism to methyl mercury results in at least one bioavailable and toxic form of the metal. Metals that are deposited onto the soil or into sediment can have very long residence times and may become mineralized. It is important to note that geological deposit and the earth's crust are comprised of a number of metals that contribute to the general background concentrations for a specific region even without anthropogenic contributions. Background levels of metals in Northeast soils and in the earth's crust are summarized in Table 1. Background metal concentrations can vary over several orders of magnitude based on the soil type, geography and other factors. Additional sources of regional and state soil metal levels can be obtained from USEPA ecological soil screening levels document (USEPA 2003). The site-specific assessments proposed for the parks will involve only a single geographic area of concern and the regional values can be used for comparison to values obtained within the park. There are also "ambient concentrations" provided on a state-by-state basis (Sanders 2003).

2.1.1 Atmospheric

The airshed that overlies a watershed can contribute large quantities of contaminants that are associated with particle deposition, gases or dissolved in rain or snow. The sources of contamination can be from both local, as well as long distance transport. Incineration of waste and production of energy using coal and other sources can contribute to atmospheric contamination. Other sources include internal combustion engines, pesticide use on production agriculture, and volatile organic compounds that are used in refrigerants, solvents, and industrial processes. The magnitude of toxic chemical releases that may occur on a yearly basis into the atmosphere is often not appreciated, nor the resident time that these contaminants have in the atmosphere (Loganathan and Kannan 1994; Kannan et al. 2007). From anthropogenic sources it is estimated that 5.4 billion metric tons of CO₂, 89.3 million metric tons of SO_x, 60.7 million metric tons of NO_x, and 0.98 million metric tons of chlorofluorocarbons (CFCs). Regional and local sources often contribute to higher local concentrations and corresponding higher concentrations entering surface water, soils, and biota.

2.1.2 Soil

Contamination of soil can occur through deliberate contamination from dumping of industrial and municipal wastes (metals, organic compound radioactive material), direct application of pesticides or herbicides, application of sewage sludge (heavy metals, nitrates, phosphates, detergents), and other soil amendments, and atmospheric deposition of long and short range contaminants (metals, sulfur dioxide, nitrogen oxides, dioxins and furans and other organic compounds). The soil characteristics (organic content, buffering capacity) can affect the fate of the contaminants deposited on the soil and their impact on flora and fauna. Erosion of soils is one of the major means by which contaminated soils can reach surface waters and also contribute to sediment contamination. Because watersheds represent large drainage basins, upstream soil contamination can impact downstream water and sediment quality as it is deposited at the mouth of the rivers and bays or simply deposited in a slow moving portion of a stream. In many instances, acceptable levels of soil contamination are based on human and terrestrial wildlife

Table 1. Levels Reported in the Earth's Crust (parts per million).¹

Atomic Number	Element	Crustal Average	Atomic Number	Element	Crustal Average
1	H	1,400	45	Rh	0.005
3	Li	20	46	Pd	0.01
4	Be	2.8	47	Ag	0.07
5	B	10	48	Cd ²	0.2
6	C	200	49	In	0.1
7	N	20	50	Sn	2
8	O	466,000	51	Sb	0.2
9	F	625	52	Te	0.01
11	Na	28,300	53	I	0.5
12	Mg	20,900	55	Cs	3
13	Al	81,300	56	Ba	425
14	Si	277,200	57	La	30
15	P	1,050	58	Ce	60
16	S	260	59	Pr	8.2
17	Cl	130	60	Nd	28
19	K	25,900	62	Sm	6.0
20	Ca	36,300	63	Eu	1.2
21	Sc	22	64	Gd	5.4
22	Ti	4,400	65	Tb	0.9
23	V	135	66	Dy	3.0
24	Cr	100	67	Ho	1.2
25	Mn	950	68	Er	2.8
26	Fe	50,000	69	Tm	0.5
27	Co	25	70	Yb	3.4
28	Ni ²	75	71	Lu	0.5
29	Cu ²	55	72	Hf	3
30	Zn ²	70	73	Ta	2
31	Ga	15	74	W	1.5
32	Ge	1.5	75	Re	0.001
33	As	1.8	76	Os	0.005
34	Se	0.05	77	Ir	0.001
35	Br	2.5	78	Pr	0.01
37	Rb	90	79	Au	0.004
38	Sr	375	80	Hg	0.08
39	Y	33	82	Pb ²	13
40	Zr	165	83	Bi	0.2
41	Nb	20	90	Th	7.2
42	Mo	7	92	U	1.8
44	Ru	0.01			

¹Values taken from Mason B. Principals of Geochemistry, Third Edition.

²Values are ppm mg/kg and the source is from NE-1001 Application of sewage biosolids to agricultural soils in the Northeast: long-term impacts and benefit uses.

http://www.lgu.umd.edu/lgu_v2/homepages/pub.cfm?trackID=31

Ranges determined from ME (n=27),NJ (n=114),NY (n=74) and PA (n=40): Ni 8.4-41.2, Cu 11-64.8,Zn 29.2-83.8, Cd 0.09-0.173 and Pb 12.6-19.6.

risk assessments, and exposure is assessed differently for terrestrial pathways. However, those same concentrations in soils, when deposited into aquatic systems can cause a different response to aquatic organisms. In some instances, studies indicate aquatic organisms are more sensitive to certain compounds in sediments, when the same level in soils would not elicit a response in terrestrial organisms.

For metals, it must be recognized that they naturally occur in the earth's crust and represent non-anthropogenic background levels. Listed in Table 1 are typical background soil metal concentrations reported for the earth's crust and in the footnote values for the Northeastern states. The footnote values represent the range of these metals from samples collected throughout the Northeast. The values in this table allow for a quick reference benchmark for comparison to soil samples collected at a park site. It should be emphasized that these are just general numbers and regional background levels should be consulted if park land values appear to be elevated. Background levels can be directly compared to samples to determine if the samples are significantly higher, and could indicate a local source. The actual concentrations would then have to be examined to see if the levels are at a toxic threshold level or higher, and determine what actions might be taken. Another approach to obtain reference background soil data is to use the Natural Resource Conservation Service's County Soils Publication and Maps to identify similar soil type in an unaltered location and collect a reference sample from this location.

2.1.3 Surface Water

Surface waters receive anthropogenic (man-made) inputs from atmospheric deposition, non-point source runoff from terrestrial sources (petroleum products from automobiles, road salt, etc.), and point source discharges (sewage treatment plants, industrial discharge, landfill leachate, etc.). There are also natural sources of contaminants such as the earth's crust and natural processes (petroleum seeps, volcanism) that release compounds and metals into water and into the atmosphere. Transport in water can occur either by being in solution or in suspension as a micelle, an electrically charged particle formed by an aggregate of molecule, or associated with particulate matter. Compounds and metals can absorb onto particulate matter in suspension and some of these contaminant-enriched particles will eventually settle out in bottom sediment. In rivers, pollutants can be transported over great distances where they can enter into estuaries and ultimately the oceans. Contaminants associated with eroding soil can be a major source of chemicals entering into surface waters. Release of pollutants into moving surface water is followed by dilution and in some cases degradation. The point of entrance will normally represent the area where the highest concentration is observed, followed by a concentration gradient downstream. The stream flow and physical characteristics may result in depositional areas that should be sampled. In some instances, such as sewage outfalls, there may be a change in the biota upstream from the outfall when compared to biota present downstream from the outfall. The difference from upstream to downstream biota may reflect a contaminant or physico-chemical parameters that impact the biota. In the case of small lakes and ponds, where there is no major outlet, chemicals may buildup in these waters. It is also important to understand that freshwater and saltwater organisms may respond differently to the same compound, and because of this the no observed adverse effect levels (NOAELs) are often different. The surface waters and the associated particulate fractions are sinks for accumulating contaminants as they move

from upland into estuaries and into the oceans. Surface waters can be contaminated from many different sources resulting in many anthropogenic compounds being present.

2.1.4 Sediment

Sediment can be either suspended in the water column and or deposited along the bottoms of rivers, estuaries, and depositional areas in the ocean. Sediment originates from the contribution of soil washing into the surface waters and from breakdown of organic matter in the receiving waters. Sediment can become contaminated from land sources, as well as from contaminants that accumulate in organisms and adhere to the sediment from the water column. The physical and chemical characteristics of the sediment will influence the amount of contamination associated with it. Sediments with high organic content and charge will have elevated levels of organic and metals, respectively. The smaller the particle size the greater the surface area to volume ratio and the higher the contaminant enrichment. Therefore, sediments with large grain size containing mainly sand will have little or no metals or organic contaminants associated with them. Sediment particle size also influences contaminant bioavailability. Bioavailability can be reduced in clay and silt sediments compared to coarser sediments. Thus, when conducting sediment analyses, it is important to evaluate both grain size and total organic carbon (TOC).

2.1.5 Groundwater

Groundwater is water located below the surface of the soil and can be found in soil pores (sometimes called pore water) or fractures in the geological deposited soils. An aquifer is a saturated zone where usable quantities of water can be withdrawn. Groundwater is recharged from rainwater leaching into the subsurface areas. Groundwater, unlike surface water, flows very slowly and discharges into seeps or springs that feed into surface waters, sometimes over decades. Therefore, contamination that reached the aquifer decades ago may only now be discharged into rivers and springs. In any one area, there can be several aquifers that are confined to different depths by geological formations. Generally, the shallow aquifers are at greatest risk of contamination. Contamination of groundwater can occur from pollutants seeping into the soil and leaching into the groundwater. Contamination can flow from septic fields, underground storage tanks, direct injection into deep wells, or leaching from surface soil applications. The rate at which a contaminant leaches into an aquifer is determined by the soil characteristics. A general rule is that sandy soil allows for easier penetration of contaminants than higher organic containing soils. Aquifers that are below bedrock areas can become contaminated through cracks and fissures in the rock or contamination on abandoned wells. Contaminants entering the groundwater can include metals, volatile organic compounds, petroleum products, and leachable pesticides. Once contamination of an aquifer occurs it is very difficult to remediate the contaminants. Degradation and mineralization of contaminants in aquifers occurs very slowly because of the lack of bacteria, light, and oxygen tension. Because of the slow recharge of aquifers, dilution of the contamination is minimal. Movement within the aquifer is determined in part by the polarity of the compound.

3.0 Ecological Risk Assessment

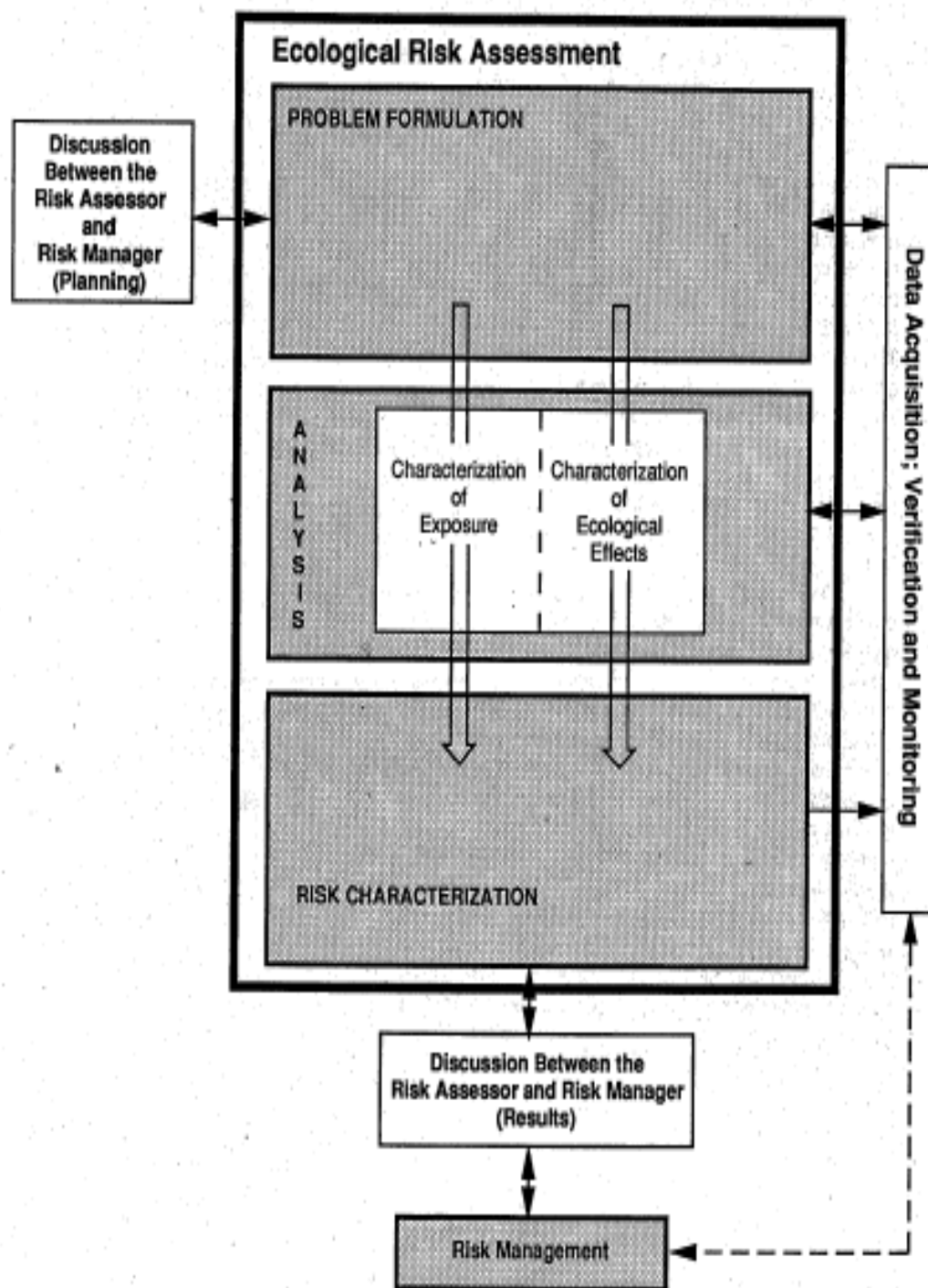
The basic underlying principle of an ecological risk assessment is based on the USEPA Guidelines for Ecological Risk Assessment (USEPA 1998). For each park it is necessary to follow a step-wise approach to evaluating potential hazards from COCs to the terrestrial and aquatic wildlife and flora. The general approach has been adopted by USEPA (1998) where there is the problem formulation where integration of available information on each park's potential COCs is carried out (Figure 3). Because each park is unique in its location and its surroundings, each require an inventory of existing threats. This can take the form of a general information questionnaire (see Appendix 2, Survey Instrument) and gathering general information about the park from literature, databases, and the internet. The analysis phase will attempt to obtain measurement for COCs (exposure analysis) or unusual abiotic conditions (stressor response profile) that exist either on or adjacent to the parks. The last phase is the risk characterization (risk estimation). The final approach is to make scientific based management recommendations that may include the following: 1) no action necessary as COCs fall below any level of concern; 2) identify specific targeted baseline sampling for historical reference for any future incident; 3) specific targeted sampling approaches for confirming elevated COCs; and 4) remediation of contaminated sites or engineering modifications to reduce impact. The amount of available information on COCs present in the biota and the different environmental matrices the parks and offsite (problem formulation and analysis phase) will affect the extent and uncertainty of the risk characterization that can be made and what management options are available. There is a need to follow up on any action that is taken to determine if the species at risk are remaining the same, increasing or decreasing. Population surveys can be a valuable long-term monitoring tool when coupled with analysis of chemical and non-chemical stressors.

3.1 Screening Level for Ecological Risk Assessment

It must be realized that a “hazard” in toxicology is determined by the risk of a compound causing an adverse effect and actual exposure to that compound ($\text{Risk} \times \text{Exposure} = \text{Hazard}$). The risk component incorporates a specified exposure dose under specific conditions. Therefore, there is no hazard if a COC has no adverse effect at a specific dose/concentration (risk component). If the organism does not come into contact with the chemical (exposure component) than there is no hazard and the compound is not a COC. In either event, there will be no adverse effect to wildlife or plants. Although there are many approaches to estimating hazards including estimating the movement through fate and transport models and food webs, those methods are beyond the scope of this appendix and project. If the concentration of a COC in an organism is greater than the environmental media (soil, water, or sediment) it is living in, then the COC is said to bioconcentrate. When the organisms COC burden is from both environmental media and food intake, then the COC is said to bioaccumulate. Biomagnification of a COC occurs when each trophic level in the food web has a higher amount of COC than the trophic level below (Newman and Unger. 2003).

Bioconcentration (BCF) and bioaccumulation (BAF) factors are two parameters that are important in both terrestrial and aquatic organisms for assessing the hazard based on steady state

Figure 3. Proposed Guidelines for Ecological Risk Assessment.



(USEPA 1992, 1997a)

body burden. The steady state tissue concentrations represent the maximum levels that are expected based on a particular level of exposure. The steady state level is achieved by the accumulation, distribution, metabolism, and elimination of a compound within an organism (Figure 2).

$$BCF = \text{concentration in organism} / \text{concentration in ambient medium} \quad \text{Eq. 1}$$

$$BAF = \text{concentration in organism} / \text{concentration in food and external media} \quad \text{Eq.2}$$
$$X(\text{ingested prey/water/soil/sediment})$$

In aquatic ecosystems where the main route of exposure is through the water column, the BCF is an appropriate means to estimate body burdens. If food, abiotic, media and ambient water concentrations are important exposure routes then Eq 2 should be used to calculate the BAF. In the case of terrestrial organisms, BCFs and BAFs can also be calculated. Although not dealt with in this report, atmospheric exposure to terrestrial wildlife can result in a steady state BCF from airborne exposure. In the majority of cases, the BAF (Eq 2) is the appropriate value to be calculated for terrestrial wildlife.

Most wildlife do not remain on a contaminated site or consume only contaminated food, which would result in an area use factor (AUF) of less than one. In order to be conservative, an AUF equal to one is used for all calculations. An AUF of one assumes that the organism ingests contaminated food or water for their entire life. While this assumption simplifies the assessment, due to the mobility and the diverse diets of most wildlife it is likely to overestimate the actual exposure experienced. It should be remembered, however, that the purpose of the screening assessment is to identify potential risks and data gaps to be filled. As more data are collected these assumptions can be modified to reflect the actual amount of time that a species spends within a specified area or park.

Our analysis involved an evaluation of the ecological risks of environmental contaminants based on a two-tiered approach. This approach follows closely with that reported by Sample (1996). In the hazard quotient (HQ) approach discussed below, the concentrations of the contaminants in the environments are compared to the NOAEL. These screening ecotoxicity values are based on literature surveys for values that have been reported to cause no adverse effect NOAEL or the LOAEL in different media.

The second approach incorporates the exposure of oral ingestion of contaminated media to reach a dose. This approach gives a benchmark that is either exceeded or not, based on known adverse effects in organisms compared to their determined dose. This approach is simple yet allows new information to be incorporated as new studies are carried out that better define the NOAEL or LOAEL values (Crane and Newman 2000). When these values are less than the toxicological benchmarks, the contaminant should be excluded from any further consideration. This process assumes there are no contributions from other compounds to increase the mixture toxicity.

3.2 Hazard Quotient Approach (HQ)

Ecological risks of environmental contaminants at the parks and evaluated with a two-tiered process. This approach follows closely that proposed by Sutter (1996). In the first tier, a screening assessment is performed where concentrations of contaminants in the environment are compared to NOAEL-based toxicological benchmarks. These benchmarks represent concentrations of chemicals (i.e., concentrations presumed to be non-hazardous to the biota) in environmental media (water, sediment, soil, food, etc.) that should not result in an adverse effect. One of the principal sources for the values that are used for this calculation is the NOAA Screening Quick Reference Tables (SQuiRT), which are available online at http://www.response.restoration.noaa.gov/book_shelf/122_squirt_cards.pdf for reference. If site-specific values or more recent literature-based information is available then these values can be used for screening purposes. Within the NOAA SQiRT tables are background levels for inorganic and organic compounds in freshwater and marine sediments, fresh and saline surface water and groundwater. These tables also give different effect levels: threshold effects levels (TEL), probable effects level (PEL), and effect range medium (ERM). The NOAA document also contains two tables summarizing specific extraction and detection methods for inorganic trace elements and organic compounds and a summary table listing appropriate containers for each analyte, preservation methods, maximum holding times, and required sample size.

In practice, when contaminant concentrations in food, water, soil, and sediment resources are less than the threshold toxicological benchmarks, the contaminants may be excluded from further consideration. As stated above, this assumes no additive or synergistic effects from similar contaminants. The PEL and ERM values allow for comparison to the increasing likelihood of an effect on the biota. In the case of sediment values, the levels are provided both for freshwater and marine sediments for inorganic and organic compounds sampled by NOAA. Another source for freshwater sediment screening values is MacDonald et al. (2000). To determine which contaminants pose a risk, an HQ is calculated, where $HQ = \text{media concentration} / \text{benchmark}$. If the $HQ \geq 1$, contaminant concentrations are sufficiently high that they may produce adverse effects. This basically means that the concentration observed in the environment is greater than or equal to a threshold or known effects level (i.e., PEL or ERM) and there is an increased likelihood that the compound may have an adverse effect on the organism and warrant further investigation. An $HQ < 1$ means there is no risk based on the laboratory derived values.

EXAMPLE CALCULATION: Values in ppb (ug/Kg) dry weight.

	Threshold Effects Level (TEL)	Probable Effects Level (PEL)	Effects Range Medium (ERM)	Source
Arsenic	7,240	41,600	70,000	NOAA SQUIRT
Arsenic sample value sediment 40,000 ppb	$40,000/7240 = 5.5$ TEL HQ > 1	$40000/41600=0.96$ PEL HQ < 1	$40000/70000=0.57$ ERM HQ < 1	

In this example arsenic would be considered a chemical of concern since it was above the TEL value. If the PEL and ERM had $HQ > 1$ the detected concentration would indicate a probability of increasing toxic responses to benthic organisms. Scientific judgment needs to be exercised when multiple compounds of similar mechanisms of toxicity may be present in a sample or another factor may result in greater sensitivity of the organism to a contaminant.

Therefore, if the concentration of a contaminant exceeds a benchmark, $HQ \geq 1$ that contaminant should be retained as a COC. Conversely, if the $HQ < 1$, the contaminant would not be retained as a COC.

3.3 Estimating Body Burdens for Comparison to NOAELs for Wildlife

Calculations can be made to determine on a daily basis the amount of a contaminant that an organism is being exposed to from its food, water or other ingestion exposure routes (e.g., sediment or soil). In this approach, both inhalation exposure and dermal adsorption are not included in the daily intake which can underestimate exposure, but normally the conservative assumptions made in estimating the other major exposure routes may negate the need to be concerned with other routes of exposure. Dermal exposure needs to be included when amphibians and reptiles are the organisms of concern. The daily exposure estimations based on known or estimated levels of a contaminant can be calculated using standard calculations and based on literature-derived life history data.

The total body burden can then be compared to LOAELs from literature studies or estimated from other reported endpoints (LOAEL, or a dose resulting in 50% death (LD_{50})). One approach to estimate a LOAEL from a NOAEL is to apply an uncertainty factor of 10 to the values.

$$LOAEL = NOAEL \text{ multiplied by an uncertainty factor of } 10 \quad \text{Eq.3}$$

In the case where there is only LD_{50} data, either examine the slope of the line and extrapolate to the x-axis, or apply a larger uncertainty factor (100 or 1000) to estimate the total body burden. The difficulty with extrapolating from these values is that the degree of uncertainty is greatly increased, but if no other value exists it may be the only alternative to estimate whether a contaminant potentially poses a risk.

The presentation of toxicity data on an mg/kg body weight (BW)/day basis allows comparisons to the calculated levels for a particular species of interest. If the levels that are calculated exceed the LOAEL then the levels in these matrices would pose a hazard to that particular species, and be considered a COC. When calculating these values care must be taken to convert any dry weight concentrations to wet weight by applying the appropriate water content values for specific prey species (see Table 6) or the value determined by the analytical laboratory at the time of analysis.

4.0 Trophic Level Evaluation

Trophic level evaluation is not required for all compounds, because there are certain characteristics which preclude biomagnification up the food web. Compounds that are rapidly metabolized, poorly absorbed from the gastrointestinal track or epidermis, or rapidly eliminated generally need not be examined in a trophic model. In these cases, the compound can be compared to the LOAEL for determining if the concentrations are above a threshold of concern (as described in the previous section). In the case of trophic level evaluations, the organism impacted is studied through direct contact with environmental matrixes and through their food sources (bioaccumulation). Therefore, when calculating the daily intake of a compound, the sources of the contaminants include water, sediment/soil, and food. Airborne exposure is not included in these calculations. In this way, representative organisms at different trophic levels can be selected, and their daily intake calculated and compared to effects levels. By using this approach, the total daily intake can be calculated using both empirical data from organisms collected on or offsite, or through estimated prey body burdens or matrix values. When the total daily intake of a compound (TDI) from all the sources is calculated, these values can be compared to the LOAEL value derived from the literature. When the TDI exceeds this benchmark effects value, the compound should be considered a COC. This is a highly conservative approach because it assumes that all of the food consumed is contaminated at a set level and that there is 100% uptake and retention. In the real world, it is unlikely that an organism will be exposed continuously to contaminated sediment/soil and prey at a constant level; there is never 100% uptake due to metabolism and elimination pathways. This conservative approach will help protect wildlife especially when tissue dose data for specific organisms is lacking.

In some instances where there are virtually no data on a chemical, the approach undertaken may have to be very simplistic. The aquatic food chain multiplier (FCM) described below is such an approach. If a large amount of data is available on empirical matrix values (i.e., water, sediment, or soil contaminant concentrations) and lower trophic level prey dose, then a better estimate of the predator dose can be calculated using the estimated dose from all source inputs. Because of the complexity of food webs even in the simplest of ecosystems, there is a need to select sentinel organisms that can represent large classes of organisms and reflect the ecosystems being evaluated when evaluating compounds that have a potential to bioaccumulate.

4.1 Estimating Aquatic Organisms' Body Burdens

If the BCF is not available for a specific compound then the following relationship developed by Lyman et al. (1982) can be used based on the octanol-water partitioning equation (P_{oct} is the partitioning coefficient for octanol-water).

$$\log_{10} BCF = 0.76 \log_{10} P_{oct} - 0.23 \quad \text{Eq. 4}$$

In a similar fashion the BCF can be calculated from the water solubility of a compound as reported by Lyman et al. (1982).

$$\text{Log}_{10} \text{BCF} = 2.791 - 0.564 \text{Log}_{10} \text{Water Solubility (mg/L)}$$

Eq. 5

Equation 4 and 5 will estimate BCF values, but tissue and matrix concentrations are more accurate for empirical BCF determinations.

4.2. Aquatic Food Chain Multiplier (FCM)

The FCM is a very simplistic approach where the concentration in a matrix is used to estimate the level in biota at different trophic levels. This approach does not differentiate between a BCF and a BAF. The differences between a BCF and BAF have been previously discussed (Screening Level for Ecological Risk Assessment).

To estimate the tissue concentration in different trophic levels the only information needed is the $\text{Log}_{10} K_{ow}$ for a chemical of interest (Sample et al. 1996). Although the FCM is a very simple approach, it is based on the assumption that the primary uptake route of these compounds is through passive diffusion, which is controlled by the lipophilicity of the compound. It is a conservative estimate since it assumes 100% uptake and does not take into account factors affecting absorption, metabolism or elimination for different species. Estimates can be made for concentrations in zooplankton (trophic level 2), small fish (trophic level 3), and piscivorous fish and top predators (trophic level 4). Table 2 shows the multipliers for estimating the amount of a compound that will accumulate in each of the higher trophic level organisms based on the $\text{Log}_{10} K_{ow}$. The FCM approach may be applicable for some metals if the organo-metallic forms (i.e., methylmercury) are known to be biomagnified in higher trophic levels based on $\text{Log}_{10} K_{ow}$ (USEPA 1995).

Table 1, located in Appendix 2, is a compilation of the $\text{Log}_{10} K_{ow}$ values and calculated concentration factors for each trophic level for the compounds that are routinely analyzed for by NOAA and USEPA. The FCM approach is useful when there is a new compound that is identified and there is very little data on levels in higher trophic level organisms. By obtaining the $\text{Log}_{10} K_{ow}$ from the literature or even doing a simple partitioning experiment one can obtain this value. It must be realized that depending on the method from which it was derived there can be differences in the actual K_{ow} values; however, they are generally similar. This value is then used to determine what multipliers (Table 2) are to be used for each trophic level. This is an approach that does not take into consideration any elimination pathways, and will overestimate tissue levels when metabolism does play a major role. The estimated FCM tissue value can then be compared to the LOAEL value determined from literature values.

For example, if a new compound has a $\text{Log}_{10} K_{ow}=6.0$ (see Table 2 for multipliers for each trophic level) and is detected at 10 mg/L in water, then it is assumed that zooplankton (level 2) will have 10 mg/kg body levels (1 x 10 mg/kg since one liter equals one kilogram). Trophic level 3 organisms would have 105.56 mg/kg and level 4 would have 159.96 mg/kg. Based on the estimated total dose these values can then be compared to LOAEL and or NOAEL values for representative species.

If for some reason there is no known K_{ow} , then an alternative would be to find a compound with a

Table 2. Aquatic Food Chain Multipliers (Taken from Sample et al., 1997 which was modified from EPA 1993).

Trophic level 2=zooplankton;

Trophic level 3=small fish;

Trophic level 4=piscivorous fish, including top predators.

Log K _{ow}	Prey Trophic Level 2	Prey Trophic Level 3	Prey Trophic Level 4
2.0	1	1.005	1.000
2.5	1	1.010	1.002
3.0	1	1.028	1.007
3.1	1	1.034	1.007
3.2	1	1.042	1.009
3.3	1	1.053	1.012
3.4	1	1.067	1.014
3.5	1	1.083	1.019
3.6	1	1.103	1.023
3.7	1	1.128	1.033
3.8	1	1.161	1.042
3.9	1	1.202	1.054
4.0	1	1.253	1.072
4.1	1	1.315	1.096
4.2	1	1.380	1.130
4.3	1	1.491	1.178
4.4	1	1.614	1.242
4.5	1	1.766	1.334
4.6	1	1.950	1.459
4.7	1	2.175	1.633
4.8	1	2.452	1.871
4.9	1	2.780	2.193
5.0	1	3.181	2.612
5.1	1	3.643	3.162
5.2	1	4.188	3.873
5.3	1	4.803	4.742
5.4	1	5.502	5.821
5.5	1	6.266	7.079
5.6	1	7.096	8.551
5.7	1	7.962	10.209
5.8	1	8.841	12.050
5.9	1	9.716	13.964
6.0	1	10.556	15.996
6.1	1	11.337	17.783
6.2	1	12.064	19.907
6.3	1	12.691	21.677

Table 2. Aquatic Food Chain Multipliers (Taken from Sample et al., 1997 which was modified from EPA 1993) (continued).

Trophic level 2=zooplankton;

Trophic level 3=small fish;

Trophic level 4=piscivorous fish, including top predators.

Log K _{ow}	Prey Trophic Level 2	Prey Trophic Level 3	Prey Trophic Level 4
6.4	1	13.228	23.281
6.5	1	13.662	24.604
6.6	1	13.980	25.645
6.7	1	14.223	26.363
6.8	1	14.355	26.669
6.9	1	14.388	26.669
7.0	1	14.305	26.242
7.1	1	14.142	25.468
7.2	1	13.852	24.322
7.3	1	13.474	22.856
7.4	1	12.987	21.038
7.5	1	21.517	18.967
7.6	1	11.708	16.749
7.7	1	10.914	14.388
7.8	1	10.069	12.050
7.9	1	9.162	9.840
8.0	1	8.222	7.798
8.1	1	7.278	6.012
8.2	1	6.361	4.519
8.3	1	5.489	3.311
8.4	1	4.683	2.371
8.5	1	3.949	1.663
8.6	1	3.296	1.146
8.7	1	2.732	0.778
8.8	1	2.246	0.521
8.9	1	1.837	0.345
9.0	1	1.493	0.226

similar structure and use that compound's K_{ow} for the estimation. These estimates can also be used for calculating levels in higher trophic level organism as described. It is important to realize that the more assumptions that are made, the less reliable the calculated body burdens. That is why it is critical to not rely solely on these estimates without empirically determined tissue levels from field samples.

Table 3 shows examples of calculated values for chemical BAF values for trophic level 3 and 4 organisms. These calculations are based on Eq. 4 and the FCM values presented in Table 2. The full list of compounds sampled by NOAA and USEPA are presented in Appendix 2, Table 1.

As shown in Table 3, acetone would not be expected to bioaccumulate into higher trophic levels. Both aldrin and benzo(a)pyrene would be assumed to accumulate into the higher trophic level organisms. This model assumes that for most trace metals that there is no bioaccumulation in higher trophic levels. Care should be exercised when there is evidence for specific metal bioaccumulation from prey species or where the metal may not be bioavailable such as with Cd (DiToro et al. 1992). In the case of organo-metals, there can be bioaccumulation in higher organisms, as seen with methyl mercury (USEPA 1997b). Selenium is also accumulated due to its similarity to calcium and using transporters and sequestration areas within the cell (Peterson and Nebeker 1992). Using this method, the calculation of tissue concentrations can be used in estimating body burdens in these trophic level organisms for comparison to LOAELs to calculate a HQ. These values can also be used to estimate concentrations in prey species for terrestrial mammals and piscivorous birds.

4.3 Terrestrial Organisms (Wildlife and Plants)

Wildlife is exposed to contaminants through the ingestion of food, the drinking of water, the breathing of air, and direct contact with the skin. In the evaluations being carried out for this project, both dermal absorption and inhalation will not be considered as major exposure pathways of terrestrial organisms to metals or organic compounds. Therefore, the major routes of exposure are through the oral route, which would include food, water, and ingested soil and sediment (Table 4). All values are expressed in terms of a body weight-normalized daily dose or mg/kg body weight per day (mg/kgBW/d). An estimated food intake rate (FIR) would be calculated as shown below.

$$FIR = \frac{(C_f \times IR) + (C_w \times IR) + (C_s \times IR)}{BW} \quad Eq.6$$

FIR = food intake rate - estimated (mg/kg/d)

C_f = concentration in food -wet weight basis (mg/kg)

C_w = concentration in water (mg/L)

C_s = concentration in soil or sediment (mg/kg)

IR = ingestion rate (kg/d)

BW = body weight (kg)

Table 3. Selected Compounds for Determining Trophic Level BAFs.

Chemical	Log ₁₀ K _{ow}	BCF ¹	Trophic Level 3 ² FCM	Trophic Level 3 BAF	Trophic Level 4 FCM	Trophic Level 4 BAF
Acetone	-0.24	0.39	1	0.39	1	0.39
Aldrin	6.5	51286.14	13.66	7000000 ⁵	24.604	13000000 ⁵
Benzo(a)pyrene	6.11	25917.91	11.34	294000 ⁵	17.783	461000 ⁵
Mercury (Methyl Mercury) ³				27900.00		140000.00
Selenium ⁴				2600.00		6800.00

1. BCF calculated using Eq. 4.
2. Level 3=small fish, Level 4=piscivorous fish, including top predators.
3. Literature citation EPA 1995.
4. Peterson and Nebeker 1992.
5. Rounded off values

Table 4. Reference Values for Representative Terrestrial Mammalian Species.

Species	Body Weight (kg)	Food Intake (kg/day)	Water Intake (L/day)	Soil Consumption Rate (kg/day)
White-footed mouse	0.022	0.0034	0.0066	0.000068
Eastern cottontail	1.2	0.237	0.116	0.015
Mink	1.0	0.137	0.099	Negligible
Red fox	4.5	0.45	0.38	0.0126
Whitetail deer	56.5	1.74	3.7	0.0348

(Modified from Sample et al. 1996)

Because wildlife does not consume dry food, these estimates must be adjusted to account for the water content of food. Water content of selected wildlife foods are given in the Wildlife Exposures Factors Handbook (USEPA 1993), and in Table 5. This adjustment is important because most analytical data generated today are on a dry-weight basis. Therefore, the concentrations used for the calculations must be decreased by the percentage of water content. When calculating the food that is consumed it must be realized that most organisms consume a variety of organisms and plant species, and this will affect their estimated daily intake. It is unlikely that there will be data on each of these food types, but when estimating the daily intake, assumptions will have to be made based on best available data. This also would indicate data gaps that if resolved would be helpful in estimating exposure and whether the tissue does approach levels of concern.

Water consumption rates are available for some species of mammalian wildlife (Table 5). Water ingestion in the equation is included when water is a route of exposure for a primary contaminant of concern. Since this is a conservative approach, if a range of data is available, either use the highest value observed or use a mean for the values.

For the terrestrial environment, the animals that were selected are listed in Table 6 and their food sources in Table 6-8. Sample et al. (1996) list data for a much larger number of animals than are presented in this appendix. The terrestrial mammals selected for discussion in this report were selected on the basis that they are commonly present at the parks and represent species that are exposed to compounds through different routes: white-footed mouse (*Peromyscus leucopus*), Eastern cottontail (*Sylvilagus floridanus*), mink (*Mustela vison*), red fox (*Vulpes vulpes*), and white-tailed deer (*Odocoiles virginianus*).

The food intake rates in Table 4 are based on dry weight and must be converted to a wet weight basis. The amount of water present in various classes of organisms was modified from Sample (1994) and represent averages within a group. In order to simplify the calculation, a single recommended value is shown in Table 5 along with the range of reported values.

EXAMPLE CALCULATION: For example if the mink consumed 0.137 kg/day (Table 4) of aquatic invertebrates then the wet weight value would be 0.685 kg/day. The dry mass equals one fifth of the total weight (wet weight consumed=0.137 kg x 5) Table 6. The same approach is used when multiple species comprise the diet of the animal of interest and requires that the total diet be proportioned to the type of prey consumed and corrected for water content.

Prey (0.137 kg/day) [Table 4]	Mink Diet [Table 6]	Water Content [Table 5]	Dry Wt (kg/day)	Wet Wt kg/day
Mammals	46%	68%	0.063	0.197
Fish & Invertebrates	31%	75% (70-80%)	0.042	0.168
Amphibians	13%	85%	0.018	0.120
Birds	10%	68%	0.014	0.044
Total	100%	-----	0.137	0.529

Table 5. Estimated Water Content for Various Types of Food Types. Recommended values were based on professional judgment and values reported by sample (1994).

Food Type	Recommended Water Content (%)	Ranges (%)
Aquatic invertebrates	80	71-87
Aquatic vertebrates	70	68-75
Aquatic plants	85	84-87
Terrestrial invertebrates	70	61-84
Mammals	68	NR
Birds	68	67-68
Reptiles	66	NR
Amphibians	85	NR
Terrestrial plants leaves	80	70-88
Terrestrial seeds/dry grass	9	7-10

NR = not reported

Table 6. Diet Composition of Representative Terrestrial Mammals Likely to be Encountered at Park Locations.

Species	Diet Composition	Percentage (%)
White-footed mouse	Seeds, fruit, vegetation	34-67
	Arthropods	30-57
Eastern cottontail	Herbaceous plants	100
Mink	Mammals	46
	Fish & invertebrates	31
	Amphibians	13
	Birds	10
Red fox	Mammals	70
	Birds	12
	Plants	10
	Insects	1
	Msc.	remainder
White-tailed deer	Herbaceous plants	100

Table 7. Avian Species That Are Recommended for Estimating Exposure Concentrations.

Species	Body weight (kg)	Food Intake (kg/day)	Water Intake (L/day)	Soil/Sediment Consumption (kg/day)
American robin	0.077	0.093	0.0106	0.0019
American woodcock	0.198	0.15	0.02	0.0156
Belted kingfisher	0.148	0.075	0.016	Negligible ¹
Great blue heron	2.39	0.42	0.1058	Negligible ¹
Red-tailed hawk	1.126	0.109	0.064	Negligible ¹
Osprey	1.5	0.3	0.077	Negligible ¹

1. Piscivorous birds assumed to be negligible and red-tailed hawk consuming mammalian prey. Piscivorous birds may be exposed to entrained sediments in the prey item.

Table 8. Diet Composition of Representative Avian Species Likely to be Encountered at Park Locations.

Species	Diet Composition	Percentage (%)
American robin	Fruit (seasonal)	7-83
	Invertebrates	8-93
American woodcock	Primarily earthworms	58-98
Belted kingfisher	Cyprinids & other fish	86.6
	Crayfish	13.3
Great blue heron	Fish (Predominantly)	100
	Other invertebrates, birds, and small mammals	
Red-tailed hawk	Small mammals	78.5
	Bird	8.5
	Snake	13.0
Osprey	Fish (Predominantly)	100

If there is no food ingestion rate (IR) data available for birds or mammals, then another approach employing (Eq. 8-12) allometric regression models based on metabolic rate is used (Nagy 1987). The BW is on a kg wet or live weight basis.

$IR = 0.0687 (BW)^{0.022}$	<i>Placental mammals</i>	Eq. 7
$IR = 0.0306 (BW)^{0.564}$	<i>Rodents</i>	Eq. 8
$IR = 0.0875 (BW)^{0.727}$	<i>Herbivores</i>	Eq. 9
$IR = 0.0582 (BW)^{0.651}$	<i>Birds</i>	Eq. 10
$IR = 0.141 (BW)^{0.850}$	<i>Passerine birds</i>	Eq. 11

Because this is a screening exercise, in many instances contamination concentrations in the food is not available, and in these circumstances estimates must be generated from existing abiotic data or regional concentrations. In these cases, uptake factors can be used to estimate the values in the food or water (Eq. 2 & 4). The same can be done from organism data by back calculating to media concentrations (Eq. 2). As seen in Table 2, tissue concentrations for aquatic species can be estimated from the $\log_{10} K_{ow}$ for any compound. These estimated concentrations can be used for evaluating the daily intake by specific organisms that consume these food organisms.

In the case of the American robin, there is seasonal variation in the foods that are consumed. However, when available, the earthworm is their primary food source. For a detailed approach to estimate earthworm concentrations, refer to Appendix 2. The same is true for the American woodcock with the earthworm being a major food item. Also, in the case of the great blue heron, osprey, and belted kingfisher, an assumption that can be made is that 100% of their prey consists of trophic level 3 and 4 fish. If there are data available on the proportion of the diet from a number of different organisms, these percentages can be used to approximate the contribution of the COC by the different prey items.

4.4 Terrestrial Plant Contamination

Estimating the amount of chemical uptake and adherence to plant material is a very complicated exercise, due in part to the variety of plants and the diversity of chemicals being applied and present in the atmosphere (Appendix 2, Calculating Uptake into Terrestrial Vegetation). In the case of direct application of a chemical (e.g., pesticide), the estimated chemical concentration can be calculated and this value used as the worst case scenario for foliar concentrations. These values can be used for estimating exposure to herbivores and omnivores. If there is concern of a compound on plant material that is being consumed, then it is recommended that the plant material be sampled directly. This will allow for “site specific” determinations that will be directly applicable to the parks.

5.0 Sample Collection and Analytical Techniques

COCs can be divided into general categories that include radionuclide, inorganic, and organic compounds. Within each of these categories there are many subgroups that may have specific common characteristics. The techniques for quantification of these compounds are generally specific and have been approved by national organizations (USEPA, NOAA, ASTM) and are rigorously followed. Any specific technique will establish which analytes will be analyzed and at what detection limit. There are also specific matrix protocols because the specific matrix will change the extractability, recovery and limit of detection of the analyte (Appendix 2, Table 4). It is critical to determine which analytes are to be tested and what is the level of detection needed.

Just as important as the analytical technique (federal or state agency approved protocols) and lab selection (state and federal certified for analytic technique) is the field collection method (Table 9 & 10, Appendix 2 - General Field Sampling Guidelines). The protocols contained in Appendix 2 have been taken directly from the USEPA Emergency Response Team website and the individual SOPs are listed

<http://www.ert.org/mainContent.asp?section=Products&subsection=List>. Because many compounds are ubiquitous, it is essential that the method of collection not introduce the analyte of interest into the sample from a spurious source. Cross contamination of samples will result in artifacts due to handling and not due to the presence of a COC (Appendix 2 - Sampling Equipment Decontamination). It is important to follow the recommended decontamination procedures, highest purity of solvents and appropriate field sample controls. Another important factor is the dissimilar holding times that are acceptable for the different COCs (Table 10). If a sample is analyzed after an unacceptable holding time (determined by analytical protocol), the results are suspect because of potential loss of analyte or parent chemical alteration.

5.1 Sampling Design

The goals of the sampling design include (1) support a decision whether a contaminant level exceeds a threshold of unacceptable hazard, (2) identify the location of “hot spots” (3) characterize the nature and extent of the contamination, and (4) determine trends in contamination levels. Prior to conducting any sample collections, a full SOP for the sampling procedures, QA/QC samples, sample storage, analytical method, and data analysis (statistics and data usage) should be outlined in detail. Any deviation from the SOP should be noted in a bound sample log. All notes and information collected while sampling should be written in the log book, and signed and dated at the bottom of each page by the person entering the information. If a misstatement or an incorrect entry is entered it should be crossed out with a single line and then initialed by the person changing the entry. All entries need to be in waterproof pen. All personnel involved in the sampling protocol need to have read the protocol and understand the procedures being carried out.

The sampling design is critical to evaluate how representative a sampling strategy is to determining the extent of a given COC at any location (USEPA 2002a). Probability-based sampling involves collection of samples in a nonsystematic fashion from the entire park. Systematic sampling involves collection of samples based on a grid or a pattern, which has been

previously statistically established. If possible, the number of samples to be collected can be determined from preliminary sampling and statistics. When judgmental sampling is performed, samples are collected only from portions of the park that are most likely to be contaminated based on expert knowledge or professional judgment and from a reference site. A grid design can be used for judgmental sampling as well. This latter approach is the one that will likely be used at most parks if for no other reason than decreased number and cost of sample analysis. Under some circumstances a combination of approaches may be used. There is no absolute number of samples that is required to establish the level of a COC at any location. It is important for comparative purposes that a minimum of three discrete independent samples with a subset of duplicates be collected at the designated site location. This will allow for, at a minimum, a mean and standard deviation to be determined, as well as for a statistical analysis to be performed (Student t-test). To prevent sample loss or the influence of outlier values, it is suggested that four to six discrete samples be collected. Increased sample number size will generally reduce the influence of any one outlier; however, sample analysis may limit the number of samples (dioxin like compounds and PCBs cost ~\$1,500 per sample) that can be analyzed. For a detailed description of sampling design and statistical interpretation refer to USEPA (2002).

Collection of duplicate or split samples can be used in place of samples that may be lost or damaged. The cost of the sampling campaign is quite high and it is often cheaper to collect the duplicate samples at the time of initial sampling than having to resample the site. For this program, it is being recommended that specific sites within the park be sampled based on suspected introduction of COCs or for the protection of an important natural resource in case of a spill (judgmental sampling). In the case of a spill situation, the samples should include reference samples outside of the spill area, samples at the point of the spill, and samples along the expected concentration gradient of the spill. There is no set number of sample sites, but an adequate number of sites should be sampled to delineate the extent of the spill.

5.2 Discrete or Composite Samples

The two most common types of sample collection are either discrete grab samples or composites of samples collected over an area or a specified time period. The matrix being sampled along with the sampling design strategy will influence the type of sample collected. As the name implies grab samples are taken at a single point in time from the matrix being sampled. This is a discrete sample that will relay the concentration within the matrix at this single point in time and location. A composite sample is a mixture of numerous individual samples that are well mixed and then sampled for analysis. The rationale for using a composite sample is that there can be variability in field samples and a composite would give an averaged concentration in the matrix. A composite sample can dilute contaminant result, so it should be noted that if you have an elevated composite sample you may wish to resample with a discrete sampling design to better understand contaminant distribution. This can be achieved if individual samples that comprise the composite can be stored until it is determined whether a point estimate is needed. Chain of custody for any sample is a critical requirement when collecting any sample. It is also important to understand for different statistics are required when comparing individual discrete samples versus composite samples (Newman and Unger 2003; USEPA 2002a).

Atmospheric sampling composite samples are usually collected because of the traditionally low levels of contaminants. There are many different types of samplers from passive designed units (wet and dry samplers, semi permeable membranes) to low volume (carbon filter mini-pumps) and high volume throughput samplers (different filter materials depending on COC). Again, the specific COC will determine the material used to trap the COC or the specific type of sampler (see Appendix 2).

As with air sampling, water sampling (surface and groundwater) can be done either using a single grab type sample or a composite sampler that collects discrete samples for a designated period of time. The composite gives an average of the COC over the time period and results in an average concentration (smoothing out highs and lows). A 24 hour composite sampler is commonly used at sewage treatment or effluent sampling to establish the average concentration over a 24 hour period. Composite sampling allows for a larger volume of sample to be collected that can be used for either analytical or biological toxicity testing. General methods for collection of surface and groundwater samples are summarized in Appendix 2 Surface Water Sampling and Groundwater Well Sampling.

In the case of soil samples, vegetation is removed and surface or core samples at various depths can be obtained. Because of spatial variability of contaminants it is important to composite samples from a specific area. A recommended protocol is to use discrete sampling from a square meter and combining five sub-samples taken from the four corners and the center of the square meter. In the case of sediment sampling, three or more cores or benthic grab samples from each location should comprise the composite. One approach in a small boat using a ponar is to sample from three locations within the boat. In larger vessels and or using larger sampling devices multiple samples from the stern of the boat can be used to make a composite sample. Another advantage to the composite sample is that there is a sufficient amount to collect duplicate samples that may be used (if needed) or as QA/QC samples. Within Appendix 2 are extensive protocols for sediment and soil sampling.

Within Table 9 are summarized the analytical methods for each of the different matrices. Table 10 summarizes for each class of analytes being examined in a specific matrix the required container, preservation method and recommended holding times. Prior to any sampling campaign contact should be made to the analytical laboratory and to determine if they have any specific requirements. What are shown in Table 10 are the generally accepted parameters. To have sufficient material for laboratory “spiking” for determining recoveries (two matrix spikes and one travel blank) and precision (eight matrix spikes) additional samples should be collected at the time of sampling. Sample size can be established following discussions with the laboratory conducting the analysis. In preparation of a spill incident, containers should be onsite along with appropriate collecting devices and identified certified laboratories that can conduct the analysis.

Breaches of protocol for analytical techniques, holding times, cross contamination, individual sample identity, and integrity (chain of custody) can result in the data being suspect and unusable for general monitoring, publication and or litigation purposes. Quality Control and Quality

Assurance Work Plan must be followed for the entire project from planning of sample collection, to analysis and interpretation.

Table 9. Recommended Analytical Methods by Matrix Being Analyzed.

Analyte	Method Number	Instrument	Matrix
PAHs	8270D	GC/MS	S, SD, X
PCBs	8270D	GC/MS	S, SD, X
Total petroleum hydrocarbon	8015B 418.1	GC/MS GC/FID	S, SD, X
Pest/PCB	8080/SW-846 608	GC/MS	S, SD, X W
Oil + grease	5520A+F	IR & Fluorescence	W
Dioxins/furans	8280B 8290A	GC/MS	S, SD, X
Metals	EPA-600/CFR40	Flame AA	W
	7000B 7010		
	6010B SW-846	ICP	S, SD, X
VOA	8240/SW-846 624/CLP	GC/MS	S, SD W
Grain size	ASTM D422-63	NA	S, SD
Total organic carbon	SW 846-9060	NA	S, SD

S=soil, SD=sediment, W=water, X=tissue, NA=not applicable, VOA=volatile organic analysis

Table 10. Summary of Collection and Holding Requirements Based on Analyte and Specimen.

Analytical Parameter	Matrix ¹	Container Type & Volume ²	Preservation	Holding Times
Pest/PCB	S	8 oz glass ~500 g	4° C	7/40 days
TAL metals	S	8 oz glass ~10-100g	4° C	6 months
TAL metals	XE	8 oz glass ~10-100g	≤ 0° C	6 months
Pest/PCB	XE	8 oz glass~10-100g	≤ 0° C	7/40 days
Pest/PCB	XM	Foil/Ziploc ~500g	≤ 0° C	7/40 days
TAL metals	XM	Foil/Ziploc ~100g	≤ 0° C	6 months
Pest/PCB	SD	8 oz glass ~500g	4° C	7/40 days
TAL metals	SD	4 oz glass ~100g	4° C	6 months
Pest/PCB	XF	Foil/Ziploc ~500g	≤ 0° C	7/40 days
TAL metals	XF	Foil/Ziploc ~500g	≤ 0° C	6 months
Pest/PCB	XI	Foil/Ziploc ~100g	≤ 0° C	7/40 days
TAL metals	XI	Foil/Ziploc ~100g	≤ 0° C	6 months
Pest/PCB	W	1 L amber~1000 ml	4° C	7/40 days
TAL metals	W	1 L poly ~1000 ml	4° C	6 months
Lipids	X	Foil/Ziploc ~1-10g	NA	7 days
Grain size	S,SD	32 oz glass ~10-1000g	NA	NA
TOC	S,SD	8 oz glass ~1-10g	4° C	28 days

1. Matrix: S=soil, W=water, SD=sediment, XE=earthworm tissue, XF=forage fish, XI=invertebrate, X=animal lipids, XM=mammal
2. The container type is indicated but the amount needed is determined by the selected analytical technique and anticipated concentration level. The values listed in the table are recommendations (Dr. Brian Buckley personnel communication EOHHSI analytical Laboratory), and actual amounts should be discussed with the analytical laboratory carrying out the analysis. Actual amounts collected can affect the detection limit for the sample.

6.0 Conclusion

Appendix 1 is a primer for assessing which chemicals may pose a threat to wildlife on NPS properties, and how samples should be collected and analyzed. Appendix 1 is presented in a manner that will allow National Park personnel to become familiar with the basic principles that underlie an environmental screening approach and to determine if a chemical concentration poses any hazard to wildlife species. It cannot be emphasized enough that the approach proposed in this chapter is a simplified approach to a very complex problem. In most environmental samples there are complex mixtures of compounds that can be assessed on an individual chemical basis, but there are likely complex chemical interactions that will influence the toxicity. Although much of Appendix 1 deals with individual compounds and their effects, most environmental situations have multiple contaminants. These contaminants, although dealt with on an individual compound by compound basis in toxicology, do not preclude the possibility that chemical compounds can result in less than additive, additive, or greater than additive effects when an organism is exposed to multiple chemicals from an environmental mixture. An exception occurs when the chemicals act through a common mechanism and the literature supports an additive approach. This is the case for dioxin-like compounds, but in the majority of cases such information is not available (Van den Berg et al. 2006). The difficulty in dealing with complex mixtures is that there is no way short of testing the mixture to determine how the chemicals interact in the biological system. The reader should also appreciate that both chemical contamination and species have a spotty distribution in the environment, which can affect the establishment of baseline values. The specific examples provided allow NPS staff to see how the equations are applied to determine if a compound is above a benchmark level that could adversely impact wildlife. It is important in any assessment to understand the activities that historically or presently (offsite and onsite) introduce chemicals into the exposure pathways of plants and animals within a park area. With this information and an understanding about the critical habitats and species an assessment can be made to predict if an adverse effect may result. It is important that both the personnel conducting chemical analysis and the natural resource personnel work together to assess impacts.

Appendix 2: Hazard Quotient Approaches and Sampling Protocols (continued)

Contents

	Page
Tables	74
Figures	75
1.0 Chemicals Analyzed During Routine Sampling	76
1.1 Calculating Uptake into Terrestrial Vegetation	77
1.2 Earthworm Uptake	77
1.3 USEPA Environmental Response Team SOPs	89
1.3.1 General Field Sampling Guidelines (USEPA-ERT)	89
1.3.2 Sampling Equipment Decontamination	93
1.3.3 General Air Sampling Guidelines.....	105
1.3.4 Surface Water Sampling	122
1.3.5 Groundwater Well Sampling	129
1.3.6 Sediment Sampling	145
1.3.7 Soil Sampling	157
1.3.8 Survey Instrument	165

Tables

	Page
Table 1. Summary of Compounds Routinely Analyzed for by NOAA and USEPA and Calculated Trophic Level BAFs.	78
Table 2. Multiplication Factors for Elements Present in Soil for Estimating Plant Concentrations in the Vegetative and Non-Vegetative Portions of the Plant.	82
Table 3. Uptake Equations for Inorganic Compounds for Plants, Earthworms, and Small Mammals.	84
Table 4. Parameters Used in Calculating Earthworm BAFs for Selected Organic Compounds.	85
Table 5. Equations for Calculating Uptake into Plants, Earthworms, and Small Mammals.	87
Table 6. Soluble Contaminants and Recommended Solvent Rinse.	96

Figures

	Page
Figure 1. Contamination Reduction Zone Layout.	99
Figure 2. Decontamination Layout.	100
Figure 3. Kemmerer Bottle.	125
Figure 4. Bacon Bomb Sampler.	127
Figure 5. Dip Sampler.	128
Figure 6. Sampling Augers.	149
Figure 7. Ekman Dredge.	152
Figure 8. Ponar Dredge.	153
Figure 9. Sample Coring Device.	155
Figure 10. Sample Trier.	162

1.0 Chemicals Analyzed During Routine Sampling

One of the largest and continuous data sets that exist for bivalve mollusks can be obtained from the NOAA Status and Trends data for estuarine environments around the country. The data set goes back to 1986 and contains data for sediment and tissue values for only a few years over this period. Tissue data is available for most of the sites on a two to five year basis. The two bivalve species that are collected at these sites are the blue mussel (*Mytilus edulis*) and the Eastern oyster (*Crassostrea virginica*). Since these are filter-feeding bivalves, they will accumulate contaminants from chemicals adhering to particulates and food organisms (algae). These data can be used to make three different interpretations concerning the waters to which the bivalves are exposed. First, this data set is useful for examining temporal trends at a given site from 1986 to present for both trace metals and organic contaminants. Selecting specific sites that are in or near park locations enables a determination to be made concerning the trends in chemical concentrations in these organisms. These trends can be used as an indicator for the improvement in a specific watershed, no change in tissue levels, or an upward trend for a particular compound. A second use for these data can be the calculation of what the suspended sediment or particulate phase concentrations are for a specific compound. The assumption being made is that this calculated particulate phase value is equivalent to actual bulk sediment, which is likely a conservative assumption. This number can be compared to the sediment matrix benchmarks and a HQ derived. This is based on site specific BAF values generated when comparing the sediment to the tissue concentrations. If the estimated sediment concentration is greater than the NOAEL for sediment, then the specific compound should be considered a COC.

Site Specific BAF = Tissue Concentration / Sediment Concentration

Estimated Sediment Concentration = Tissue Concentration / Site Specific BAF

Eq. 1

Third, the tissue concentrations can be used to establish exposure from food ingestion by mammals and birds that have bivalves as a portion of their diets. These data along with that generated in other trophic level organisms can be used to estimate a higher trophic levels organism's exposure through ingestion.

The EPA has also begun a long-term monitoring program that is examining not only chemical concentrations in sediment but also in fish and crustaceans inhabiting estuarine and near shore areas along the United States. There is also a biological component that examines toxicity associated with sediment and surface water. These data are useful when attempting to establish, whether there is an impact from multiple contaminants that may be present in an environmental sample. Examining whole organism toxicity allows for the total impact of all of the bioavailable compounds to be assessed as to whether there is an impact on the organism. These responses can be sublethal and lethal responses.

Other data sets that are useful include data from state and local authorities that have conducted regional or local collections. Local industry and federal government installations also are sources of contaminant information. NPS surveys are also useful in establishing the extent and number of COCs at any one location.

1.1 Calculation Uptake into Terrestrial Vegetation

Travis and Arms (1988) reported that uptake into vegetation from soil contaminated with organic compounds can be calculated by with Eq. 13. The concentration in the plant (B_v) is inversely proportional to the square-root of the octanol-partitioning coefficient (K_{ow}).

$$\text{Log}_{10} B_v = 1.588 - 0.578 \text{Log}_{10} K_{ow} \quad \text{Eq. 2}$$

A recent reevaluation of this approach has supported the initial assumptions with several minor qualifications (Birak et al. 2001). Compounds that are readily metabolized will be overestimated in the plant material; the concentration of compounds with a $\text{Log}_{10} K_{ow}$ greater than 6.5 may be overestimated in the plants.

In the case of elements present in soil, the concentration in plants can be estimated using specific elemental transport parameters developed by Baes et al. (1984) for both the vegetative and non-vegetative portions of plants. These values were developed to estimate the amount of transfer to agricultural crops and are a good tool for estimating soil to plant uptake. The transfer coefficients were derived to represent the ratio of the elemental concentration in the plant and soil at harvest, and were broken down into vegetative portions and non-vegetative (reproductive) portions (Table 2). To calculate the concentration in the plant, multiply the transfer coefficient of the specific element by the soil dry-weight concentration. Multiplication by a factor of four for conversion from dry to wet weight should be used for non-grain or grasses. For grains and dry grasses a factor of 1.1 should be used (Table 6, Appendix 1).

Within Table 1 are derived equations for estimating uptake by plants for a number of routinely sampled metals. Derived equations for a number of organic compounds are shown in Table 2. These tables were obtained from the ECOTOX database (<http://cfpub.epa.gov/ecotox/>).

1.2 Earthworm Uptake

Earthworms (oligochaeta) are an important food source for a number of vertebrate species and may comprise the majority of their food intake. Secondary poisoning from contaminated worms has been reported (Sheppard et al. 1997). Uptake of organic compounds can be estimated based on the method of Menzie et al. (1992) as shown in the equation below.

$$UF = (Y_L)/(0.66 \times f_{oc}) \quad \text{Eq. 2}$$

UF =uptake factor

Y_L =earthworm lipid content (if not measured assume 0.84%)

f_{oc} =organic carbon content of soil

The soil organic carbon should be measured on a site by site basis. If this information is not available, estimations can be made based on the soil conservation information available from the U.S. Department of Agriculture Natural Resources Conservation Service Web Soil Survey (<http://soils.usda.gov/>).

Table 1. Summary of Compounds Routinely Analyzed for by NOAA and USEPA and Calculated Trophic Level BAFs.

Analyte	Class	Log Kow	Kow	BCF*	Trophic Level 3 FCM	Trophic Level 3 BAF	Trophic Level 4 FCM	Trophic Level 4 BAF	Carcinogen	Mutagen	Teratogen	Reference
1,2,3,4-Tetrachlorobenzene	Pesticide	4.67	4.68E+04	2.09E+03	2.175	4.54E+03	1.633	3.41E+03				5
1,6,7-Trimethylnaphthalene	PAH	4.30	2.00E+04	1.09E+03	1.491	1.63E+03	1.178	1.29E+03	X			7
1-Methylnaphthalene	PAH	3.84	6.87E+03	4.88E+02	1.161	5.67E+02	1.042	5.08E+02	X			1
1-Methylphenanthrene	PAH	5.04	1.09E+05	3.98E+03	3.181	1.27E+04	2.612	1.04E+04	X			1
2,4'-DDD	Pesticide	6.20	1.58E+06	3.03E+04	12.064	3.66E+05	19.907	6.04E+05	X			1
2,4'-DDE	Pesticide	7.00	1.00E+07	1.23E+05	14.305	1.76E+06	26.242	3.23E+06	X			1
2,4'-DDT	Pesticide	6.19	1.55E+06	2.98E+04	12.064	3.60E+05	19.907	5.93E+05	X	X		1
2,6-Dimethylnaphthalene	PAH	4.37	2.36E+04	1.23E+03	1.614	1.99E+03	1.242	1.53E+03	X			1
2-Methylnaphthalene	PAH	3.86	7.19E+03	5.05E+02	1.202	6.07E+02	1.054	5.33E+02	X			1
4,4'-DDD	Pesticide	6.20	1.58E+06	3.03E+04	12.064	3.66E+05	19.907	6.04E+05	X			1
4,4'-DDE	Pesticide	7.00	1.00E+07	1.23E+05	14.305	1.76E+06	26.424	3.25E+06	X			1
4,4'-DDT	Pesticide	6.19	1.55E+06	2.98E+04	12.064	3.60E+05	19.907	5.93E+05	X	X		1
Acenaphthene	PAH	4.01	1.03E+04	6.57E+02	1.253	8.23E+02	1.072	7.04E+02	X			1
Acenaphthylene	PAH	3.22	1.67E+03	1.65E+02	1.042	1.72E+02	1.009	1.66E+02	X			1
Aldrin	Pesticide	5.66	4.57E+05	1.18E+04	7.962	9.39E+04	10.209	1.20E+05	X			1
Alpha-Chlordane	Pesticide	6.00	1.00E+06	2.14E+04	10.556	2.26E+05	15.996	3.42E+05	X			6
Alpha-Hexachlorocyclohexane	Pesticide	3.80	6.31E+03	4.45E+02	1.161	5.17E+02	1.042	4.64E+02	X			8
Aluminum	Metal	NA	NA	NA	NA	NA	NA	NA				2
Anthracene	PAH	4.53	3.42E+04	1.63E+03	1.766	2.88E+03	1.334	2.18E+03	X			1
Antimony	Metal	NA	NA	NA	NA	NA	NA	NA				2
Arsenic	Metal	NA	NA	NA	NA	NA	NA	NA	X			2
Benz[a]anthracene	PAH	5.67	4.71E+05	1.20E+04	7.962	9.55E+04	10.209	1.23E+05	X			1
Benzo[a]pyrene	PAH	6.11	1.28E+06	2.59E+04	11.337	2.94E+05	17.783	4.61E+05	X			1
Benzo[b]fluoranthene	PAH	6.27	1.85E+06	3.43E+04	12.691	4.35E+05	21.677	7.43E+05	X			1
Benzo[e]pyrene	PAH	6.14	1.36E+06	2.71E+04	11.337	3.07E+05	17.783	4.82E+05	X			1
Benzo[g,h,i]perylene	PAH	6.51	3.21E+06	5.22E+04	13.662	7.13E+05	24.604	1.28E+06	X			1
Benzo[k]fluoranthene	PAH	6.29	1.95E+06	3.55E+04	12.691	4.51E+05	21.677	7.70E+05	X			1
Beta-Hexachlorocyclohexane	Pesticide	3.78	6.03E+03	4.39E+02	1.161	5.10E+02	1.042	4.57E+02	X			8
Biphenyl	PAH	3.95	8.91E+03	5.92E+02	1.253	7.41E+02	1.072	6.34E+02	X			1
C1-Chrysenes	PAH	6.42	2.63E+06	4.46E+04	13.228	5.90E+05	23.281	1.04E+06	X			7
C1-Dibenzothiophenes	PAH	NA	NA	NA	NA	NA	NA	NA	X			
C1-Fluoranthenes/Pyrenes	PAH	5.29	1.94E+05	6.17E+03	4.803	2.96E+04	4.742	2.93E+04	X			1
C1-Fluorenes	PAH	4.72	5.25E+04	2.28E+03	2.175	4.95E+03	1.633	3.72E+03	X			1
C1-Naphthalenes	PAH	3.80	6.31E+03	4.55E+02	1.161	5.28E+02	1.042	4.74E+02	X			1
C1-Phenanthrenes/Anthracenes	PAH	5.04	1.10E+05	3.98E+03	3.181	1.27E+04	2.612	1.04E+04	X			1

Table 1. Summary of Compounds Routinely Analyzed for by NOAA and USEPA and Calculated Trophic Level BAFs (continued).

Analyte	Class	Log Kow	Kow	BCF*	Trophic Level 3 FCM	Trophic Level 3 BAF	Trophic Level 4 FCM	Trophic Level 4 BAF	Carcinogen	Mutagen	Teratogen	Reference
C2-Chrysenes	PAH	6.88	7.59E+06	9.97E+04	14.388	1.43E+06	26.669	2.66E+06	X			7
C2-Dibenzothiophenes	PAH	NA	NA	NA	NA	NA	NA	NA	X			
C2-Fluoranthenes/Pyrenes	PAH	5.29	1.94E+05	6.17E+03	4.803	2.96E+04	4.742	2.93E+04	X			
C2-Fluorenes	PAH	5.20	1.58E+05	5.27E+03	4.188	2.21E+04	3.873	2.04E+04	X			1
C2-Naphthalenes	PAH	4.30	2.00E+04	1.09E+03	1.491	1.63E+03	1.178	1.29E+03	X			1
C2-Phenanthrenes/Anthracenes	PAH	5.46	2.88E+05	8.31E+03	6.266	5.21E+04	7.079	5.88E+04	X			1
C3-Chrysenes	PAH	7.44	2.75E+07	2.66E+05	12.987	3.45E+06	21.038	5.59E+06	X			7
C3-Dibenzothiophenes	PAH	NA	NA	NA	NA	NA	NA	NA	X			
C3-Fluoranthenes/Pyrenes	PAH	5.29	1.94E+05	6.17E+03	4.803	2.96E+04	4.742	2.93E+04	X			
C3-Fluorenes	PAH	5.70	5.01E+05	1.26E+04	7.962	1.01E+05	10.209	1.29E+05	X			1
C3-Naphthalenes	PAH	4.80	6.31E+04	2.62E+03	2.452	6.42E+03	1.871	4.90E+03	X			1
C3-Phenanthrenes/Anthracenes	PAH	5.92	8.32E+05	1.86E+04	9.716	1.81E+05	13.964	2.60E+05	X			1
C4-Chrysenes	PAH	8.00	1.00E+08	7.08E+05	8.222	5.82E+06	7.798	5.52E+06	X			7
C4-Naphthalenes	PAH	5.30	2.00E+05	6.28E+03	4.803	3.02E+04	4.742	2.98E+04	X			1
C4-Phenanthrenes/Anthracenes	PAH	6.32	2.09E+06	3.74E+04	12.691	4.75E+05	21.677	8.11E+05	X			1
Cadmium	Metal	NA	NA	NA	NA	NA	NA	NA	X			2
Chlorpyrifos	Pesticide	5.26	1.82E+05	5.86E+03	4.803	2.81E+04	4.742	2.78E+04				5
Chromium	Metal	NA	NA	NA	NA	NA	NA	NA	X			2
Chrysene	PAH	5.71	5.16E+05	1.29E+04	7.962	1.02E+05	10.209	1.31E+05	X			1
Cis-Nonachlor	Pesticide	5.70	5.01E+05	1.26E+04	7.962	1.01E+05	10.209	1.29E+05				6
Copper	Metal	NA	NA	NA	NA	NA	NA	NA				2
Delta-Hexachlorocyclohexane	Pesticide	4.14	1.38E+04	8.25E+02	1.315	1.08E+03	1.096	9.04E+02	X			8
Dibenzo[a,h]anthracene	PAH	6.71	5.16E+06	7.41E+04	14.223	1.05E+06	26.363	1.95E+06	X			1
Dibenzofuran		4.12	1.32E+04	7.97E+02	1.315	1.05E+03	1.069	8.51E+02				5
Dibenzothiophene	PAH	4.49	3.09E+04	1.52E+03	1.766	2.69E+03	1.334	2.03E+03	X			1
Dibutyltin	Organotin	NA	NA	NA	NA	NA	NA	NA				2
Dieldrin	Pesticide	5.16	1.45E+05	4.92E+03	4.188	2.06E+04	3.873	1.90E+04		X		1
Endosulfan	Pesticide	2.23	4.10E+00	2.90E+01	1.005	2.91E+01	1.000	2.90E+01				2
Endrin	Pesticide	4.56	3.63E+04	1.72E+03	1.950	3.35E+03	1.459	2.51E+03				1
Fluoranthene	PAH	5.08	1.21E+05	4.27E+03	3.643	1.56E+04	3.162	1.35E+04	X			1
Fluorene	PAH	4.21	1.61E+04	9.32E+02	1.380	1.29E+03	1.130	1.05E+03	X			1
Gamma-Chlordane	PAH	6.00	1.00E+06	2.14E+04	10.556	2.26E+05	15.996	3.42E+05	X		X	1
Gamma-Hexachlorocyclohexane	Pesticide	3.61	4.07E+03	3.26E+02	1.103	3.60E+02	1.023	3.34E+02	X			8
Heptachlor	Pesticide	5.44	2.75E+05	8.02E+03	5.502	4.41E+04	5.821	4.67E+04	X			1
Heptachlor-Epoide	Pesticide	5.40	2.51E+05	7.48E+03	5.502	4.12E+04	5.821	4.36E+04	X			1
Hexachlorobenzene	Pesticide	5.66	4.57E+05	1.18E+04	7.962	9.39E+04	10.209	1.20E+05	X	X		1
Indeno[1,2,3-c,d]pyrene	PAH	6.72	5.27E+06	7.54E+04	14.223	1.07E+06	26.363	1.99E+06	X			1
Iron	Metal	NA	NA	NA	NA	NA	NA	NA				2
Lead	Metal	NA	NA	NA	NA	NA	NA	NA	X			2
Manganese	Metal	NA	NA	NA	NA	NA	NA	NA				2
Mercury	Metal	NA	NA	NA	NA	NA	NA	NA				2
Mirex	PAH	6.89	7.76E+06	1.01E+05	14.388	1.46E+06	26.669	2.71E+06	X			1
Monobutyltin	Organotin	NA	NA	NA	NA	NA	NA	NA				2
Naphthalene	PAH	3.36	2.27E+03	2.09E+02	1.067	2.23E+02	1.014	2.12E+02	X			1
Nickel	Metal	NA	NA	NA	NA	NA	NA	NA	X			2

Table 1. Summary of Compounds Routinely Analyzed for by NOAA and USEPA and Calculated Trophic Level BAFs (continued).

Analyte	Class	Log Kow	Kow	BCF*	Trophic Level 3 FCM	Trophic Level 3 BAF	Trophic Level 4 FCM	Trophic Level 4 BAF	Carcinogen	Mutagen	Teratogen	Reference
Oxychlordane	Pesticide	2.60	3.98E+02	5.57E+01	1.028	5.73E+01	1.007	5.61E+01				6
PCB101/90	PCB	6.64	4.37E+06	6.55E+04	13.980	9.16E+05	25.645	1.68E+06	X			3
PCB105	PCB	6.91	8.13E+06	1.05E+05	14.388	1.51E+06	26.669	2.80E+06	X			3
PCB118	PCB	7.40	2.52E+07	2.48E+05	12.987	3.22E+06	21.038	5.21E+06	X			4
PCB128	PCB	7.02	1.05E+07	1.27E+05	14.305	1.82E+06	26.242	3.34E+06	X			3
PCB138	PCB	7.11	1.29E+07	1.49E+05	14.142	2.11E+06	25.468	3.80E+06	X			3
PCB153/132/168	PCB	6.86	7.24E+06	9.63E+04	14.388	1.39E+06	26.669	2.57E+06	X			3
PCB170/190	PCB	7.57	3.72E+07	3.34E+05	11.708	3.91E+06	16.749	5.59E+06	X			3
PCB18	PCB	5.60	3.98E+05	1.06E+04	7.096	7.53E+04	8.551	9.08E+04	X			4
PCB180	PCB	7.66	4.57E+07	3.90E+05	10.914	4.26E+06	14.388	5.62E+06	X			3
PCB187	PCB	7.47	2.95E+07	2.80E+05	21.517	6.03E+06	18.967	5.31E+06	X			3
PCB195/208	PCB	7.88	7.59E+07	5.74E+05	9.162	5.26E+06	9.840	5.65E+06	X			3
PCB206	PCB	7.88	7.59E+07	5.74E+05	9.162	5.26E+06	9.840	5.65E+06	X			3
PCB209	PCB	7.88	7.59E+07	5.74E+05	9.162	5.26E+06	9.840	5.65E+06	X			3
PCB28	PCB	5.89	7.76E+05	1.76E+04	9.716	1.71E+05	13.964	2.46E+05	X			3
PCB44	PCB	5.99	9.77E+05	2.10E+04	10.556	2.22E+05	15.996	3.36E+05	X			3
PCB52	PCB	6.08	1.20E+06	2.46E+04	11.337	2.79E+05	17.783	4.37E+05	X			3
PCB66	PCB	6.44	2.75E+06	4.62E+04	13.228	6.11E+05	23.281	1.07E+06	X			3
PCB8/5	PCB	5.27	1.86E+05	5.96E+03	4.803	2.86E+04	4.742	2.83E+04	X			3
Pentachloroanisole	Pesticide	NA	NA	NA	NA	NA	NA	NA	X			
Pentachlorobenzene	Pesticide	5.26	1.82E+05	5.86E+03	4.803	2.81E+04	4.742	2.78E+04	X			5
Perylene	PAH	6.14	1.36E+06	2.73E+04	11.337	3.10E+05	17.783	4.86E+05	X			1
Phenanthrene	PAH	4.57	3.72E+04	1.75E+03	1.950	3.41E+03	1.459	2.55E+03				1
Pyrene	PAH	4.92	8.36E+04	3.23E+03	2.780	8.98E+03	2.193	7.08E+03	X			1
Selenium	Metal	NA	NA	NA	NA	NA	NA	NA				2
Silicon	Metal	NA	NA	NA	NA	NA	NA	NA				2
Silver	Metal	NA	NA	NA	NA	NA	NA	NA				2
Tetrabutyltin	Organotin	NA	NA	NA	NA	NA	NA	NA				2
Tin	Metal	NA	NA	NA	NA	NA	NA	NA				2
Total butyltins	Organotin	NA	NA	NA	NA	NA	NA	NA				2
Total chlordanes	Pesticide	5.50	3.16E+05	8.91E+03	6.266	5.58E+04	7.079	6.31E+04	X		X	6
Total DDT	Pesticide	6.19	1.55E+06	2.98E+04	12.064	3.60E+05	19.907	5.93E+05	X	X		1
Total dieldrin	Pesticide	4.60	3.98E+04	1.85E+03	1.950	3.60E+03	1.459	2.69E+03		X		6,2
Total PAH	PAH	5.98	9.55E+05	2.06E+04	9.716	2.01E+05	13.964	2.88E+05	X			1
Total PAHmw (4 or more rings)	PAH	5.98	9.55E+05	2.06E+04	9.716	2.01E+05	13.964	2.88E+05	X			1
Total PAHlmw (2-3 rings)	PAH	5.98	9.55E+05	2.06E+04	9.716	2.01E+05	13.964	2.88E+05	X			1
Trans-Nonachlor	Pesticide	5.70	5.01E+05	1.26E+04	7.962	1.01E+05	10.209	1.29E+05	X			6
Tributyltin	Organotin	NA	NA	NA	NA	NA	NA	NA				2
Zinc	Metal	NA	NA	NA	NA	NA	NA	NA				2

$\log BCF = (0.76)(\log Kow) - (0.23)$

BAF = (BCF)(FCM) NA=not available

Table 1. Summary of Compounds Routinely Analyzed for by NOAA and EPA and Calculated Trophic Level BAFs (continued).

References

- Davis, J.A. 2003. The Long Term Fate of PCBs in San Francisco Bay. RMP Technical Report: SFEI Contribution 47. San Francisco Estuary Institute, Oakland, CA.
- Gobas, F. and Wilcockson, J. 2003. RMP Technical Report:SFEI Contribution 90. San Francisco Estuary Institute, Oakland, CA.
- Irwin, R.J. 1997. Environmental Contaminants Ecyclopedia Chrysene Entry. NPS Water Resources Divisions, Water Operations Branch.
- Jarvinen, A.W. and Ankley, G.T. 1999. Linkage of Effects to Tissue Residues: Development of a Comprehensive Database for Aquatic Organisms Exposed to Inorganic and Organic Chemicals. Society of Environmental Toxicology and Chemistry (SETAC).
- Karickhoff, S.W. and J.M. Long. Environmental Research Laboratory. U.S. EPA.1995. Internal Report on Summary of Measured, Calculated and Recommended Log Kow Values.
- Leatherbarrow, J.E., David, N., Greenfield, B.K., Oram, J.J., and Davis, J.A. 2006. Organochlorine Pesticide Fate in San Francisco Bay. SFEI Contribution 433. San Francisco Estuary Institute, Oakland, CA.
- Syracuse Research Corporation. CHEMFATE Chemical Search.
<http://www.syrres.com/eSc/chemfate.htm>.
- US Army Corp of Engineers. www.nae.usace.army.mil/projects/ma/blackstone/wqcg.pdf.
- Information of Carcinogenicity was obtained from the analytes MSDS at Physical and Theoretical Chemical Laboratory. University of Oxford. <http://physchem.ox.ac.uk/>.

Table 2. Multiplication Factors for Elements Present in Soil for Estimating Plant Concentrations in the Vegetative and Non-Vegetative Portions of the Plant¹.

Element	Vegetative	Non-Vegetative
Hafnium (Hf)	0.0035	0.0009
Tantalum (Ta)	0.0100	0.0025
Tungsten (W)	0.0450	0.0100
Rhenium (Re)	1.5000	0.3500
Osmium (Os)	0.0150	0.0035
Iridium (Ir)	0.0550	0.0150
Platinum (Pt)	0.0950	0.0250
Gold (Au)	0.4000	0.1000
Mercury (Hg)	0.9000	0.2000
Thallium (Tl)	0.0040	0.0004
Lead (Pb)	0.0450	0.0090
Bismuth (Bi)	0.0350	0.0050
Polonium (Po)	0.0025	0.0004
Astatine (At)	1.0000	0.1500
Francium (Fr)	0.0300	0.0300
Radium (Ra)	0.0150	0.1500
Lanthanum (La)	0.0100	0.0040
Cerium (Ce)	0.0100	0.0040
Prasiodinium (Pr)	0.0100	0.0040
Neodymium (Nd)	0.0100	0.0040
Promethium (Pm)	0.0100	0.0040
Samarium (Sm)	0.0100	0.0040
Europium (Eu)	0.0100	0.0040
Gadolinium (Gd)	0.0100	0.0040
Terbium (Tb)	0.0100	0.0040
Dysprosium (Dy)	0.0100	0.0040
Holmium (Ho)	0.0100	0.0040
Erbium (Er)	0.0100	0.0040
Thulium (Tm)	0.0100	0.0040
Ytterbium (Yb)	0.0100	0.0040
Lutetium (Lu)	0.0100	0.0040
Actinium (Ac)	0.0035	0.0004
Thorium (Th)	0.0010	0.0001
Protactinium (Pa)	0.0025	0.0003
Uranium (U)	0.0085	0.0040
Neptunium (Np)	0.1000	0.0100
Plutonium (Pu)	0.0005	0.00005
Americium (Am)	0.0055	0.0003
Curium (Cu)	0.0009	0.00002

1. Source: Baes, C.F., Sharp, R.D., Sjoeren, A.L., and Shor, R.W. (1984). A Review and Analyses of Parameters for Assessing transport of Environmentally Released Radionuclide's through Agriculture. Oakridge National Laboratory. Managed by Martin Marietta Systems, INC. for the U.S. Department of Energy.

An alternative model has been proposed by Jager (1998), which is currently being recommended by USEPA for determining the BCF in earthworms (Connell and Markwell 1990; Sample et al. 1997). The model is based on the theory that bioconcentration in earthworms is governed by thermodynamic partitioning between surrounding water and the water and lipid phases inside the organism (Eq 15). For risk assessment the equations below can be used to predict BCFs for chemicals taken up by earthworms in the $\text{Log}_{10} K_{ow}$ range of zero to eight. Tables 3-5 are based on the Jager (1998) model.

$$C_{worm} = K_{ww} \times C_w \quad \text{Eq. 3}$$

C_{worm} = concentration in worm (mg/kg dry weight)

K_{ww} = biota to soil water partitioning coefficient (L soil pore water/kg ww tissue)

C_w = concentration in soil pore water (mg/L)

Jager (1998) derived the following equations for determining K_{ww} and C_w .

$$\text{Log}_{10} (K_{ww}) = 0.87 \times \text{Log}_{10}(K_{ow}) - 2.0$$

$$C_w = C_s / K_d$$

C_s = concentration in soil (mg/kg soil)

K_d = soil to water partitioning coefficient (L soil pore water/kg dw soil)

For non-ionic organic compounds, K_d may be estimated using the following equation.

$$K_d = F_{oc} \times K_{oc}$$

F_{oc} = fraction of organic carbon in soil (kg organic carbon/kg soil)

K_{oc} = soil organic carbon to water partitioning coefficient
(volume soil pore water (L)/kg organic carbon)

We are recommending using Eq. 2 as the default if insufficient information is available. If the chemical is listed in Tables 1-3, utilize the equations to estimate tissue concentrations. Tables 1-3 were taken from the Ecological Soil Screening Levels Attachment 4-1 (2005), which is updated periodically as new information becomes available and is available through the ECOTOX database (<http://cfpub.epa.gov/ecotox/>). When sufficient data are available, and then utilize Eq. 3 to estimate the earthworm concentrations.

Table 3. Uptake Equations for Inorganic Compounds for Plants, Earthworms, and Small Mammals.

Analyte	Soil to Plants		Soil to Earthworms		Soil to Small Mammals	
	Equation	Source	Equation	Source	Equation	Source
Antimony	$\ln(C_p) = 0.938 * \ln(C_s) - 3.233$	a	$C_e = C_s$	g	$C_m = 0.001 * 50 * C_d$	f
Arsenic	$C_p = 0.03752 * C_s$	b	$\ln(C_e) = 0.706 * \ln(C_s) - 1.421$	e	$\ln(C_m) = 0.8188 * \ln(C_s) - 4.8471$	d
Barium	$C_p = 0.156 * C_s$	b	$C_e = 0.091 * C_s$	c	$C_m = 0.00015 * 50 * C_d$	f
Beryllium	$\ln(C_p) = 0.7345 * \ln(C_s) - 0.5361$	h	$C_e = 0.045 * C_s$	c	$C_m = 0.001 * 50 * C_d$	f
Cadmium	$\ln(C_p) = 0.546 * \ln(C_s) - 0.475$	b	$\ln(C_e) = 0.795 * \ln(C_s) + 2.114$	e	$\ln(C_m) = 0.4723 * \ln(C_s) - 1.2571$	d
Chromium	$C_p = 0.041 * C_s$	b	$C_e = 0.306 * C_s$	e	$\ln(C_m) = 0.7338 * \ln(C_s) - 1.4599$	d
Cobalt	$C_p = 0.0075 * C_s$	b	$C_e = 0.122 * C_s$	c	$\ln(C_m) = 1.307 * \ln(C_s) - 4.4669$	d
Copper	$\ln(C_p) = 0.394 * \ln(C_s) + 0.668$	b	$C_e = 0.515 * C_s$	e	$\ln(C_m) = 0.1444 * \ln(C_s) + 2.042$	d
Lead	$\ln(C_p) = 0.561 * \ln(C_s) - 1.328$	b	$\ln(C_e) = 0.807 * \ln(C_s) - 0.218$	e	$\ln(C_m) = 0.4422 * \ln(C_s) + 0.0761$	d
Manganese	$C_p = 0.079 * C_s$	b	$\ln(C_e) = 0.682 * \ln(C_s) - 0.809$	e	$C_m = 0.0205 * C_s$	d
Nickel	$\ln(C_p) = 0.748 * \ln(C_s) - 2.223$	b	$C_e = 1.059 * C_s$	e	$\ln(C_m) = 0.4658 * \ln(C_s) - 0.2462$	d
Selenium	$\ln(C_p) = 1.104 * \ln(C_s) - 0.677$	b	$\ln(C_e) = 0.733 * \ln(C_s) - 0.075$	e	$\ln(C_m) = 0.3764 * \ln(C_s) - 0.4158$	d
Silver	$C_p = 0.014 * C_s$	b	$C_e = 2.045 * C_s$	c	$C_m = 0.004 * C_s$	d
Vanadium	$C_p = 0.00485 * C_s$	b	$C_e = 0.042 * C_s$	c	$C_m = 0.0123 * C_s$	d
Zinc	$\ln(C_p) = 0.554 * \ln(C_s) + 1.575$	b	$\ln(C_e) = 0.328 * \ln(C_s) + 4.449$	e	$\ln(C_m) = 0.0706 * \ln(C_s) + 4.3632$	d

Source:

- a. Regression derived from measured data [Appendix A]
- b. Bechtel-Jacobs 1998
- c. Sample et al. 1998b
- d. Sample et al. 1998a
- e. Sample et al. 1999
- f. Baes et al. 1984
- g. Assumed
- h. Regression derived from measured data [Appendix A].

Abbreviations:

- C_s = Concentration in soil (mg/kg)
 - C_p = Concentration in plant tissue (mg/kg dry weight)
 - C_e = Concentration in earthworm (mg/kg dry weight)
 - C_m = Concentration in small mammal tissue (mg/kg dry weight)
 - C_d = Concentration in diet (mg/kg dry weight)
- where small mammal diet is assumed to be 100% earthworms

Table 4. Parameters Used in Calculating Earthworm BAFs for Selected Organic Compounds.

Chemical	K _{ow} : octanol to water partitioning coefficient			K _{ww} : worm to soil water partitioning coefficient			K _{oc} : water to soil organic carbon partitioning coefficient					K _d : soil to water partitioning coefficient	Soil to Earthworm BAF ⁵
	log K _{ow}	K _{ow}	Source	log K _{ww} ¹	K _{ww} (L/kg worm ww)	K _{ww} ² (L/kg worm dw)	slope	intercept	log K _{oc}	K _{oc} ³	Source	K _d ⁴ (L/kg soil dw)	
Acenaphthene	3.92	8.32E+03	EPA 1996	1.41	2.57E+01	1.61E+02	0.762	1.051	4.04	1.09E+04	estimated (a)	1.09E+02	1.47
Acenaphthylene	4.07	1.17E+04	SRC, PP	1.54	3.47E+01	2.17E+02			2.98	9.47E+02	SRC, CF	9.47E+00	22.9
Anthracene	4.55	3.55E+04	EPA 1996	1.96	9.09E+01	5.68E+02			4.37	2.35E+04	EPA 1996	2.35E+02	2.42
Benzo(a)anthracene	5.7	5.01E+05	EPA 1996	2.96	9.10E+02	5.69E+03			5.55	3.58E+05	EPA 1996	3.58E+03	1.59
Benzo(a)pyrene	6.11	1.29E+06	EPA 1996	3.32	2.07E+03	1.29E+04			5.99	9.69E+05	EPA 1996	9.69E+03	1.33
Benzo(b)fluoranthene	6.2	1.58E+06	EPA 1996	3.39	2.48E+03	1.55E+04	0.762	1.051	5.78	5.96E+05	estimated (a)	5.96E+03	2.60
Benzo(e)pyrene	6.44	2.75E+06	SRC, PP	3.60	4.01E+03	2.50E+04	0.762	1.051	5.96	9.08E+05	estimated (a)	9.08E+03	2.76
Benzo(ghi)perylene	6.7	5.01E+06	EPA 1995	3.83	6.75E+03	4.22E+04	0.762	1.051	6.16	1.43E+06	estimated (a)	1.43E+04	2.94
Benzo(k)fluoranthene	6.2	1.58E+06	EPA 1996	3.39	2.48E+03	1.55E+04	0.762	1.051	5.78	5.96E+05	estimated (a)	5.96E+03	2.60
Chrysene	5.7	5.01E+05	EPA 1996	2.96	9.10E+02	5.69E+03	0.762	1.051	5.39	2.48E+05	estimated (a)	2.48E+03	2.29
Coronene	7.64	4.37E+07	SRC, PP	4.65	4.43E+04	2.77E+05	0.762	1.051	6.87	7.46E+06	estimated (a)	7.46E+04	3.72
Dibenzo(ah)anthracene	6.69	4.90E+06	EPA 1996	3.82	6.61E+03	4.13E+04			6.25	1.79E+06	EPA 1996	1.79E+04	2.31
Fluoranthene	4.95	8.91E+04	SRC, PP	2.31	2.03E+02	1.27E+03			4.62	4.17E+04	SRC, CF	4.17E+02	3.04
Fluorene	4.18	1.51E+04	SRC, PP	1.64	4.33E+01	2.71E+02			3.45	2.83E+03	SRC, CF	2.83E+01	9.57
Indeno(123 cd)pyrene	6.584	3.84E+06	SRC, PP	3.73	5.35E+03	3.34E+04	0.762	1.051	6.07	1.17E+06	estimated (a)	1.17E+04	2.86
Naphthalene	3.36	2.29E+03	EPA 1996	0.92	8.38E+00	5.24E+01			3.08	1.19E+03	EPA 1996	1.19E+01	4.40
Phenanthrene	4.55	3.55E+04	EPA 1995	1.96	9.09E+01	5.68E+02	0.762	1.051	4.52	3.30E+04	estimated (a)	3.30E+02	1.72
Pyrene	4.88	7.59E+04	SRC, PP	2.25	1.76E+02	1.10E+03			4.80	6.27E+04	SRC, CF	6.27E+02	1.75

Table 4. Parameters Used in Calculating Earthworm BAFs for Selected Organic Compounds (continued).

¹ $\log K_{ww} = 0.87 * \log K_{ow} - 2.0$ [model from Jager, 1998]

² Converted from wet weight to dry weight assuming 16% solids (Jager, 1998)

³ Measured K_{oc} values from SRC Chem Fate Database or EPA, 1996 ($n > 2$).

If no measured K_{oc} values available, values modeled based on chemical class-specific models from Gerstl (1990).

where: $\log K_{oc} = \text{slope} * \log K_{ow} + \text{intercept}$

(a) slope and intercept for PAHs

⁴ $K_d = f_{oc} * K_{oc}$ (assumes an f_{oc} of 1% [0.01])

⁵ $BAF = K_{ww} \text{ (L/kg worm dw)} / K_d \text{ (L/kg soil dw)}$

Source Citations:

EPA (1995) = Internal report on summary of measured, calculated, and recommended Log Kow values. U.S. Environmental Protection Agency, Office of Water, Washington, D.C. 38 pp.

EPA (1996) = Soil Screening Guidance: Technical Background Document. EPA/540/R-95/128

SRC, PP = Syracuse Research Corp. Physical Properties Database. <http://esc.syrres.com/interkow/PhysProp.htm>

SRC, CF = Syracuse Research Corp. Chem Fate Database. <http://www.syrres.com/esc/chemfate.htm>

Table 5. Equations for Calculating Uptake into Plants, Earthworms, and Small Mammals.

Chemical	Soil to Plants		Soil to Earthworms		Soil to Small Mammals	
	Equation	Source	Equation	Source	Equation	Source
Non-PAHs						
Dieldrin	$C_p = 0.41 * C_s$	a	$\ln(C_e) = 0.8756 * \ln(C_d) + 2.2757$	a	$\ln(C_m) = 0.6076 * \ln(C_d) + 1.9582$	a
DDT, DDD and DDE Combined	$\ln(C_p) = 0.7524 * \ln(C_s) - 2.5119$	b	$\ln(C_e) = 0.8561 * \ln(C_d) + 2.1287$	b	$\ln(C_m) = 0.663 * \ln(C_d) + 2.3833$	b
DDT	Not Available		$\ln(C_e) = 0.8689 * \ln(C_d) + 2.1247$	b	$\ln(C_m) = 0.7254 * \ln(C_d) + 1.1788$	b
DDD	Not Available		$\ln(C_e) = 0.6975 * \ln(C_d) + 1.1613$	b	Not Available	
DDE	Not Available		$\ln(C_e) = 0.8804 * \ln(C_d) + 2.4771$	b	$\ln(C_m) = 0.641 * \ln(C_d) + 3.6401$	b
TNT	$C_p = 4.23 * C_s$	c	Not Available		$C_m = 0$	f
RDX	$C_p = 0.43 * C_s$	c	Not Available		$C_m = 0$	f
PAHs						
Acenaphthene	$\ln(C_p) = -0.8556 * \ln(C_s) - 5.562$	d	$C_e = 1.47 * C_s$	e	$C_m = 0$	f
Acenaphthylene	$\ln(C_p) = 0.791 * \ln(C_s) - 1.144$	g	$C_e = 22.9 * C_s$	e	$C_m = 0$	f
Anthracene	$\ln(C_p) = 0.7784 * \ln(C_s) - 0.9887$	d	$C_e = 2.42 * C_s$	e	$C_m = 0$	f
Benzo(a)anthracene	$\ln(C_p) = 0.5944 * \ln(C_s) - 2.7078$	d	$C_e = 1.59 * C_s$	e	$C_m = 0$	f
Benzo(a)pyrene	$\ln(C_p) = 0.9750 * \ln(C_s) - 2.0615$	d	$C_e = 1.33 * C_s$	e	$C_m = 0$	f
Benzo(b)fluoranthene	$C_p = 0.310 * C_s$	c	$C_e = 2.60 * C_s$	e	$C_m = 0$	f
Benzo(e)pyrene	$C_p = 0.19 * C_s$	c	$C_e = 2.76 * C_s$	e	$C_m = 0$	f
Benzo(ghi)perylene	$\ln(C_p) = 1.1829 * \ln(C_s) - 0.9313$	d	$C_e = 2.94 * C_s$	e	$C_m = 0$	f
Benzo(k)fluoranthene	$\ln(C_p) = 0.8595 * \ln(C_s) - 2.1579$	d	$C_e = 2.60 * C_s$	e	$C_m = 0$	f
Chrysene	$\ln(C_p) = 0.5944 * \ln(C_s) - 2.7078$	d	$C_e = 2.29 * C_s$	e	$C_m = 0$	f
Coronene	$C_p = 0.68 * C_s$	c	$C_e = 3.72 * C_s$	e	$C_m = 0$	f
Dibenz(ah)anthracene	$C_p = 0.13 * C_s$	c	$C_e = 2.31 * C_s$	e	$C_m = 0$	f
Fluoranthene	$C_p = 0.50 * C_s$	c	$C_e = 3.04 * C_s$	e	$C_m = 0$	f
Fluorene	$\ln(C_p) = -0.8556 * \ln(C_s) - 5.562$	d	$C_e = 9.57 * C_s$	e	$C_m = 0$	f
Indeno(123 cd)pyrene	$C_p = 0.11 * C_s$	c	$C_e = 2.86 * C_s$	e	$C_m = 0$	f
Naphthalene	$C_p = 12.2 * C_s$	c	$C_e = 4.40 * C_s$	e	$C_m = 0$	f
Phenanthrene	$\ln(C_p) = 0.6203 * \ln(C_s) - 0.1665$	d	$C_e = 1.72 * C_s$	e	$C_m = 0$	f
Pyrene	$C_p = 0.72 * C_s$	c	$C_e = 1.75 * C_s$	e	$C_m = 0$	f

Table 5. Equations for Calculating Uptake into Plants, Earthworms, and Small Mammals (continued).

Source:

- a. Regression derived from measured data [Appendix E].
- b. Regression derived from measured data [Appendix D].
- c. Median BAF calculated from measured data [Appendix C].
- d. Regression derived from measured data [Appendix C].
- e. Modeled from K_{ow} based on Jager (1998) [Table 5].
- f. Assumed to be negligible
- g. Modeled using the rinsed PAH-specific equation [Figure 3]

Abbreviations:

- C_s = Concentration in soil (mg/kg)
- C_p = Concentration in plant tissue (mg/kg dry weight)
- C_e = Concentration in earthworm (mg/kg dry weight)
- C_m = Concentration in small mammal or bird tissue (mg/kg dry weight)
- C_d = Concentration in diet (mg/kg dw) where diet is assumed to be 100% earthworms.

Chemical	Soil to Plants		Soil to Earthworms		Soil to Small Mammals	
	Equation	Source	Equation	Source	Equation	Source
Pentachlorophenol	$C_p = 5.93 * C_s$	a	$\ln(C_e) = 0.3308 * \ln(C_s) + 5.5463$	b	$C_m = 0.00452 * C_d + 0.198$	c

1.3 USEPA Environmental Response Team SOPs

1.3.1 General Field Sampling Guidelines (USEPA-Environmental Response Team)

SOP#: 2001

DATE:08/11/94

REV. #: 0.0

Scope and Application: The purpose of this SOP is to provide general field sampling guidelines that will assist personnel in choosing sampling strategies, location, and frequency for proper assessment of site characteristics. This SOP is applicable to all field activities that involve sampling. These are standard (i.e., typically applicable) operating procedures that may be varied or changed as required depending on site conditions, equipment limitations, and limitations imposed by the procedure. In all instances, the ultimate procedures employed should be documented and reported. Mention of trade names or commercial products does not constitute USEPA endorsement or recommendation for use.

Method Summary: Sampling is the selection of a representative portion of a larger population, universe, or body. Through examination of a sample, the characteristics of the larger body from which the sample was drawn can be inferred. In this manner, sampling can be a valuable tool for determining the presence, type, and extent of contamination by hazardous substances in the environment. The primary objective of all sampling activities is to characterize a hazardous waste site accurately so that its impact on human health and the environment can be properly evaluated. It is only through sampling and analysis that site hazards can be measured and the job of cleanup and restoration can be accomplished effectively with minimal risk. The sampling itself must be conducted so that every sample collected retains its original physical form and chemical composition. In this way, sample integrity is assured, quality assurance standards are maintained, and the sample can accurately represent the larger body of material under investigation.

The extent to which valid inferences can be drawn from a sample depends on the degree to which the sampling effort conforms to the project's objectives. For example, as few as one sample may produce adequate, technically valid data to address the project's objectives. Meeting the project's objectives requires thorough planning of sampling activities, and implementation of the most appropriate sampling and analytical procedures. These issues will be discussed in this procedure.

Sample Preservation, Containers, Handling, and Storage: The amount of sample to be collected, and the proper sample container type (i.e., glass, plastic), chemical preservation, and storage requirements are dependent on the matrix being sampled and the parameter(s) of interest. Sample preservation, containers, handling, and storage for air and waste samples are discussed in the specific SOPs for air and waste sampling techniques.

Interferences and Potential Problems: The nature of the object or materials being sampled may be a potential problem to the sampler. If a material is homogeneous, it will generally have a uniform composition throughout. In this case, any sample increment can be considered representative of the material. On the other hand, heterogeneous samples present problems to the

sampler because of changes in the material over distance, both laterally and vertically. Samples of hazardous materials may pose a safety threat to both field and laboratory personnel. Proper health and safety precautions should be implemented when handling this type of sample. Environmental conditions, weather conditions, or non-target chemicals may cause problems and interferences when performing sampling activities or when sampling for a specific parameter. Refer to the specific SOPs for sampling techniques.

Equipment/Apparatus: The equipment/apparatus required to collect samples must be determined on a site specific basis. Due to the wide variety of sampling equipment available, refer to the specific SOPs for sampling techniques, which include lists of the equipment/apparatus required for sampling.

Reagents: Reagents may be utilized for preservation of samples and for decontamination of sampling equipment. The preservatives required are specified by the analysis to be performed. Decontamination solutions are specified in ERT SOP #2006, Sampling Equipment Decontamination.

Procedure: *Types of Samples:* In relation to the media to be sampled, two basic types of samples can be considered: the environmental sample and the hazardous sample. Environmental samples are those collected from streams, ponds, lakes, and wells; there are offsite samples that are not expected to be contaminated with hazardous materials. They usually do not require the special handling procedures typically used for concentrated wastes. However, in certain instances, environmental samples can contain elevated concentrations of pollutants and in such cases would have to be handled as hazardous samples. Hazardous or concentrated samples are those collected from drums, tanks, lagoons, pits, waste piles, fresh spills, or areas previously identified as contaminated, and require special handling procedures because of their potential toxicity or hazard. These samples can be further subdivided based on their degree of hazard; however, care should be taken when handling and shipping any wastes believed to be concentrated regardless of the degree.

The importance of making the distinction between environmental and hazardous samples is two-fold:

- (1) Personnel safety requirements: Any sample thought to contain enough hazardous materials to pose a safety threat should be designated as hazardous and handled in a manner which ensures the safety of both field and laboratory personnel.
- (2) Transportation requirements: Hazardous samples must be packaged, labeled, and shipped according to the International Air Transport Association Dangerous Goods Regulations or Department of Transportation (DOT) regulations and USEPA guidelines.

Sample Collection Techniques: In general, two basic types of sample collection techniques are recognized, both of which can be used for either environmental or hazardous samples.

Grab Samples: A grab sample is defined as a discrete aliquot representative of a specific location at a given point in time. The sample is collected all at once at one particular point in the sample medium. The representativeness of such samples is defined by the nature of the materials

being sampled. In general, as sources vary over time and distance, the representativeness of grab samples will decrease.

Composite Samples: Composites are nondiscrete samples composed of more than one specific aliquot collected at various sampling locations and/or different points in time. Analysis of this type of sample produces an average value and can in certain instances be used as an alternative to analyzing a number of individual grab samples and calculating an average value. It should be noted, however, that compositing can mask problems by diluting isolated concentrations of some hazardous compounds below detection limits. Compositing is often used for environmental samples and may be used for hazardous samples under certain conditions. For example, compositing of hazardous waste is often performed after compatibility tests have been completed to determine an average value over a number of different locations (group of drums). This procedure generates data that can be useful by providing an average concentration within a number of units, can serve to keep analytical costs down, and can provide information useful to transporters and waste disposal operations. For sampling situations involving hazardous wastes, grab sampling techniques are generally preferred because grab sampling minimizes the amount of time sampling personnel must be in contact with the wastes, reduces risks associated with compositing unknowns, and eliminates chemical changes that might occur due to compositing.

Types of Sampling Strategies: The number of samples that should be collected and analyzed depends on the objective of the investigation. There are three basic sampling strategies: random, systematic, and judgmental sampling. Random sampling involves collection of samples in a nonsystematic fashion from the entire site or a specific portion of a site. Systematic sampling involves collection of samples based on a grid or a pattern that has been previously established. When judgmental sampling is performed, samples are collected only from the portion(s) of the site most likely to be contaminated. Often, a combination of these strategies is the best approach depending on the type of the suspected/known contamination, the uniformity and size of the site, the level/type of information desired, etc.

Quality Analysis Work Plans (QAWP): A QAWP is required when it becomes evident that a field investigation is necessary. It should be initiated in conjunction with, or immediately following, notification of the field investigation. This plan should be clear and concise and should detail the following basic components, with regard to sampling activities:

1. Objective and purpose of the investigation.
2. Basis upon which data will be evaluated.
3. Information known about the site including location, type and size of the facility, and length of operations/abandonment.
4. Type and volume of contaminated material, contaminants of concern (including concentration), and basis of the information/data.
5. Technical approach including media/matrix to be sampled, sampling equipment to be used, sample equipment decontamination (if necessary), sampling design and rationale, and SOPs or description of the procedure to be implemented.
6. Project management and reporting, schedule, project organization and responsibilities, manpower and cost projections, and required deliverables.
7. QA objectives and protocols including tables summarizing field sampling and QA/QC analysis and objectives.

Note that this list of QAWP components is not all inclusive and that additional elements may be added or altered depending on the specific requirements of the field investigation. It should also be recognized that although a detailed QAWP is quite important, it may be impractical in some instances. Emergency responses and accidental spills are prime examples of such instances where time might prohibit the development of site-specific QAWPs prior to field activities. In such cases, investigators would have to rely on general guidelines and personal judgment, and the sampling or response plans might simply be a strategy based on preliminary information and finalized on site. In any event, a plan of action should be developed, no matter how concise or informal, to aid investigators in maintaining a logical and consistent order to the implementation of their task.

Legal Implications: The data derived from sampling activities are often introduced as critical evidence during litigation of a hazardous waste site cleanup. Legal issues in which sampling data are important may include cleanup cost recovery, identification of pollution sources and responsible parties, and technical validation of remedial design methodologies. Because of the potential for involvement in legal actions, strict adherence to technical and administrative SOPs is essential during both the development and implementation of sampling activities. Technically valid sampling begins with thorough planning and continues through the sample collection and analytical procedures. Administrative requirements involve thorough, accurate documentation of all sampling activities. Documentation requirements include maintenance of a chain of custody, as well as accurate records of field activities and analytical instructions. Failure to observe these procedures fully and consistently may result in data that are questionable, invalid and indefensible in court, and the consequent loss of enforcement proceedings.

Calculations: Refer to the specific SOPs for any calculations which are associated with sampling techniques.

QA/QC: Refer to the specific SOPs for the type and frequency of QA/QC samples to be analyzed, the acceptance criteria for the QA/QC samples, and any other QA/QC activities which are associated with sampling techniques.

Data Validation: Refer to the specific SOPs for data validation activities that are associated with sampling techniques.

Health and Safety: When working with potentially hazardous materials follow USEPA, OSHA, and corporate health and safety procedures.

1.3.2 Sampling Equipment Decontamination (USEPA - Environmental Response Team)

SOP#: 2006

DATE:08/11/94

REV. #: 0.0

Scope and Application: The purpose of this SOP is to provide a description of the methods used for preventing, minimizing, or limiting cross-contamination of samples due to inappropriate or inadequate equipment decontamination and to provide general guidelines for developing decontamination procedures for sampling equipment to be used during hazardous waste operations as per 29 Code of Federal Regulations (CFR) 1910.120. This SOP does not address personnel decontamination.

These are standard (i.e., typically applicable) operating procedures that may be varied or changed as required depending on site conditions, equipment limitation, or limitations imposed by the procedure. In all instances, the ultimate procedures employed should be documented and reported.

Mention of trade names or commercial products does not constitute USEPA endorsement or recommendation for use.

Method Summary: Removing or neutralizing contaminants from equipment minimizes the likelihood of sample cross contamination, reduces or eliminates transfer of contaminants to clean areas, and prevents the mixing of incompatible substances.

Gross contamination can be removed by physical decontamination procedures. These abrasive and non-abrasive methods include the use of brushes, air and wet blasting, and high and low pressure water cleaning.

The first step, a soap and water wash, removes all visible particulate matter, residual oils, and grease. This may be preceded by a steam or high-pressure water wash to facilitate residuals removal. The second step involves a tap water rinse and a distilled/deionized water rinse to remove the detergent. An acid rinse provides a low pH media for trace metals removal and is included in the decontamination process if metal samples are to be collected. It is followed by another distilled/deionized water rinse. If sample analysis does not include metals, the acid rinse step can be omitted. Next, a high purity solvent rinse is performed for trace organics removal if organics are a concern at the site. Typical solvents used for removal of organic contaminants include acetone, hexane, or water. Acetone is typically chosen because it is an excellent solvent, miscible in water, and not a target analyte on the priority pollutant list. If acetone is known to be a contaminant of concern at a given site or if target compound list analysis (which includes acetone) is to be performed, another solvent may be substituted. The solvent must be allowed to evaporate completely and then a final distilled/deionized water rinse is performed. This rinse removes any residual traces of the solvent.

The decontamination procedure described above may be summarized as follows:

1. Physical removal
2. Non-phosphate detergent wash
3. Tap water rinse
4. Distilled/deionized water rinse
5. 10% nitric acid rinse
6. Distilled/deionized water rinse
7. Solvent rinse (pesticide grade)
8. Air dry
9. Distilled/deionized water rinse

If a particular contaminant fraction is not present at the site, the nine step decontamination procedure specified above may be modified for site specificity. For example, the nitric acid rinse may be eliminated if metals are not of concern at a site. Similarly, the solvent rinse may be eliminated if organics are not of concern at a site. Modifications to the standard procedure should be documented in the site specific work plan or subsequent report.

Sample Preservation, Containers, Handling, and Storage: The amount of sample to be collected and the proper sample container type (i.e., glass, plastic), chemical preservation, and storage requirements are dependent on the matrix being sampled and the parameter(s) of interest.

More specifically, sample collection and analysis of decontamination waste may be required before beginning proper disposal of decontamination liquids and solids generated at a site. This should be determined prior to initiation of site activities.

Interferences and Potential Problems: The use of distilled/deionized water commonly available from commercial vendors may be acceptable for decontamination of sampling equipment provided that it has been verified by laboratory analysis to be analyte free (specifically for the contaminants of concern).

The use of an untreated potable water supply is not an acceptable substitute for tap water. Tap water may be used from any municipal or industrial water treatment system.

If acids or solvents are utilized in decontamination they raise health and safety, and waste disposal concerns.

Damage can be incurred by acid and solvent washing of complex and sophisticated sampling equipment.

Equipment/Apparatus: Decontamination equipment, materials, and supplies are generally selected based on availability. Other considerations include the ease of decontaminating or disposing of the equipment. Most equipment and supplies can be easily procured. For example, softwash bristle scrub brushes or long-handled bottle brushes can be used to remove contaminants. Large galvanized wash tubs, stock tanks, or buckets can hold softwash and rinse solutions. Children's wading pools can also be used. Large plastic garbage cans or other similar containers lined with plastic bags can help segregate contaminated equipment. Contaminated liquid can be stored temporarily in metal or plastic cans or drums.

The following standard materials and equipment are recommended for decontamination activities:

Decontamination Solutions: Non-phosphate detergent, selected solvents (acetone, hexane, nitric acid, etc.), tap water, distilled or deionized water.

Decontamination Tools/Supplies: Long and short handled brushes, bottle brushes, drop cloth/plastic sheeting, paper towels, plastic or galvanized tubs or buckets, pressurized sprayers, solvent sprayers, and aluminum foil.

Health and Safety Equipment: Appropriate personal protective equipment (i.e., safety glasses or splash shield, appropriate gloves, aprons or coveralls, respirator, and emergency eye wash).

Waste Disposal: Trash bags, trash containers, 55-gallon drums, and metal/plastic buckets/containers for storage and disposal of decontamination solutions.

Reagents: There are no reagents used in this procedure aside from the actual decontamination solutions. Table 6 lists solvent rinses which may be required for elimination of particular chemicals. In general, the following solvents are typically utilized for decontamination purposes: 10% nitric acid is typically used for inorganic compounds such as metals. An acid rinse may not be required if inorganics are not a contaminant of concern.

Acetone (pesticide grade)(1)

Hexane (pesticide grade)(1)

Methanol(1)

(1)- Only if sample is to be analyzed for organics.

Procedures: As part of the health and safety plan, a decontamination plan should be developed and reviewed. The decontamination line should be set up before any personnel or equipment enter the areas of potential exposure. The equipment decontamination plan should include:

- The number, location, and layout of decontamination stations.
- Decontamination equipment needed.
- Appropriate decontamination methods.
- Methods for disposal of contaminated clothing, equipment, and solutions.

Procedures can be established to minimize the potential for contamination. This may include: (1) work practices that minimize contact with potential contaminants; (2) using remote sampling techniques; (3) covering monitoring and sampling equipment with plastic, aluminum foil, or other protective material; (4) watering down dusty areas; (5) avoiding laying down equipment in areas of obvious contamination; and (6) use of disposable sampling equipment.

Table 6. Soluble Contaminants and Recommended Solvent Rinse.

Solvent¹	Examples of Solvents	Soluble Contaminants
Water	Deionized water Tap water	Low-chain hydrocarbons Inorganic compounds Salts Some organic acids and other polar compounds
Dilute acids	Nitric acid Acetic acid Boric acid	Basic (caustic) compounds (e.g., amines and hydrazines)
Dilute bases	Sodium bicarbonate (e.g., soap detergent)	Acidic compounds Phenol Thiols Some nitro and sulfonic compounds
Organic solvents ²	Alcohols Ethers Ketones Aromatics Straight chain alkalines (e.g., hexane) Common petroleum products (e.g., fuel, oil, kerosene)	Nonpolar compounds (e.g., some organic compounds)
Organic solvent ²	Hexane	PCBs

- Material safety data sheets are required for all decontamination solvents or solutions as required by the hazard communication standard
- WARNING: Some organic solvents can permeate and/or degrade the protective clothing

Decontamination Methods: All samples and equipment leaving the contaminated area of a site must be decontaminated to remove any contamination that may have adhered to equipment. Various decontamination methods will remove contaminants by: (1) flushing or other physical action, or (2) chemical complexing to inactivate contaminants by neutralization, chemical reaction, disinfection, or sterilization. Physical decontamination techniques can be grouped into two categories: abrasive methods and non-abrasive methods, as follows:

Abrasive Cleaning Methods: Abrasive cleaning methods work by rubbing and wearing away the top layer of the surface containing the contaminant. The mechanical abrasive cleaning methods are most commonly used at hazardous waste sites. The following abrasive methods are available:

Mechanical: Mechanical methods of decontamination include using metal or nylon brushes. The amount and type of contaminants removed will vary with the hardness of bristles, length of time brushed, degree of brush contact, degree of contamination, nature of the surface being cleaned, and degree of contaminant adherence to the surface.

Air Blasting: Air blasting equipment uses compressed air to force abrasive material through a nozzle at high velocities. The distance between nozzle and surface cleaned, air pressure, time of application, and angle at which the abrasive strikes the surface will dictate cleaning efficiency. Disadvantages of this method are the inability to control the amount of material removed and the large amount of waste generated.

Wet Blasting: Wet blast cleaning involves use of a suspended fine abrasive. The abrasive/water mixture is delivered by compressed air to the contaminated area. By using a very fine abrasive, the amount of materials removed can be carefully controlled.

Non-Abrasive Cleaning Methods: Non-abrasive cleaning methods work by forcing the contaminant off a surface with pressure. In general, the equipment surface is not removed using non-abrasive methods.

Low-Pressure Water: This method consists of a container that is filled with water. The user pumps air out of the container to create a vacuum. A slender nozzle and hose allow the user to spray in hard-to-reach places.

High-Pressure Water: This method consists of a high-pressure pump, an operator controlled directional nozzle, and a highpressure hose. Operating pressure usually ranges from 340 to 680 atmospheres (atm) and flow rates usually range from 20 to 140 liters per minute.

Ultra-High-Pressure Water: This system produces a water jet that is pressured from 1,000 to 4,000 atmospheres. This ultra-high-pressure spray can remove tightly-adhered surface films. The water velocity ranges from 500 meters/second (m/s) (1,000 atm) to 900 m/s (4,000 atm). Additives can be used to enhance the cleaning action.

Rinsing: Contaminants are removed by rinsing through dilution, physical attraction, and solubilization.

Damp Cloth Removal: In some instances, due to sensitive, non-waterproof equipment or due to the unlikelihood of equipment being contaminated, it is not necessary to conduct an extensive decontamination procedure. For example, air sampling pumps hooked on a fence, placed on a drum, or wrapped in plastic bags are not likely to become heavily contaminated. A damp cloth should be used to wipe off contaminants that may have adhered to equipment through airborne contaminants or from surfaces upon which the equipment was set.

Disinfection/Sterilization: Disinfectants are a practical means of inactivating infectious agents. Unfortunately, standard sterilization methods are impractical for large equipment. This method of decontamination is typically performed offsite.

Field Sampling Equipment Decontamination Procedures: The decontamination line is setup so that the first station is used to clean the most contaminated item. It progresses to the last station where the least contaminated item is cleaned. The spread of contaminants is further reduced by separating each decontamination station by a minimum of one meter. Ideally, the contamination should decrease as the equipment progresses from one station to another farther along in the line.

A site is typically divided up into the following boundaries: hot zone or exclusion zone, the contamination reduction zone (CRZ), and the support or safe zone. The decontamination line should be setup in the contamination reduction corridor (CRC) which is in the CRZ. Figure 1 shows a typical contaminant reduction zone layout. The CRC controls access into and out of the exclusion zone and confines decontamination activities to a limited area. The CRC boundaries should be conspicuously marked. The far end is the hotline, the boundary between the exclusion zone and the contamination reduction zone. The size of the decontamination corridor depends on the number of stations in the decontamination process, overall dimensions of the work zones, and amount of space available at the site. Whenever possible, it should be a straight line.

Anyone in the CRC should be wearing the level of protection designated for the decontamination crew. Another corridor may be required for the entry and exit of heavy equipment. Sampling and monitoring equipment and sampling supplies are all maintained outside of the CRC. Personnel don their equipment away from the CRC and enter the exclusion zone through a separate access control point at the hotline. One person (or more) dedicated to decontaminating equipment is recommended.

Decontamination Setup: Starting with the most contaminated station, the decontamination setup should be as follows:

Station 1: Segregate Equipment Drop

Place plastic sheeting on the ground (Figure 2). Size will depend on amount of equipment to be decontaminated. Provide containers lined with plastic if equipment is to be segregated. Segregation may be required if sensitive equipment or mildly contaminated equipment is used at the same time as equipment that is likely to be heavily contaminated.

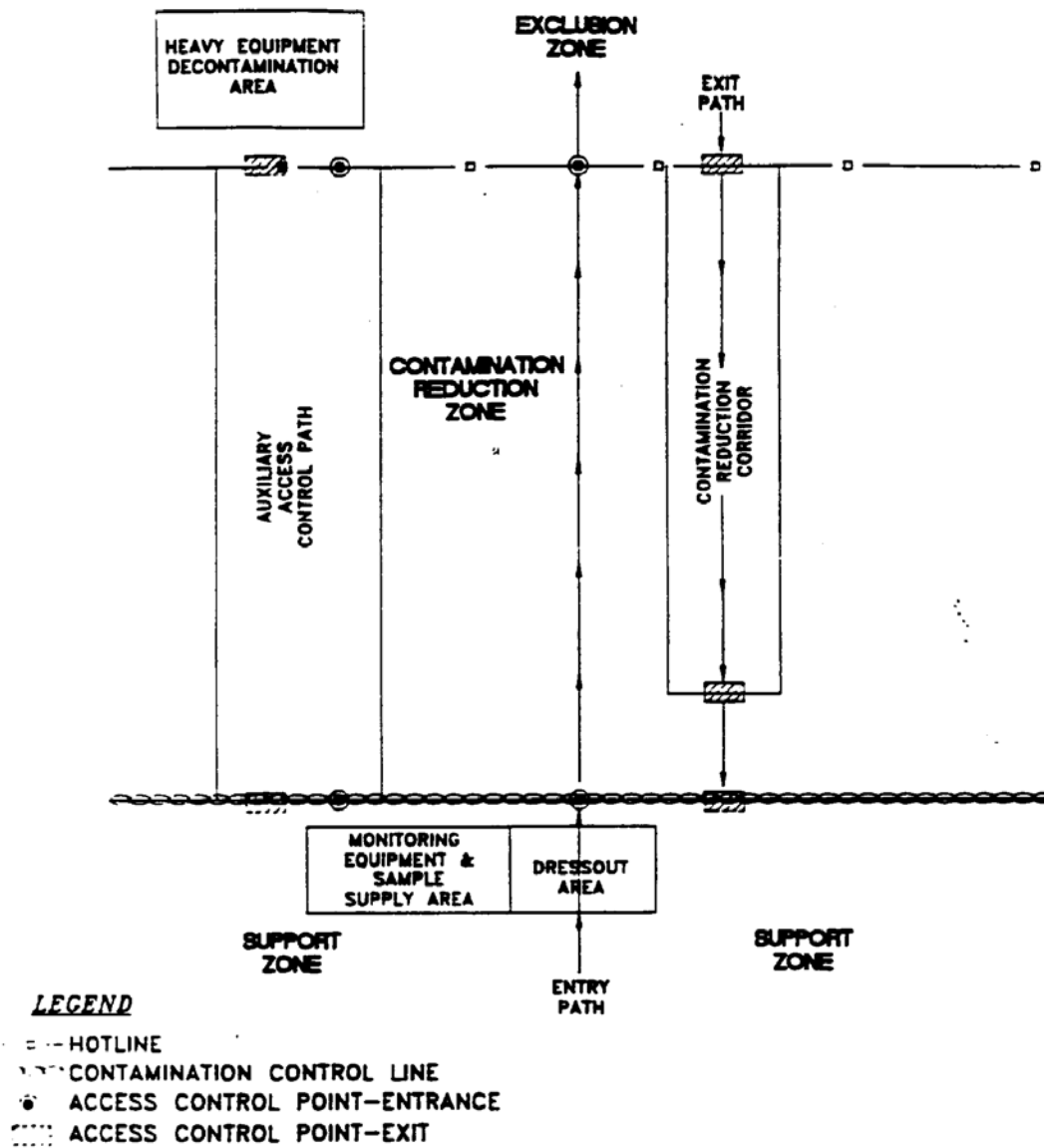


Figure 1. Contamination Reduction Zone Layout.

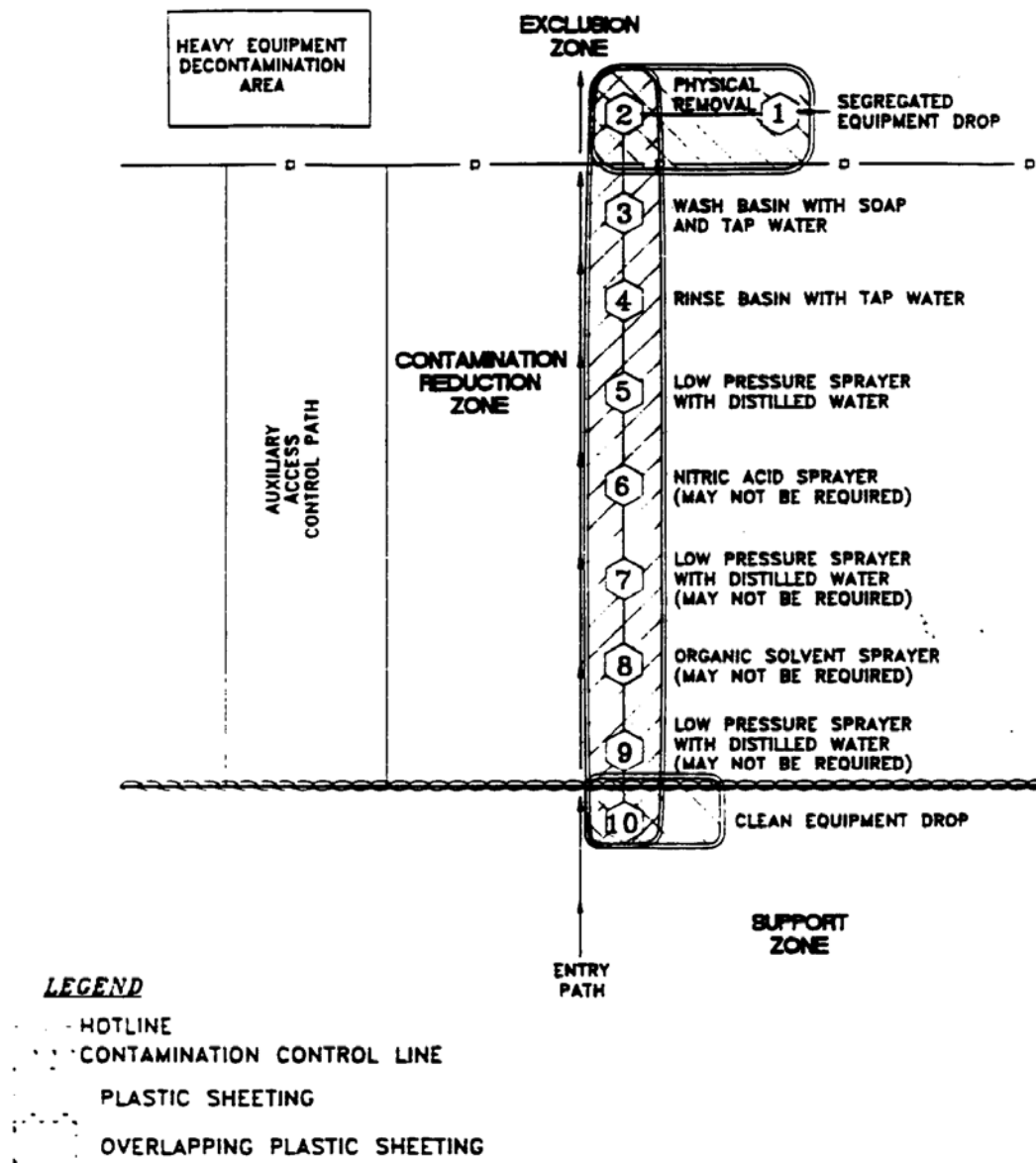


Figure 2. Decontamination Layout.

Station 2: Physical Removal with a High-Pressure Washer (Optional)

A high-pressure wash may be required for compounds that are difficult to remove by washing with brushes. The elevated temperature of the water from the high-pressure washers is excellent at removing greasy/oily compounds. High pressure washers require water and electricity.

A decontamination pad may be required for the high- pressure wash area. An example of a wash pad may consist of an approximately a half meter deep basin lined with plastic sheeting and sloped to a sump at one corner. A layer of sand can be placed over the plastic and the basin is filled with gravel or shell. The sump is also lined with visqueen and a barrel is placed in the hole to prevent collapse. A sump pump is used to remove the water from the sump for transfer into a drum.

Typically heavy machinery is decontaminated at the end of the day unless site sampling requires that the machinery be decontaminated frequently. A separate decontamination pad may be required for heavy equipment.

Station 3: Physical Removal With Brushes and a Wash Basin

Prior to setting up Station 3, place plastic sheeting on the ground to cover areas under Station 3 through Station 10.

Fill a wash basin, a large bucket, or child's swimming pool with non-phosphate detergent and tap water. Several bottle and bristle brushes to physically remove contamination should be dedicated to this station. Approximately 38 – 189 liters of water may be required initially depending upon the amount of equipment to decontaminate and the amount of gross contamination.

Station 4: Water Basin

Fill a wash basin, a large bucket, or child's swimming pool with tap water. Several bottle and bristle brushes should be dedicated to this station. Approximately 38 – 189 liters of water may be required initially depending upon the amount of equipment to decontaminate and the amount of gross contamination.

Station 5: Low-Pressure Sprayers

Fill a low-pressure sprayer with distilled/deionized water. Provide a 5-gallon bucket or basin to contain the water during the rinsing process. Approximately 38 – 76 liters of water may be required initially depending upon the amount of equipment to decontaminate and the amount of gross contamination.

Station 6: Nitric Acid Sprayers

Fill a spray bottle with 10% nitric acid. An acid rinse may not be required if inorganics are not a contaminant of concern. The amount of acid will depend on the amount of equipment to be decontaminated. Provide a 5-gallon bucket or basin to collect acid during the rinsing process.

Station 7: Low-Pressure Sprayers

Fill a low-pressure sprayer with distilled/deionized water. Provide a 5-gallon bucket or basin to collect water during the rinsate process.

Station 8: Organic Solvent Sprayers

Fill a spray bottle with an organic solvent. After each solvent rinse, the equipment should be rinsed with distilled/deionized water and air dried. Amount of solvent will depend on the amount of equipment to decontaminate. Provide a 5-gallon bucket or basin to collect the solvent during the rinsing process.

Solvent rinses may not be required unless organics are a contaminant of concern, and may be eliminated from the station sequence.

Station 9: Low-Pressure Sprayers

Fill a low-pressure sprayer with distilled/deionized water. Provide a 5-gallon bucket or basin to collect water during the rinsate process.

Station 10: Clean Equipment Drop

Lay a clean piece of plastic sheeting over the bottom plastic layer. This will allow easy removal of the plastic in the event that it becomes dirty. Provide aluminum foil, plastic, or other protective material to wrap clean equipment.

Decontamination Procedures:

Station 1: Segregate Equipment Drop

Deposit equipment used on-site (e.g., tools, sampling devices and containers, monitoring instruments radios, and clipboards) on the plastic drop cloth/sheet or in different containers with plastic liners. Each will be contaminated to a different degree.

Segregation at the drop reduces the probability of cross contamination. Loose leaf sampling data sheets or maps can be placed in plastic Ziploc bags if contamination is evident.

Station 2: Physical Removal With a High-Pressure Washer (Optional)

Use high pressure wash on grossly contaminated equipment. Do not use high-pressure wash on sensitive or non-waterproof equipment.

Station 3: Physical Removal With Brushes and a Wash Basin

Scrub equipment with soap and water using bottle and bristle brushes. Only sensitive equipment (i.e., radios, air monitoring and sampling equipment) that is waterproof should be washed. Equipment that is not waterproof should have plastic bags removed and wiped down with a damp cloth. Acids and organic rinses may also ruin sensitive equipment. Consult the manufacturers for recommended decontamination solutions.

Station 4: Equipment Rinse

Wash soap from equipment with water by immersing the equipment in the water while brushing. Repeat as many times as necessary.

Station 5: Low-Pressure Rinse

Rinse sampling equipment with distilled/deionized water with a low-pressure sprayer.

Station 6: Nitric Acid Sprayers (required only if metals are a contaminant of concern)

Using a spray bottle rinse sampling equipment with nitric acid. Begin spraying (inside and outside) at one end of the equipment allowing the acid to drip to the other end into a 5-gallon bucket. A rinsate blank may be required at this station.

Station 7: Low-Pressure Sprayers

Rinse sampling equipment with distilled/deionized water with a low-pressure sprayer.

Station 8: Organic Solvent Sprayers

Rinse sampling equipment with a solvent. Begin spraying (inside and outside) at one end of the equipment allowing the solvent to drip to the other end into a 5-gallon bucket. Allow the solvent to evaporate from the equipment before going to the next station. A QC rinsate sample may be required at this station.

Station 9: Low-Pressure Sprayers

Rinse sampling equipment with distilled/deionized water with a low-pressure washer.

Station 10: Clean Equipment Drop

Lay clean equipment on plastic sheeting. Once air dried, wrap sampling equipment with aluminum foil, plastic, or other protective material.

Post Decontamination Procedures:

1. Collect high-pressure pad and heavy equipment decontamination area liquid and waste and store in appropriate drum or container. A sump pump can aid in the collection process. Refer to the DOT requirements for appropriate containers based on the contaminant of concern.
2. Collect high-pressure pad and heavy equipment decontamination area solid waste and store in appropriate drum or container. Refer to the DOT requirements for appropriate containers based on the contaminant of concern.
3. Empty soap and water liquid wastes from basins and buckets and store in appropriate drum or container. Refer to the DOT requirements for appropriate containers based on the contaminant of concern.
4. Empty acid rinse waste and place in appropriate container or neutralize with a base and place in appropriate drum. pH paper or an equivalent pH test is required for neutralization. Consult DOT requirements for appropriate drum for acid rinse waste.
5. Empty solvent rinse sprayer and solvent waste into an appropriate container. Consult DOT requirements for appropriate drum for solvent rinse waste.
6. Using low-pressure sprayers, rinse basins, and brushes. Place liquid generated from this process into the wash water rinse container.
7. Empty low-pressure sprayer water onto the ground.

8. Place all solid waste materials generated from the decontamination area (e.g., gloves and plastic sheeting) in an approved DOT drum. Refer to the DOT requirements for appropriate containers based on the contaminant of concern.
9. Write appropriate labels for waste and make arrangements for disposal. Consult DOT regulations for the appropriate label for each drum generated from the decontamination process.

Calculations: This section is not applicable to this SOP.

QA/QC: A rinsate blank is one specific type of quality control sample associated with the field decontamination process. This sample will provide information on the effectiveness of the decontamination process employed in the field. Rinsate blanks are samples obtained by running analyte-free water over decontaminated sampling equipment to test for residual contamination. The blank water is collected in sample containers for handling, shipment, and analysis. These samples are treated identical to samples collected that day.

A rinsate blank is used to assess cross contamination brought about by improper decontamination procedures. Where dedicated sampling equipment is not utilized, collect one rinsate blank per day per type of sampling device samples to meet quality assurance objectives.

If sampling equipment requires the use of plastic tubing it should be disposed of as contaminated and replaced with clean tubing before additional sampling occurs.

Data Validation: Results of quality control samples will be evaluated for contamination. This information will be utilized to qualify the environmental sample results in accordance with the project's data quality objectives.

Health and Safety: When working with potentially hazardous materials, follow OSHA, USEPA, corporate, and other applicable health and safety procedures.

Decontamination can pose hazards under certain circumstances. Hazardous substances may be incompatible with decontamination materials. For example, the decontamination solution may react with contaminants to produce heat, explosion, or toxic products. Also, vapors from decontamination solutions may pose a direct health hazard to workers by inhalation, contact, fire, or explosion.

The decontamination solutions must be determined to be acceptable before use. Decontamination materials may degrade protective clothing or equipment; some solvents can permeate protective clothing. If decontamination materials do pose a health hazard, measures should be taken to protect personnel or substitutions should be made to eliminate the hazard. The choice of respiratory protection based on contaminants of concern from the site may not be appropriate for solvents used in the decontamination process.

Safety considerations should be addressed when using abrasive and non-abrasive decontamination equipment. Maximum air pressure produced by abrasive equipment could cause physical injury. Displaced material requires control mechanisms.

Material generated from decontamination activities requires proper handling, storage, and disposal. Personal protective equipment may be required for these activities.

Material safety data sheets are required for all decontamination solvents or solutions as required by the Hazard Communication Standard (i.e., acetone, alcohol, and trisodiumphosphate). In some jurisdictions, phosphate containing detergents (i.e., TSP) are banned.

1.3.3 General Air Sampling Guidelines (USEPA - Environmental Response Team SOPs)



GENERAL AIR SAMPLING GUIDELINES

SOP#: 2008
DATE: 11/16/94
REV. #: 0.0

1.0 SCOPE AND APPLICATION

This Standard Operating Procedure (SOP) provides guidance in developing and implementing sampling plans to assess the impact of hazardous waste sites on ambient air. It presents the United States Environmental Protection Agency/Environmental Response Team's (U.S. EPA/ERT's) approach to air sampling and monitoring and identifies equipment requirements. It is not within the scope of this SOP to provide a generic air sampling plan. Experience, objectives, site characteristics, and chemical characteristics will dictate sampling strategy. This SOP does not address indoor air sampling.

Two basic approaches can be used to assess ambient air (also referred to as air pathway assessments): modeling and measurements. The modeling approach initially estimates or measures the overall site emission rate(s) and pattern(s). These data are input into an appropriate air dispersion model, which predicts either the maximum or average air concentrations at selected locations or distances during the time period of concern. This overall modeling strategy is presented in the first three volumes of the Air Superfund National Technical Guidance Series on Air Pathway Assessments^(1,2,3). Specific applications of this strategy are presented in several additional Air Superfund Technical Guidance documents⁽⁴⁾.

The measurement approach involves actually measuring the air impact at selected locations during specific time periods. These measurements can be used to document actual air impacts during specific time intervals (i.e., during cleanup operations) or to extrapolate the probable "worst case" concentrations at that and similar locations over a longer time period than was sampled.

This SOP addresses issues associated with this second assessment strategy. This SOP also discusses the U.S. EPA/ERT's monitoring instruments, air sampling

kits, and approach to air sampling and monitoring at hazardous waste sites.

These are standard (i.e., typically applicable) operating procedures which may be varied or changed as required, depending on site conditions, equipment limitations, or limitations imposed by the procedure. In all instances, the ultimate procedures employed should be documented and associated with the final report.

Mention of trade names or commercial products does not constitute U.S. EPA endorsement or recommendation for use.

2.0 METHOD SUMMARY

Air monitoring is defined as the use of direct-reading instruments and other screening or monitoring equipment and techniques that provide instantaneous (real-time) data on the levels of airborne contaminants. The U.S. EPA/ERT maintains numerous monitors for real-time measurements. Examples of air monitoring equipment are hand-held photoionization detectors (PID), flame ionization detectors (FID), oxygen/combustible gas detectors, and remote optical sensors.

Air sampling is defined as those sampling and analytical techniques that require either off- or on-site laboratory analysis and therefore do not provide immediate results. Typically, air sampling occurs after use of real-time air monitoring equipment has narrowed the number of possible contaminants and has provided some qualitative measurement of contaminant concentration. Air sampling techniques are used to more accurately detect, identify and quantify specific chemical compounds relative to the majority of air monitoring technologies.

In the Superfund Removal Program, On-Scene Coordinators (OSCs) may request the U.S. EPA/ERT to conduct air monitoring and sampling during the

following situations: emergency responses, site assessments, and removal activities. Each of these activities has a related air monitoring/sampling objective that is used to determine the potential hazards to workers and/or the community.

C Emergency Response

Emergency responses are immediate responses to a release or threatened release of hazardous substances presenting an imminent danger to public health, welfare, or the environment (i.e., chemical spills, fires, or chemical process failures resulting in a controlled release of hazardous substances). Generally these situations require rapid on-site investigation and response. A major part of this investigation consists of assessing the air impact of these releases.

C Removal Site Assessment

Removal site assessments (referred to as site assessments) are defined as any of several activities undertaken to determine the extent of contamination at a site and which help to formulate the appropriate response to a release or threatened release of hazardous substances. These activities may include a site inspection, multimedia sampling, and other data collection.

C Removal Actions

Removal actions clean up or remove hazardous substances released into the environment. Removal actions include any activity conducted to abate, prevent, minimize, stabilize, or eliminate a threat to public health or welfare, or to the environment.

Personal risk from airborne contaminants can be determined by comparing the results of on-site monitoring and sampling to health-based action levels such as the American Conference of Governmental Industrial Hygienists (ACGIH) Threshold Limit Values (TLVs) and the Occupational Safety and Health Administration (OSHA) Permissible Exposure Limits (PELs). Residential risk can be determined by comparing the results of off-site monitoring or sampling to health-based action levels such as those developed by the Agency for Toxic Substance and

Disease Registry (ATSDR).

The extent to which valid inferences can be drawn from air monitoring/sampling depends on the degree to which the monitoring/sampling effort conforms to the objectives of the event. Meeting the project's objectives requires thorough planning of the monitoring/sampling activities, and implementation of the most appropriate monitoring/sampling and analytical procedures. These issues will be discussed in this SOP.

3.0 SAMPLE PRESERVATION, CONTAINERS, HANDLING, AND STORAGE

Preservation, containers, handling and storage for air samples are discussed in the specific SOPs for the technique selected. In addition, the analytical method (i.e., U.S. EPA, National Institute for Occupational Safety and Health [NIOSH], and OSHA Methods) may be consulted for storage temperature, holding times and packaging requirements. After sample collection, the sampling media (i.e., cassettes or tubes) are immediately sealed. The samples are then placed into suitable containers (i.e., whirl bags, resealable bags or culture tubes) which are then placed into a shipping container.

Use bubble wrap or styrofoam peanuts when packing air samples for shipment. DO NOT USE VERMICULITE.

4.0 INTERFERENCES AND POTENTIAL PROBLEMS

Upwind sources can contribute to sample concentration. Natural sources, such as biological waste, can produce hydrogen sulfide and methane which may contribute to the overall contaminant level. Extraneous anthropogenic contaminants (i.e., burning of fossil fuels; emissions from vehicular traffic, especially diesel; volatile compounds from petrochemical facilities; and effluvium from smoke stacks) may also contribute. Air sampling stations should be strategically placed to identify contributing sources.

Photoreactivity or reaction of the parameters of concern may occur with nonrelated compounds [i.e., nitrogen compounds and polyaromatic hydrocarbons

(PAHs)]. Some sorbent media/samples should not be exposed to light during or after sampling due to photochemical effects (i.e., PAHs).

Various environmental factors, including humidity, temperature and pressure, also impact the air sampling methodology, collection efficiency and detection limit. Since the determination of air contaminants is specifically dependent on the collection parameters and efficiencies, the collection procedure is an integral part of the analytical method.

Detection limits depend on the contaminants being investigated and the particular site situation. It is important to know why the data are needed and how the data will be used. Care should be taken to ensure the detection limits are adequate for the intended use of the final results.

Some equipment may be sensitive to humidity and temperature extremes.

5.0 EQUIPMENT/APPARATUS

5.1 Direct Reading Instruments (Air Monitoring Instruments)

There are two general types of direct reading instruments: portable screening devices and specialized analytical instruments. Generally all these techniques involve acquiring, for a specific location or area, continuous or sequential direct air concentrations in either a real-time or semi-real-time mode. None of these instruments acquires true time-weighted average concentrations. In addition, these instruments are not capable of acquiring simultaneous concentration readings at multiple locations, although several are able to sequentially analyze samples taken remotely from different locations. The document, "Guide to Portable Instruments for Assessing Airborne Pollutants Arising from Hazardous Waste Sites⁽⁵⁾," provides additional information about air sampling and monitoring. The hazard levels for airborne contaminants vary. See the ACGIH TLVs and the OSHA PELs for safe working levels. Common screening devices and analytical instruments are described in Appendix A.

5.2 Air Sampling Equipment and Media/Devices

The U.S. EPA/ERT uses the following analytical

methods for sampling: *NIOSH Manual of Analytical Methods*⁽⁶⁾, *American Society for Testing and Materials (ASTM) Methods*⁽⁷⁾, *U.S. EPA Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air*^(8,9), and *OSHA Methods*⁽¹⁰⁾. Additional air sampling references include *Industrial Hygiene and Toxicology* (3rd Ed.)⁽¹¹⁾ and *Air Sampling Instruments for Evaluation of Atmospheric Contaminants*⁽¹²⁾. These methods typically specify equipment requirements for sampling. Since air sampling is such a diverse technology, no single method or reference is best for all applications. Common sampling equipment and media/devices are described in Appendix B.

5.3 Tools/Material and Equipment List

In addition to equipment and materials identified in Appendices A and B, the following equipment and materials may be required to conduct air sampling and monitoring at hazardous waste sites:

- C Camera
- C Site logbook
- C Clipboard
- C Chain of custody records
- C Custody seals
- C Air sampling worksheets
- C Sample labels
- C Small screwdriver set
- C Aluminum foil
- C Extension cords
- C Glass cracker
- C Multiple plug outlet
- C Whirl bags or culture tubes
- C Teflon tape
- C Calibration devices
- C Tygon and/or Teflon[®] tubing
- C Surgical gloves
- C Lint-free gloves
- C Ice
- C Sample container

Use the following additional equipment when decontaminating glassware on site:

- C Protective equipment (i.e., gloves, splash goggles, etc.)
- C Appropriate solvent(s)
- C Spray bottles
- C Liquinox (soap)
- C Paper towels

- C Distilled/deionized water
- C Five-gallon buckets
- C Scrub brushes and bottle brushes

6.0 REAGENTS

Impinger sampling involves using reagents contained in a glass vial to absorb contaminants of concern (for example, NIOSH Method 3500 for formaldehyde uses 1% sodium bisulfite solution). Impinger solutions vary and are method-dependent.

Reagents such as acetone and hexane are required to decontaminate glassware and some air sampling equipment. Decontamination solutions are specified in the Sampling Equipment Decontamination SOP.

7.0 PROCEDURES

7.1 Air Monitoring Design

7.1.1 Initial Surveys

In general, the initial survey is considered to be a relatively rapid screening process for collecting preliminary data at hazardous waste sites. However, initial surveys may require many hours to complete and may consist of more than one entry.

Some information is generally known about the site; therefore, real-time instrumentation for specific compounds (i.e., detector tubes and electrochemical sensors) can be used to identify hot spots. Sufficient data should be obtained with real-time instruments during the initial entry to screen the site for various contaminants. When warranted, intrinsically safe or explosion-proof instruments should be used. An organic vapor analyzer (OVA) is typically used during this survey. These gross measurements may be used on a preliminary basis to (1) determine levels of personal protection, (2) establish site work zones, and (3) map candidate areas for more thorough qualitative and quantitative studies involving air sampling.

In some situations, the information obtained may be sufficient to preclude additional monitoring. Materials detected during the initial survey may call for a more comprehensive evaluation of hazards and analyses for specific compounds. Since site activities and weather conditions change, a continuous program to monitor the ambient atmosphere must be established.

7.1.2 Off-Site Monitoring

Typically, perimeter monitoring with the same instruments employed for on-site monitoring is utilized to determine site boundaries. Because air is a dynamic matrix, physical boundaries like property lines and fences do not necessarily delineate the site boundary or area influenced by a release. Whenever possible, atmospheric hazards in the areas adjacent to the on-site zone should be monitored with direct-reading instruments. Monitoring at the fenceline or at varying locations off site provides useful information regarding pollutant migration. Three to four locations downwind of the source (i.e., plume) at breathing-zone height, provide a basic fingerprint of the plume. Negative instrument readings off site should not be interpreted as the complete absence of airborne toxic substances; rather, they should be considered another piece of information to assist in the preliminary evaluation. The interpretation of negative readings is instrument-dependent. The lack of instrument readings off site should not be interpreted as the complete absence of all airborne toxic substances; rather, it is possible that the particular compound or class of compounds to which the monitoring instrument responds is not present or that the concentration of the compound(s) is below the instrument's detection limit.

7.2 Air Sampling Design

7.2.1 Sampling Plan Design

The goal of air sampling is to accurately assess the impact of a contaminant source(s) on ambient air quality. This impact is expressed in terms of overall average and/or maximum air concentrations for the time period of concern and may be affected by the transport and release of pollutants from both on- and off-site sources. The location of these sources must be taken into account as they impact the selection of sampling locations. Unlike soil and groundwater concentrations, air concentrations at points of interest can easily vary by orders of magnitude over the period of concern. This variability plays a major role in designing an air sampling plan.

Downwind air concentration is determined by the amount of material being released from the site into the air (the emission rate) and by the degree that the contamination is diluted as it is transported. Local

meteorology and topography govern downwind dilution. Contaminant emission rates can also be heavily influenced by on-site meteorology and on-site activities. All of these concerns must be incorporated into an air sampling plan.

A sampling strategy can be simple or complex, depending on the sampling program objectives. Programs involving characterization of the pollutant contribution from a single point source tend to be simple, whereas sampling programs investigating fate and transport characteristics of components from diverse sources require a more complex sampling strategy. In addition, resource constraints may affect the complexity of the sampling design.

An optimal sampling strategy accounts for the following site parameters:

- C Location of stationary as well as mobile sources
- C Analytes of concern
- C Analytical detection limit to be achieved
- C Rate of release and transport of pollutants from sources
- C Availability of space and utilities for operating sampling equipment
- C Meteorological monitoring data
- C Meteorological conditions in which sampling is to be conducted

The sampling strategy typically requires that the concentration of contaminants at the source or area of concern as well as background contributions be quantified. It is important to establish background levels of contaminants in order to develop a reference point from which to evaluate the source data. Field blanks and lot blanks, as well as various other types of QA/QC samples, can be utilized to determine other sources. The impact of extraneous sources on sampling results can frequently be accounted for by placing samplers upwind, downwind and crosswind from the subject source. The analytical data from these different sampling locations may be compared to determine statistical differences.

7.2.2 Sampling Objectives

The objectives of the sampling must be determined prior to developing the sampling plan. Does the sampling plan verify adequate levels of protection for on-site personnel, or address potential off-site impacts

associated with the site or with site activities? In addition, the assumptions associated with the sampling program must be defined. These assumptions include whether the sampling is to take place under "typical," "worst case," or "one-time" conditions. If the conditions present at the time of sampling are different from those assumed during the development of the sampling plan, then quality of the data collected may be affected. The following definitions have been established:

- C Typical: routine daily sampling or routine scheduled sampling at pre-established locations.
- C Worst case: sampling conducted under the worst meteorological and/or site conditions which would result in elevated ambient concentrations.
- C One-time: only one chance is given to collect a sample without regard to time or conditions.

Qualitative data acquired under these conditions are usually applicable only to the time period during which the data were collected and may not provide accurate information to be used in estimating the magnitude of an air impact during other periods or over a long time interval.

The sampling objectives also dictate the detection limits. Sampling methods for airborne contaminants will depend upon the nature and state (solid, liquid or gas) of the contaminant. Gases and vapors may be collected in aqueous media or adsorbents, in molecular sieves, or in suitable containers. Particulates are collected by filters or impactors. The volume of sample to be collected is dependent upon an estimate of the contaminant concentration in the air, the sensitivity of the analytical method, and the standard or desired detection limit. A sufficient amount of sample must be collected to achieve the desired detection limit without interference from other contaminants. In addition, the selected method must be able to detect the target compound(s).

7.2.3 Location and Number of Individual Sampling Points

Choose the number and location of sampling points according to the variability, or sensitivity, of the

sampling and analytical methods being utilized, the variability of contaminant concentration over time at the site, the level of precision required and cost limitations. In addition, determine the number of locations and placement of samplers by considering the nature of the response, local terrain, meteorological conditions, location of the site (with respect to other conflicting background sources), size of the site, and the number, size, and relative proximity of separate on-site emission sources and upwind sources. The following are several considerations for sampler placement:

- C Location of potential on-site emission sources, as identified from the review of site background information or from preliminary on-site inspections.
- C Location of potential off-site emission sources upwind of the sampling location(s). Review local wind patterns to determine the location of off-site sources relative to wind direction.
- C Topographic features that affect the dispersion and transport of airborne toxic constituents.

Avoid natural obstructions when choosing air sampling station locations, and account for channelization around those obstructions.

- C Large water bodies, which affect atmospheric stability and the dispersion of air contaminants.
- C Roadways (dirt or paved), which may generate dust that could mask site contaminants.
- C Vegetation, such as trees and shrubs, which stabilizes soil and retards subsurface contaminants from becoming airborne. It also affects air flow and scrubs some contaminants from the air. Sometimes thick vegetation can make an otherwise ideal air monitoring location inaccessible.

Consider the duration of sampling activities when choosing the location and number of samples to be collected. For example, if the sampling period is limited to a few hours, one or two upwind and several downwind samples would typically be adequate,

especially around major emission sources.

A short-term monitoring program ranges from several days to a few weeks and generally includes gathered data for site assessments, removal actions, and source determination data (for further modeling). Activities involved in a short-term sampling strategy must recognize the most of the limited possibilities for data collection. Consider moving upwind/downwind locations determined based on National Oceanic and Atmospheric Administration (NOAA) weather forecasts. Weather monitoring becomes critical where complex terrain and local meteorological effects frequently change wind direction. Often, a number of alternatives fulfill the same objective.

Prevailing winds running the length of a valley usually require a minimum number of sampler locations; however, a complex valley may require more sampler locations to account for the wide variety of wind patterns. Ocean/lake effects may require a radical plan to collect enough samples to reach a low detection limit. Two sets of samplers may be placed next to each other: one set would be activated during the sea breeze while the other set is turned off, and vice versa when there is no sea breeze. After the sampling event, the respective upwind and downwind samples would be combined. Another alternative for sampling near a large body of water may be to use automatic, wind vector-operated samplers, which turn the sample only when the wind comes from a specified vector. At sites located on hillsides, wind will move down the valley and produce an upward fetch at the same time. Sampling locations may have to ring the site to measure the wind's impact.

Off-site sources may affect on-site monitoring. In this case, on-site meteorological data, concurrent with sampling data, is essential to interpreting the acquired data. Also, additional upwind sampling sites may be needed to fully characterize ambient background contaminant levels. Multiple off-site sources may require several monitoring locations, but if the sources are at a sufficient distance, only one monitoring location is needed.

Topography and weather are not the only factors in sampler location; the sampling sites must be secured from vandals and mishap. Secure all sampling locations to maintain chain of custody, and to prevent tampering with samples or loss of sampling equipment. High-volume sampling methods often require the use of 110 VAC electric power. When port

generators are used, the power quality may affect sampler operation. Also, be aware that the generators themselves could be a potential pollution source if their placement is not carefully considered.

Air quality dispersion models can be used to place samplers. The models incorporate source information, surrounding topography, and meteorological data to predict the general distance and directions of maximum ambient concentrations. Modeling results should be used to select sampling locations in areas of maximum pollutant concentrations.

7.2.4 Time, Duration and Frequency of Sampling Events

After choosing appropriate sampling or monitoring locations, determine the sampling frequency and the number of samples to be collected. The time of day, duration and frequency of sampling events is governed by:

- C The effects of site activities and meteorology on emission rates
- C The diurnal effect of the meteorology on downwind dispersion
- C The time period(s) of concern as defined by the objective
- C The variability in the impact from other non-site-related sources
- C If defined, the degree of confidence needed for either the mean or maximum downwind concentrations observed
- C The precision requirements for single measurements
- C Cost and other logistical considerations

The duration of the removal action and the number of hours per day that site work is conducted determine the time, duration, and frequency of samples. Short-term sampling programs may require daily sampling, while long-term programs may require 24-hour sampling every sixth or twelfth day. If the site will be undergoing removal activities 24 hours a day, continuous air sampling may be warranted. However, if the site activities will be conducted for only eight hours a day, and there are no emissions likely to occur during the remaining 16 hours, then sampling would be appropriate prior to the start of daily activities, would continue during operations, and end at the conclusion of the daily activities. An off-peak sample collection can ensure that emissions are not persisting

after the conclusion of daily cleanup activities. For some sites, emissions are still a factor several hours after daily site activities have been completed. Because of the typically decreased downwind dispersion in the evening, higher downwind concentrations than were present during daytime site activities may be detected. For sites where this is possible, the sampling duration needs to be lengthened accordingly.

Sampling duration and flow rate dictate the volume of air collected, and to a major degree, the detection limit. The analytical method selected will provide a reference to flow rate and volume. Flow rates are limited to the capacity of the pumps being employed and the contact time required by the collection media.

The duration or period of air sampling is commonly divided into two categories (1) samples collected over a brief time period are referred to as "instantaneous" or "grab" samples and are usually collected in less than five minutes and (2) average or integrated samples are collected over a significantly longer period of time. Integrated samples provide an average concentration over the entire sampling period. Integrated samples are not suited to determining cyclical releases of contaminants because periodic or cyclical events are averaged out by the proportionally long sampling duration.

Air quality dispersion models can predict the maximum air contaminant concentration expected from a source. The meteorological and site conditions expected to cause the highest concentration are known as worst-case conditions and can be identified by analyzing the modeling results. Depending upon the objective, one may sample when the model predicts worst-case conditions will exist.

7.2.5 Meteorological and Physical/Chemical Considerations

A meteorological monitoring program is an integral part of site monitoring activities. Meteorological data, which define local terrain impacts on air flow paths, are needed to interpret air concentration data. Meteorological data may be available from an existing station located near the site (i.e., at a local airport), otherwise a station should be set up at the site. This data will document the degree that samples actually were downwind and verify whether other worst-case assumptions were met. Meteorological parameters to

be monitored are, at a minimum, wind speed, wind direction, and sigma theta (which is the horizontal wind direction standard deviation and an indicator of atmospheric stability). The remaining parameters primarily affect the amount of a contaminant available in the air.

C Wind Speed

When the contaminant of concern is a particulate, wind speed is critical in determining whether the particulate will become airborne, the quantity of the particulate that becomes airborne, and the distance the particulate will travel from the source. Wind speed also contributes to the volatilization of contaminants from liquid sources.

C Wind Direction

Wind direction highly influences the path of airborne contaminants. In addition, variations in wind direction increase the dispersion of pollutants from a given source.

C Atmospheric Stability

Atmospheric stability refers to the degree to which the atmosphere tends to dampen vertical and horizontal motion. Stable atmospheric conditions (i.e., evenings) result in low dispersion, and unstable atmospheric conditions (i.e., hot sunny days) result in higher dispersion.

C Temperature

Higher temperatures increase the rate of volatilization of organic and some inorganic compounds and affect the initial rise of gaseous or vapor contaminants. Therefore, worst-case emission of volatiles and semivolatiles occurs at the hottest time of day, or on the hottest day.

C Humidity

High humidity affects water-soluble chemicals and particulates. Humid conditions may dictate the sampling media used to collect the air sample, or limit the volume of air sampled and thereby increase

the detection limit.

C Atmospheric Pressure

Migration of landfill gases through the landfill surface and through surrounding soils are governed by changes in atmospheric pressure. Atmospheric pressure will influence upward migration of gaseous contaminants from shallow aquifers into the basements of overlying structures.

In many cases, the transport and dispersion of air pollutants is complicated by local meteorology. Normal diurnal variations (i.e., temperature inversions) affect dispersion of airborne contaminants. Terrain features can enhance or create air inversions and can also influence the path and speed of air flow, complicating transport and dispersion patterns.

The chemical characteristics of a contaminant (i.e., molecular weight, physical state, vapor pressure, aerodynamic size, temperature, reactive compounds, and photodegradation) affects its behavior and can influence the method used to sample and analyze it.

8.0 CALCULATIONS

Volume is obtained by multiplying the sample time in minutes by the flow rate. Sample volume should be indicated on the chain of custody record. Adjustments for temperature and pressure differences may be required.

Results are usually provided in parts per million (ppm), parts per billion (ppb), milligrams per cubic meter (mg/m³) or micrograms per cubic meter (µg/m³).

Refer to the analytical method or regulatory guidelines for other applicable calculations.

9.0 QUALITY ASSURANCE/ QUALITY CONTROL

The manufacturer's instructions should be reviewed prior to instrument use. Instruments must be utilized in accordance with manufacturer's instructions. Equipment checkout and calibration activities must

occur prior to and after monitoring and sampling and must be documented.

9.1 QA/QC Samples

QA/QC samples provide information on the variability and usability of environmental sample results. Various QA/QC samples may be collected to detect error. QA/QC samples are submitted with the field samples for analysis to aid in identifying the origin of analytical discrepancies; then a determination can be made as to how the analytical results should be used. Collocated samples, background samples, field blanks, and lot blanks are the most commonly collected QA/QC field samples. Performance evaluation (PE) samples and matrix spikes provide additional measures of data QA/QC control. QA/QC results may suggest the need for modifying sample collection, preparation, handling, or analytical procedures if the resultant data do not meet site-specific QA or data quality objectives.

9.2 Sample Documentation

All sample and monitoring activities should be documented legibly, in ink. Any corrections or revisions should be made by lining through the incorrect entry and by initialing the error. All samples must be recorded on an Air Sampling Worksheet. A chain of custody record must be maintained from the time a sample is taken to the final disposition of the sample. Custody seals demonstrate that a sample container has not been opened or tampered with during transport or storage of samples.

10.0 DATA VALIDATION

Results for QA/QC samples should be evaluated for contamination. This information should be utilized to qualify the environmental sample results accordingly with data quality objectives.

11.0 HEALTH AND SAFETY

Personal protection equipment (PPE) requirements identified in federal and/or state regulations and 29 Code of Federal Regulations (CFR) 1910.120 for hazardous waste site work must be followed.

The majority of physical precautions involved in air sampling are related to the contaminant sampled. Attention should be given when sampling in

potentially explosive, flammable or acidic atmospheres. On rare occasions, the collection media may be hazardous; for example, in the instance where an acidic or basic solution is utilized in an impinger.

When working with potentially hazardous materials, follow U.S. EPA, OSHA and corporate health and safety procedures.

12.0 REFERENCES

- (1) U.S. EPA. *Air Superfund National Technical Guidance Series. Volume I. Application of Air Pathway Analyses for Superfund Activities.* EPA/450/1-89/001.
 - (2) U.S. EPA. *Air Superfund National Technical Guidance Series. Volume II. Estimation of Baseline Air Emissions at Superfund Sites.* EPA/450/1-89/002.
 - (3) U.S. EPA. *Air Superfund National Technical Guidance Series. Volume III. Estimations of Air Emissions from Cleanup Activities at Superfund Sites.* EPA/450/1-89/003.
 - (4) U.S. EPA. *Air Superfund National Technical Guidance Series. Volume IV. Procedures for Dispersion Air Modeling and Air Monitoring for Superfund Air Pathway Analysis.* EPA/450/1-89/004.
 - (5) *Guide to Portable Instruments for Assessing Airborne Pollutants Arising from Hazardous Wastes,* International Organization of Legal Metrology (OIML) U.S. National Working Group (NWG) for OIML, American Conference of Governmental Industrial Hygienists, Cincinnati, OH
 - (6) NIOSH. *Manual of Analytical Methods, Second Edition. Volumes 1-7.* U.S. Department of Health and Human Services Publication No. 84-100.
- NIOSH. *Manual of Analytical Methods,* February 1984. U.S. Department of Health and Human Services Publication No. 84-100.

- (7) ASTM. 1990. *Annual Book of Standards, Volume 11.03*.
- (8) Riggin, R.M. *Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air*. EPA/600/4-84/041.
- (9) Winberry, W.T. *Supplement to U.S. EPA/600/4-84/041: Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air*. EPA/600/4-87/006.
- (10) OSHA. *Analytical Methods Manual, Second Edition. Part 1, Organic Substances*, January 1990. *Part 2, Inorganic Substances* August 1991.
- (11) Patty, F.A., *Industrial Hygiene and Toxicology, Third Edition*, John Wiley and Sons, Inc., New York, NY.
- (12) *Air Sampling Instruments for Evaluation of Atmospheric Contaminants, Seventh Edition*, 1989, American Conference of Governmental Industrial Hygienists, Cincinnati, OH

BIBLIOGRAPHY

Removal Program Representative Sampling Guidance, Volume 2: Air, Environmental Response Branch, Emergency Response Division, Office of Emergency and Remedial Response, Office of Solid Waste and Emergency Response, U.S. Environmental Protection Agency, April 1992, Interim Final.

APPENDIX A

Portable Screening Devices and Specialized Analytical Instruments

PORTABLE SCREENING DEVICES

Where possible, a datalogger should be used to minimize the length of time required for site personnel to be in a potentially contaminated area. Datalogger cable is available from manufacturers for linear output instruments and some nonlinear output instruments. U.S. EPA ERT/REAC has output cables for organic vapor analyzers (i.e., HNU and OVA), toxic gas analyzers (i.e., monitox) and real-time aerosol monitors (i.e., RAM and miniram).

C Total Hydrocarbon Analyzers

Total hydrocarbon analyzers used to detect a variety of volatile organic compounds (VOCs) at hazardous waste sites principally employ either a photoionization detector (PID) or a flame ionization detector (FID). Compounds are ionized by a flame or an ultraviolet lamp. PIDs depend on the ionization potential of the compounds. PIDs are sensitive to aromatic and olefinic (unsaturated) compounds such as benzene, toluene, styrene, xylenes, and acetylene. Greater selectivity is possible by using low-voltage lamps. The ionization potential of individual compounds can be found in the NIOSH Pocket Guide to Chemical Hazards. These instruments are not compound-specific and are typically used as screening instruments. FIDs are sensitive to volatile organic vapor compounds such as methane, propanol, benzene and toluene. They respond poorly to organic compounds lacking hydrocarbon characteristics.

C Oxygen and Combustible Gas Indicators

Combustible Gas Indicators (CGIs) provide efficient and reliable methods to test for potentially explosive atmospheres. CGI meters measure the concentration of a flammable vapor or gas in air and present these measurements as a percentage of the

lower explosive limit (LEL).

The measurements are temperature-dependent. The property of the calibration gas determines sensitivity.

LELs for individual compounds can be found in the NIOSH Pocket Guide to Chemical Hazards. If readings approach or exceed 10% of the LEL, extreme caution should be exercised in continuing the investigation. If readings approach or exceed 25% LEL, personnel should be withdrawn immediately.

CGIs typically house an electrochemical sensor to determine the oxygen concentration in ambient air. Normally, air contains approximately 20.9% oxygen by volume. Oxygen measurements are of particular importance for work in enclosed spaces, low-lying areas, or in the vicinity of accidents that have produced heavier-than-air vapors which could displace ambient air. The meters are calibrated for sea level and may indicate a false negative (i.e., O₂ content) at higher altitudes. Since the air has been displaced by other substances, these oxygen-deficient areas are also prime locations for taking additional organic vapor and combustible gas measurements. Oxygen-enriched atmospheres increase the potential for fires by their ability to contribute to combustion or to chemically react with flammable compounds and promote auto-ignition.

C Toxic Atmosphere Analyzers

The toxic atmosphere analyzer is a compound-specific instrument, designed and calibrated to identify and quantify a specific compound or class of compounds in either gaseous or vapor form. Cross-sensitivity to air pollutants not of interest may lead to erroneous results.

U.S. EPA/ERT has the following toxic atmosphere analyzers: carbon monoxide, phosgene, nitrous oxide, hydrogen cyanide, sulfur dioxide, hydrogen sulfide, and chlorine gas.

C Aerosol/Particulate Monitors

A Real-Time Aerosol/Particulate Monitor (RAM) displays readings for total particulates. The instrument employs a pulse light emitting diode which generates a narrow band emission in conjunction with a photovoltaic cell to detect light scattered from particulates.

The U.S. EPA/ERT uses the RAM when the contaminant of concern is associated with particulates, and when responding to fires involving hazardous materials, to identify plume levels. The instrument is very useful in determining the presence of a plume when it is not visible. The U.S. EPA/ERT typically uses RAMs on tripods to obtain particulate concentrations at the breathing zone level. Personal dataloggers are used with the RAMs to document minimum, average and maximum concentrations. This provides real-time data without requiring those in personal protective equipment to be constantly present in the plume.

C Chemical Detector Tubes (Colorimetric Tubes)

A chemical detector tube is a hollow, tube-shaped, glass body containing one or more layers of chemically impregnated inert material. To use, the fused ends are broken off and a manufacturer-specified volume of air is drawn through the tube with a pump to achieve a given detection limit. The chemicals contained within the packing material undergo a chemical reaction with the airborne pollutant present, producing a color change during the intake of each pump stroke. The concentration of a pollutant is indicated by the length of discoloration on a calibrated scale printed on the detector tube.

C Radiation Meters

Radiation meters determine the presence and level of radiation. The meters use a gas or solid ion detection media which becomes ionized when radiation is present. The meters are normally calibrated to one probe. Meters that detect alpha, beta, and gamma radiation are available.

C Gold Film (Hydrogen Sulfide and Mercury Vapor) Monitors

Hydrogen sulfide (H_2S) and Mercury (Hg) monitors operate on the principle that electric resistivity increases across a gold film as a function of H_2S and Hg concentration. The monitors provide rapid and relatively low detection limits for H_2S and Hg in air. After extensive sampling periods or high concentrations of H_2S and Hg, the gold film must be heated to remove contamination and return the monitor to its original sensitivity.

C Infrared Detectors

Infrared detectors such as the Miniature Infrared Analyzer (MIRAN) use infrared (IR) absorption as a function of specific compounds. MIRAN instruments apply to situations where the contaminants are identified but concentrations are not. MIRAN instruments generally require AC power.

SPECIALIZED ANALYTICAL INSTRUMENTS

The continuous monitors described above provide qualitative measurement of air contaminants. Quantitative measurements in the field can be obtained using more sophisticated instruments, such as portable Gas Chromatographs, to analyze grab samples.

C Direct Air Sampling Portable Gas Chromatographs (GCs)

Portable GCs use gas chromatography to identify and quantify compounds. The time it takes for a compound to move through a chromatographic column is a function of that specific compound or group of compounds. A trained technician with knowledge of the range of expected concentrations of compounds can utilize a portable GC in the field to analyze grab samples. GCs generally require AC power and shelter to operate. This method is limited by its reliance on a short-term grab sample to be representative of the air quality at a site.

C Remote Optical Sensing

This technique, also referred to as long-path or open-path monitoring, involves transmitting either an infrared or ultraviolet light beam across a long open path and measuring the absorbance at specific wavelengths. The technique is capable of analyzing any preselected organic or inorganic volatile compound that can be resolved from compounds naturally occurring in ambient air. Current projected removal applications include perimeter monitoring during site cleanups and measurement of emission source strengths during site assessments.

C TAGA Direct Air Sampling Mass Spectrometer/Mass Spectrometer

The Trace Atmospheric Gas Analyzer (TAGA), which is operated by the U.S. EPA/ERT, is capable of real-time detection of preselected organic compounds at low parts-per-billion concentrations. The instrument has been successfully used by the U.S. EPA/ERT for isolating individual emission plumes and tracking those plumes back to their sources.

APPENDIX B

Air Sampling Equipment and Media/Devices

AIR SAMPLING EQUIPMENT

C High-Volume, Total Suspended Particulate (TSP) Samplers

High-volume TSP samplers collect all suspended particles by drawing air across an 8- by 10-inch glass-quartz filter. The sample rate is adjusted to 40 cubic feet per minute (CFM), or 1134 liters per minute (L/min), and it is held constant by a flow controller over the sample period. The mass of TSPs can be determined by weighing the filter before and after sampling. The composition of the filter varies according to the analytical method and the detection limit required.

C PM-10 Samplers

PM-10 samplers collect particulates with a diameter of 10 microns or less from ambient air. Particulates of this size represent the respirable fraction, and thus are of special significance. PM-10 samplers can be high-volume or low-volume. The high-volume sampler operates in the same manner as the TSP sampler at a constant flow rate of 40 CFM; it draws the sample through a special impactor head which collects particulates of 10 microns or less. The particulate is collected on an 8- by 10-inch filter. The low-volume sampler operates at a rate of approximately 17 L/min. The flow must remain constant through the impactor head to maintain the 10-micron cut-off point. The low-volume PM-10 collects the sample on 37-mm Teflon filters.

C High-Volume PS-1 Samplers

High-volume PS-1 samplers draw a sample through polyurethane foam (PUF) or a combination foam and XAD-2 resin plug, and a glass quartz filter at a rate of 5-10 CFM (144 to 282 L/min). This system is

excellent for measuring low concentrations of semivolatiles, PCBs, pesticides, or chlorinated dioxins in ambient air.

C Area Sampling Pumps

These pumps provide flow-rate ranges of 2-20 L/min and have a telescopic sampling mast with the sampling train. Because of the higher volume, this pump is suitable for sampling low concentrations of airborne contaminants (i.e., asbestos sampling). These pumps are also used for metals, pesticides and PAH sampling which require large sample volumes.

C Personal Sampling Pumps

Personal sampling pumps are reliable portable sampling devices that draw air samples through a number of sampling media including resin tubes, impingers, and filters. Flow rates are usually adjustable from 0.1 to 4 L/min (or 0.01 to .75 L/min with a restrictive orifice) and can remain constant for up to 8 hours on one battery charge or continuously with an AC charger/converter.

C Canister Samplers

Evacuated canister sampling systems use the pressure differential between the evacuated canister and ambient pressure to bleed air into the canister. The sample is bled into the canister at a constant rate over the sampling period using a critical orifice, a mechanically compensated regulator, or a mass flow control device until the canister is near atmospheric pressure.

Pressure canister sampling systems use a pump to push air into the canister. To maintain a higher, more controlled flow, the pump typically controls the pressure differential across a critical orifice at the

inlet of the canister, resulting in a pressurized canister at the completion of sampling.

AIR SAMPLING MEDIA/DEVICES

If possible, before employing a specific sampling method, consult the laboratory that will conduct the analyses. Many of the methods can be modified to provide better results or a wider range of results.

C Summa[®] Canisters

Summa canisters are highly polished passivated stainless steel cylinders. The Summa polishing process brings chrome and nickel to the surface of the canisters, which results in an inert surface. This surface restricts adsorption or reactions that occur on the canister's inner surface after collection. At the site, the canister is either placed in a sampler to control sample collection rate, or opened to collect a grab sample. Samples can be collected by allowing air to bleed into or be pumped into the canister. U.S. EPA/ERT uses 6-liter Summa canisters for VOC and permanent gas analysis.

C Passive Dosimeters

Passive dosimeters are clip-on vapor monitors (samplers) in which the diffused contaminants are absorbed on specially prepared active surfaces. Industrial hygienists commonly use dosimeters to obtain time-weighted averages or concentrations of chemical vapors, as they can trap over 130 organic compounds. Selective dosimeters have also been developed for a number of chemicals including formaldehyde, ethylene oxide, hydrogen sulfide, mercury vapor, nitrogen dioxide, sulfur dioxide, and ozone. Dosimeters must be sent to a laboratory for analysis.

C Polyurethane Foam (PUF)

PUF is a sorbent used with a glass filter for the collection of semivolatile organic compounds such as pesticides, PCBs, chlorinated dioxins and furans, and PAHs. Fewer artifacts (chemical changes that occur

to collected compounds) are produced than with some other solid sorbents. PUF is used with the PS-1 sampler and U.S. EPA Method TO13. PUF can also be used with personal sampling pumps when sampling for PAHs using the Lewis/McCloud method. Breakthrough of the more volatile PCBs and PAHs may occur when using PUF.

C Sampling Bags (Tedlar[®])

Sampling bags, like canisters, transport air samples to the laboratory for analysis. Samples are generally pumped into the bags, but sometimes a lung system is used, in which a pump creates a vacuum around the bag in a vacuum box. Then the sample flows from a source into the bag. This method is used for VOCs, fixed gases (CO₂, O₂, and N₂) and methane.

C Impingers

An impinger allows an air sample to be bubbled through a solution, which collects a specific contaminant by either chemical reaction or absorption. For long sampling periods, the impinger may need to be kept in an ice bath to prevent the solution from evaporating during sampling. The sample is drawn through the impinger by using a sampling pump or more elaborate sampling trains with multiple impingers.

C Sorbent Tubes/Cartridges

A variety of sampling media are available in sorbent tubes, which are used primarily for industrial hygiene. A few examples are carbon cartridges, carbon molecular sieves, Tenax tubes and tube containing the XAD-2 polymer. Depending upon the sorbent material, tubes can be analyzed using either a solvent extraction or thermal desorption. The former technique uses standard laboratory equipment and allows for multiple analyses of the same sample. The latter technique requires special, but readily available, laboratory equipment and allows only one analysis per sample. In addition, thermal desorption typically allows for lower detection limits by two or more orders of magnitude. Whenever sorbent tubes are

being used for thermal desorption, they should be certified as "clean" by the laboratory doing the analysis.

Thermally Desorbed Media

During thermal desorption, high-temperature gas streams are used to remove the compounds collected on a sorbent medium. The gas stream is injected and often cryofocused into an analytical instrument, such as a GC, for compound analysis:

C Tenax Tubes

Tenax tubes are made from commercially available polymer (p-phenylene oxide) packed in glass or stainless steel tubes through which air samples are drawn or sometimes pumped. These tubes are used in U.S. EPA Method TO1 and VOST for volatile nonpolar organic, some polar organic, and some of the more volatile semivolatile organics. Tenax is not appropriate for many of the highly volatile organics (with vapor pressure greater than approximately 200 mm Hg).

C Carbonized Polymers

The carbonized molecular sieve (CMS), a carbonized polymer, is a commercially available, carbon sorbent packed in stainless-steel sampling tubes through which air samples are drawn or sometimes pumped. These are used in U.S. EPA Method TO2 for highly volatile nonpolar compounds which have low-breakthrough volumes on other sorbents. When high-thermal desorption temperatures are used with CMS, more variability in analysis may occur than with other sorbents.

C Mixed Sorbent Tubes

Sorbent tubes can contain two type of sorbents. Combining the advantages of each sorbent into one tube increases the possible types of compounds to be sampled. The combination of two sorbents can also reduce the chance that highly volatile compounds will break through the sorbent media. An example of a mixed sorbent tube is the combination of Tenax and charcoal with a

carbonized molecular sieve. A potential problem with mixed sorbent tubes is the breakthrough of a compound from an earlier sorbent to a later sorbent from which it cannot be desorbed.

Solvent-Extracted Media

Solvent-extracted media use the principle of chemical extraction to remove compounds collected on a sorbent media. The chemical solvent is injected into an instrument, such as a GC, for analysis of compounds. Examples of solvent-extracted media follow:

C Chemically Treated Silica Gel

Silica gel is a sorbent which can be treated with various chemicals. The chemically treated silica gel can then be used to sample for specific compounds in air. Examples include the DNPH-coated silica gel cartridge used with U.S. EPA Method TO11.

C XAD-2 Polymers

XAD-2 polymers usually are placed in tubes, custom-packed sandwich-style with polyurethane foam, and prepared for use with U.S. EPA Method TO13 or the semi-VOST method. The polymers are used for the collection of semivolatile polar and nonpolar organic compounds. The compounds collected on the XAD-2 polymer are chemically extracted for analysis.

C Charcoal Cartridges

Charcoal cartridges, consisting of primary and backup sections, trap compounds by adsorption. Ambient air is drawn through them so that the backup section verifies that breakthrough of the analytes on the first section did not occur, and the sample collection was therefore quantitative. Quantitative sample collection is evident by the presence of target chemicals on the first charcoal section and the absence on the second section. Next, the adsorbed compounds must be eluted, usually with a solvent extraction, and analyzed by GC with a detector, such as a Mass Spectrometer (MS).

C Tenax Tubes

Cartridges are used in OSHA and NIOSH methods in a manner similar to charcoal cartridges but typically for less volatile compounds.

Particulate Filters

Particulate filters are used by having a sampling pump pass air through them. The filter collects the particulates present in the air and is then analyzed for particulate mass or chemical or radiological composition. Particulate filters are made from different materials which are described below.

C Mixed Cellulose Ester (MCE)

MCE is manufactured from mixed esters of cellulose which are a blend of nitro-cellulose and cellulose acetate. MCE filters are used often for particulate sampling.

C Glass Fiber

Glass fiber is manufactured from glass fibers without a binder. Particulate filters with glass fiber provide high flow rates, wet strength, and high, solid holding capacity. Generally, the filters are used for gravimetric analysis of particulates.

C Polyvinyl Chloride

Particulate filters with polyvinyl chloride are resistant to concentrated acids and alkalis. Their low moisture pickup and light tare weight make them ideal for gravimetric analysis.

C Teflon

Teflon is manufactured from polytetrafluorethylene (PTFE). Particulate filters with Teflon are easy to handle and exceptionally durable. Teflon filters are used for metal collection.

C Silver

Particulate filters manufactured from pure silver have high collection efficiency and uniform pore size. These filters are used for mercury collection and analysis.

C Cellulose

Particulate filters with cellulose contain less than 0.01% ash. These filters are used to collect particulates.

1.3.4 Surface Water Sampling (USEPA - Environmental Response Team SOPs)

SOP#: 2013

DATE: 11/17/94

REV. #: 0.0

Scope and Application: This SOP is applicable to the collection of representative liquid samples, both aqueous and non-aqueous from streams, rivers, lakes, ponds, lagoons, and surface impoundments. It includes samples collected from depth, as well as samples collected from the surface. These are standard (i.e., typically applicable) operating procedures that may be varied or changed as required, depending on site conditions, equipment limitations or limitations imposed by the procedure or other procedure limitations. In all instances, the ultimate procedures employed should be documented and associated with the final report. Mention of trade names or commercial products does not constitute USEPA endorsement or recommendation for use.

Method Summary: Sampling situations vary widely, therefore, no universal sampling procedure can be recommended. However, sampling of both aqueous and non-aqueous liquids from the above mentioned sources is generally accomplished through the use of one of the following samplers or techniques:

- Kemmerer bottle
- Bacon bomb sampler
- Dip sampler
- Direct method

These sampling techniques will allow for the collection of representative samples from the majority of surface waters and impoundments encountered.

Sample Preservation Containers, Handling, and Storage: Once samples have been collected, the following procedure should be followed:

1. Transfer the sample(s) into suitable, labeled sample containers.
2. Preserve the sample if appropriate, or use pre-preserved sample bottles. Do not overfill bottles if they are pre-preserved.
3. Cap the container, place in a Ziploc plastic bag and cool to 4°C.
4. Record all pertinent data in the site logbook and on field data sheets.
5. Complete the chain of custody record.
6. Attach custody seals to cooler prior to shipment.
7. Decontaminate all sampling equipment prior to the collection of additional samples with that sampling device.

Interferences and Potential Problems: There are two primary interferences or potential problems with surface water sampling. These include cross contamination of samples and improper sample collection.

1. Cross contamination problems can be eliminated or minimized through the use of dedicated sampling equipment. If this is not possible or practical, then decontamination of sampling equipment is necessary. Refer to the Sampling Equipment Decontamination SOP.
2. Improper sample collection can involve using contaminated equipment, disturbance of the stream or impoundment substrate, and sampling in an obviously disturbed area. Following proper decontamination procedures and minimizing disturbance of the sample site will eliminate these problems.

Equipment/Apparatus: Equipment needed for collection of surface water samples may include (depending on technique chosen):

- Kemmerer bottles
- Bacon bomb sampler
- Dip sampler
- Line and messengers
- Sample bottles/preservatives
- Ziploc bags
- Ice
- Coolers
- Chain of Custody records, custody seals
- Field data sheets
- Decontamination equipment
- Maps/plot plan
- Safety equipment
- Compass
- Tape measure
- Survey stakes, flags, or buoys and anchors
- Camera and film
- Logbook/waterproof pen
- Sample bottle labels

Reagents: Reagents will be utilized for preservation of samples and for decontamination of sampling equipment. The preservatives required are specified by the analysis to be preserved.

Procedures: *Preparation:*

1. Determine the extent of the sampling effort, the sampling methods to be employed, and the types and amounts of equipment and supplies needed.
2. Obtain the necessary sampling and monitoring equipment.
3. Decontaminate or pre-clean equipment, and ensure that it is in working order.
4. Prepare scheduling and coordinate with staff, clients, and regulatory agency, if appropriate.
5. Perform a general site survey prior to site entry, in accordance with the site specific health and safety plan.

6. Use stakes, flagging, or buoys to identify and mark all sampling locations. If required the proposed locations may be adjusted based on site access, property boundaries, and surface obstructions. If collecting sediment samples, this procedure may disturb the bottom.

Representative Sampling Considerations: In order to collect a representative sample, the hydrology and morphometrics of a stream or impoundment should be determined prior to sampling. This will aid in determining the presence of phases or layers in lagoons, or impoundments, flow patterns in streams, and appropriate sample locations and depths. Water quality data should be collected in impoundments, and to determine if stratification is present. Measurements of dissolved oxygen, pH, and temperature can indicate if strata exist that would affect analytical results. Measurements should be collected at one-meter intervals from the substrate to the surface using the appropriate instrument (i.e., a Hydrolab or equivalent).

Water quality measurements such as dissolved oxygen, pH temperature, conductivity, and oxidation-reduction potential can assist in the interpretation of analytical data and the selection of sampling sites and depths when surface water samples are collected. Generally, the deciding factors in the selection of a sampling device for sampling liquids in streams, rivers, lakes, ponds, lagoons, and surface impoundments are:

1. Will the sample be collected from shore or from a boat?
2. What is the desired depth at which you wish to collect the sample?
3. What is the overall depth and flow direction of river or stream?
4. What type of sample will be collected (i.e., water or lagoon liquids)?

Sampler Composition: The appropriate sampling device must be of a proper composition. Selection of samplers constructed of glass, stainless steel, PVC or PTFE (Teflon) should be based upon the analyses to be performed.

Sample Collection: Kemmerer Bottle: A Kemmerer bottle (Figure 3) may be used in most situations where site access is from a boat or structure such as a bridge or pier, and where samples at depth are required. Sampling procedures are as follows:

1. Use a properly decontaminated Kemmerer bottle. Set the sampling device so that the sampling end pieces (upper and lower stoppers) are pulled away from the sampling tube (body), allowing the substance to be sampled to pass through this tube.
2. Lower the pre-set sampling device to the predetermined depth. Avoid bottom disturbance.
3. When the Kemmerer bottle is at the required depth, send down the messenger, closing the sampling device.

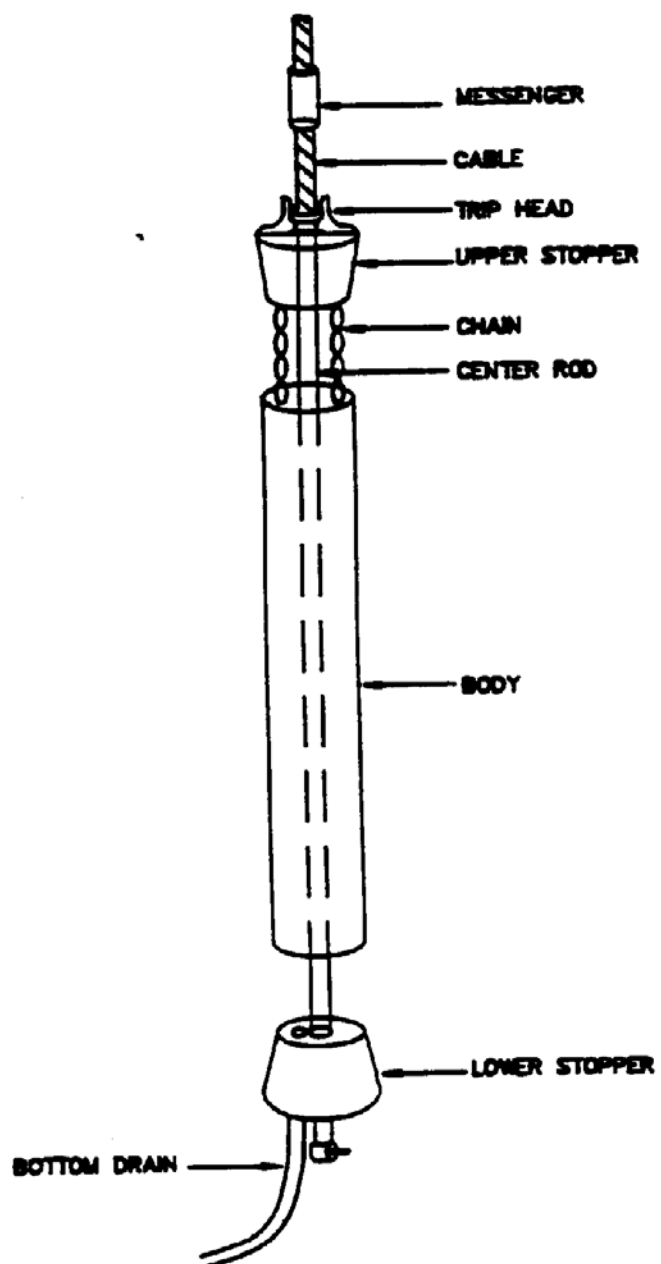


Figure 3. Kemmerer Bottle.

4. Retrieve the sampler and discharge from the bottom drain from the first 10-20 mL to clear any potential contamination of the valve. Transfer the sample to the appropriate sample container.

Bacon Bomb Sampler: A bacon bomb sampler (Figure 4) may be used in situations similar to those outlined for the Kemmerer bottle. Sampling procedures are as follows:

1. Lower the bacon bomb sampler carefully to the desired depth, allowing the line for the trigger to remain slack at all times. When the desired depth is reached, pull the trigger line until taut. This will allow the sampler to fill.
2. Release the trigger line and retrieve the sampler.
3. Transfer the sample to the appropriate sample container by pulling up on the trigger.

Dip Sampler: A dip sampler (Figure 5) is useful in situations where a sample is to be recovered from an outfall pipe or along a lagoon bank where direct access is limited. The long handle on such a device allows access from a discrete location. Sampling procedures are as follows:

1. Assemble the device in accordance with the manufacturer's instructions.
2. Extend the device to the sample location and collect the sample by dipping the sampler into the substance.
3. Retrieve the sampler and transfer the sample to the appropriate sample container.

Direct Method: For streams, rivers, lakes, and other surface waters, the direct method may be utilized to collect water samples from the surface directly into the sample bottle. This method is not to be used for sampling lagoons or other impoundments where contact with contaminants is a concern. Using adequate protective clothing, access the sampling station by appropriate means. For shallow stream stations, collect the sample under the water surface while pointing the sample container upstream; the container must be upstream of the collector. Avoid disturbing the substrate. For lakes and other impoundments, collect the sample under the water surface avoiding surface debris and the boat wake. When using the direct method, do not use prepreserved sample bottles as the collection method may dilute the concentration of preservative necessary for proper sample preservation.

Calculations: This section is not applicable to this SOP.

QA/QC: There are no specific QA activities which apply to the implementation of these procedures. However, the following general QA procedures apply:

1. All data must be documented on field data sheets or within site logbooks.
2. All instrumentation must be operated in accordance with operating instructions as supplied by the manufacturer, unless otherwise specified in the work plan. Equipment checkout and calibration activities must occur prior to sampling/operation and they must be documented.

Data Validation: This section is not applicable to this SOP.

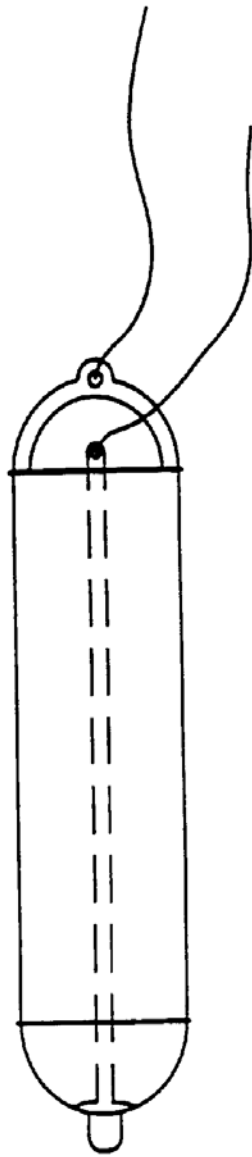


Figure 4. Bacon Bomb Sampler.

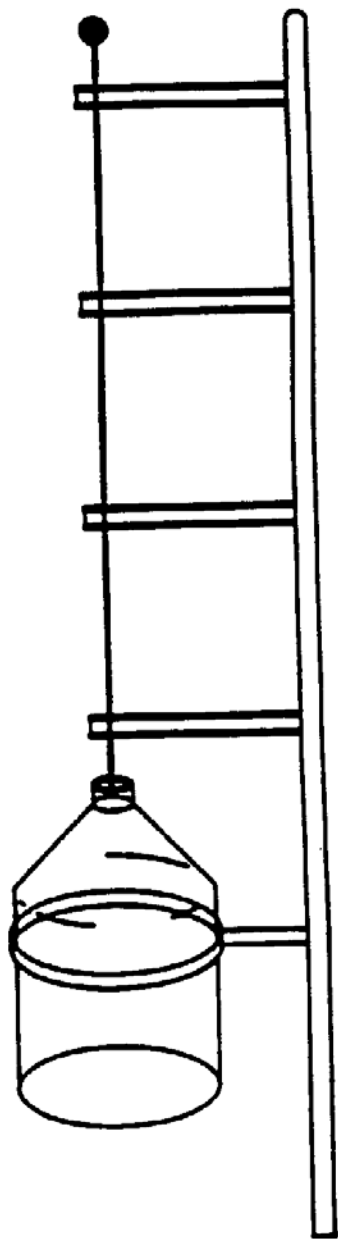


Figure 5. Dip Sampler

Health and Safety: When working with potentially hazardous materials, follow USEPA, OSHA, and corporate health and safety procedures. More specifically, when sampling lagoons or surface impoundments containing known or suspected hazardous substances, adequate precautions must be taken to ensure the safety of sampling personnel. The sampling team members collecting the samples should not get too close to the edge of the impoundment, where bank failure may cause them to lose their balance. The persons performing the samplings should be on a lifeline and be wearing adequate protective equipment. When conducting sampling from a boat in an impoundment or flowing waters, appropriate boating safety procedures should be followed.

1.3.5 Groundwater Well Sampling (USEPA - Environmental Response Team)

SOP#: 2007

DATE: 01/26/95

REV. #: 0.0

Scope and Application: The objective of this SOP is to provide general reference information on sampling of groundwater wells. This guideline is primarily concerned with the collection of water samples from the saturated zone of the subsurface. Every effort must be made to ensure that the sample is representative of the particular zone of water being sampled. These procedures are designed to be used in conjunction with analyses for the most common types of groundwater contaminants (e.g., volatile and semivolatile organic compounds, pesticides, metals, biological parameters). These are standard (i.e., typically applicable) operating procedures that may be varied or changed as required, depending on site conditions, equipment limitations, or limitations imposed by the procedure. In all instances, the ultimate procedures employed should be documented and reported. Mention of trade names or commercial products does not constitute USEPA endorsement or recommendation for use.

Method Summary: In order to obtain a representative groundwater sample for chemical analysis it is important to remove stagnant water in the well casing and the water immediately adjacent to the well before collection of the sample. This may be achieved with one of a number of instruments. The most common of these are the bailer, submersible pump, non-contact gas bladder pump, inertia pump and suction pump. At a minimum, three well volumes should be purged, if possible. Equipment must be decontaminated prior to use and between wells. Once purging is completed and the correct laboratory-cleaned sample containers have been prepared, sampling may proceed. Sampling may be conducted with any of the above instruments and need not be the same as the device used for purging. Care should be taken when choosing the sampling device as some will affect the integrity of the sample. Sampling should occur in a progression from the least to most contaminated well, if this information is known. The growing concern over the past several years over low levels of volatile organic compounds in water supplies has led to the development of highly sophisticated analytical methods that can provide detection limits at part per trillion levels. While the laboratory methods are extremely sensitive, well controlled and quality assured, they cannot compensate for a poorly collected sample. The collection of a sample should be as sensitive, highly developed, and quality assured as the analytical procedures.

Sample Preservation, Containers, Handling, and Storage: The type of analysis for which a sample is being collected determines the type of bottle, preservative, holding time, and filtering

requirements. Samples should be collected directly from the sampling device into appropriate laboratory cleaned containers. Check that a Teflon liner is present in the cap, if required. Attach a sample identification label. Complete a field data sheet, a chain of custody form, and record all pertinent data in the site logbook. Samples shall be appropriately preserved, labeled, logged, and placed in a cooler to be maintained at 4°C. Samples must be shipped well before the holding time is up and ideally should be shipped within 24 hours of collection. It is imperative that samples be shipped or delivered daily to the analytical laboratory in order to maximize the time available for the laboratory to perform the analyses. The bottles should be shipped with adequate packing and cooling to ensure that they arrive intact.

Sample retrieval systems suitable for the valid collection of volatile organic samples include positive displacement bladder pumps, gear driven submersible pumps, syringe samplers and bailers (Barcelona, 1984; Nielsen, 1985). Field conditions and other constraints will limit the choice of appropriate systems. The focus of concern must remain to provide a valid sample for analysis, one which has been subjected to the least amount of turbulence possible. Treatment of the sample with sodium thiosulfate preservative is required only if there is residual chlorine in the water that could cause free radical chlorination and change the identity of the original contaminants. It should not be used if there is no chlorine in the water. Holding time for volatiles analysis is seven days. It is imperative that the sample be shipped or delivered daily to the analytical laboratory. The bottles must be shipped on their sides to aid in maintaining the airtight seal during shipment; with adequate packing and cooling to ensure that they arrive intact. For collection of volatile organic samples, refer to the work plan to ensure that 40 mL glass sample vials with Teflon lined septa are ordered and in sufficient numbers. Check sampling supplies: field kit for chlorine, preservatives, parafilm, foam sleeves and coolers. Due to the extreme trace levels at which volatile organics are detectable, cross contamination and introduction of contaminants must be avoided. Trip blanks are incorporated into the shipment package to provide a check against cross contamination.

Interferences and Potential Problems: *General:* The primary goal in performing groundwater sampling is to obtain a representative sample of the groundwater body. Analysis can be compromised by field personnel in two primary ways: (1) taking an unrepresentative sample, or (2) by incorrect handling of the sample. There are numerous ways of introducing foreign contaminants into a sample, and these must be avoided by following strict sampling procedures and utilizing trained field personnel.

Purging: In a nonpumping well, there will be little or no vertical mixing of the water, and stratification will occur. The well water in the screened section will mix with the groundwater due to normal flow patterns, but the well water above the screened section will remain isolated, become stagnant, and may lack the contaminants representative of the groundwater. Persons sampling should realize that stagnant water may contain foreign material inadvertently or deliberately introduced from the surface, resulting in an unrepresentative sample. To safeguard against collecting nonrepresentative stagnant water, the following guidelines and techniques should be adhered to during sampling:

1. As a general rule, all monitor wells should be pumped or bailed prior to sampling. Purged water should be containerized onsite or handled as specified in the site specific project

plan. Evacuation of a minimum of one volume of water in the well casing, and preferably three to five volumes, is recommended for a representative sample. In a high-yielding groundwater formation and where there is no stagnant water in the well above the screened section, evacuation prior to sample withdrawal is not as critical. However, in all cases where the monitoring data are to be used for enforcement actions, evacuation is recommended.

2. When purging with a pump (not a bailer), the pump should be set at the screened interval, or if the well is an open-rock well, it should be set at the same depth the sample will be collected. When sampling a screened well, the sample should also be collected from the same depth the pump was set at.
3. The well should be sampled as soon as possible after purging.
4. Analytical parameters typically dictate whether the sample should be collected through the purging device, or through a separate sampling instrument.
5. For wells that can be pumped or bailed to dryness with the equipment being used, the well should be evacuated and allowed to recover prior to collecting a sample. If the recovery rate is fairly rapid and time allows, evacuation of more than one volume of water is preferred. If recovery is slow, sample the well upon recovery after one evacuation.
6. A non-representative sample can also result from excessive pre-pumping of the monitoring well. Stratification of the leachate concentration in the groundwater formation may occur, or heavier-than-water compounds may sink to the lower portions of the aquifer. Excessive pumping can dilute or increase the contaminant concentrations from what is representative of the sampling point of interest.

Materials: Materials of construction for samplers and evacuation equipment (bladders, pump, bailers, tubing, etc.) should be limited to stainless steel, Teflon, and glass in areas where concentrations are expected to be at or near the detection limit. The tendency of organics to leach into and out of many materials make the selection of materials critical for trace analyses. The use of plastics, such as PVC or polyethylene, should be avoided when analyzing for organics. However, PVC may be used for evacuation equipment as it will not come in contact with the sample, and in highly contaminated wells, disposable equipment (i.e., polypropylene bailers) may be appropriate to avoid cross-contamination.

Materials of construction (bladders/ pumps, bailers, tubing, etc.) suitable for collecting and handling volatile organic samples should be limited to stainless steel, Teflon, and glass in areas in which detection limit range concentrations are expected. The tendency of organics to leach into and out of many materials, make the selection of materials critical for these trace analyses. The use of plastics should be avoided. There are numerous ways of introducing foreign contaminants into a sample, and these must be avoided by following strict sampling procedures and utilization of trained personnel.

Advantages/Disadvantages of Certain Equipment:

Bailers:

<u>Advantages</u>	<u>Disadvantages</u>
Only practical limitations on size and materials	Time-consuming to flush a large well of stagnant water

Portable

Transfer of sample may cause aeration

Inexpensive, so it can be dedicated and hung in a well, thereby reducing the chances of cross contamination

Stoppers at the bottom of the bailer usually leak thus the bailer must be brought to the surface rapidly

Minimal outgassing of volatile organics while sample is in bailer

If the bailer is allowed to hit the bottom of the well boring, gravel can displace the ball valve not allowing the bailer to hold water

No power source needed

Readily available

Removes stagnant water first

Rapid, simple method for removing small volumes of purge water

Submersible Pumps:

Advantages

Portable and can be transported to several wells

Depending upon the size of the pump and the pumping depths, relatively high pumping rates are possible

Generally very reliable and does not require priming

Disadvantages

Potential for effects on analysis of trace organics

Heavy and cumbersome to deal with, particularly in deeper wells

Expensive

Power source needed

Sediment in water may cause problems with the pumps

Impractical in low yielding or shallow wells

Non-Contact Gas Bladder Pumps:

Advantages

Maintains integrity of sample

Easy to use

Disadvantages

Difficulty in cleaning, though dedicated tubing and bladder may be used

Only useful to about 30.5 meters

Can sample from discrete locations within the monitor well

Supply of gas for operation, gas bottles and compressors are often difficult to obtain and are cumbersome

Relatively low pumping rates

Requires air compressor or pressurized gas source and control box

Suction Pumps:

Advantages

Portable, inexpensive, and readily available

Disadvantages

Restricted to areas with water levels within

Vacuum can cause loss of dissolved gasses

Pump must be primed and vacuum is often pumping approximately 6 to 8 meters of the ground surface and volatile organics difficult to maintain during initial stages of pumping

Inertia Pumps

Advantages

Portable, inexpensive, and readily available

Disadvantages

Restricted to areas with water levels within these manual pumps diameter wells approximately 21 meters of the ground surface

Offers a rapid method for purging relatively shallow wells

May be time consuming to purge wells

Labor intensive

WaTerra pumps are only effective in 51 millimeters

Equipment Apparatus: *Equipment Checklist:*

General

- Water level indicator
- Electric sounder
- Steel tape
- Transducer
- Reflection sounder
- Airline
- Depth sounder
- Appropriate keys for well cap locks
- Steel brush

- Hnu or ova (whichever is most appropriate)
- Logbook
- Calculator
- Field data sheets and samples labels
- Chain of custody records and seals
- Sample containers
- Engineer's rule
- Sharp knife (locking blade)
- Tool box (to include at least: screwdrivers, pliers, hacksaw, hammer, flashlight, adjustable wrench)
- Leather work gloves
- Appropriate health and safety gear
- Plastic sheeting
- Shipping containers
- Packing materials
- Bolt cutters
- Ziploc plastic bags
- Containers for evacuation liquids
- Decontamination solutions
- Tap water
- Non phosphate soap
- Several brushes
- Pails or tubs
- Aluminum foil
- Garden sprayer
- Preservatives
- Distilled or deionized water
- Fire extinguisher (if using a generator for your power source)

Bailers

- Clean, decontaminated bailers of appropriate size and construction material
- Nylon line, enough to dedicate to each well
- Teflon-coated bailer wire
- Sharp knife
- Aluminum foil (to wrap clean bailers)
- Five gallon bucket

Submersible Pump

- Pump(s)
- Generator (110, 120, or 240 volt) or 12 volt battery if inaccessible to field vehicle – amp meter is useful
- 25.5 mm black PVC coil tubing - enough to dedicate to each well
- Hose clamps
- Safety cable

- Tool box supplement
- Pipe wrenches
- Wire strippers
- Electrical tape
- Heat shrink
- Hose connectors
- Teflon tape
- Winch, pulley or hoist
- Gasoline for generator/gas can
- Flow meter with gate valve
- 25.5 mm nipples and various plumbing (i.e., pipe connectors)
- Control box (if necessary)

Non-Gas Contact Bladder Pump

- Non-gas contact bladder pump
- Compressor or nitrogen gas tank
- Batteries and charger
- Teflon tubing - enough to dedicate to each well
- Swagelock fitting
- Toolbox supplements - same as submersible pump
- Control box (if necessary)

Suction Pump

- Pump
- 25.5 mm black PVC coil tubing - enough to dedicate to each well
- Gasoline - if required
- Toolbox
- Plumbing fittings
- Flow meter with gate valve

Inertia Pump

- Pump assembly (WaTerra pump, piston pump)
- Five gallon bucket

Reagents: Reagents may be utilized for preservation of samples and for decontamination of sampling equipment. The preservatives required are specified by the analysis to be performed. Decontamination solutions are specified in ERT SOP #2006, Sampling Equipment Decontamination.

Procedure: *Preparation:*

1. Determine the extent of the sampling effort, the sampling methods to be employed, and the types and amounts of equipment and supplies needed (i.e, diameter and depth of wells to be sampled).

2. Obtain necessary sampling and monitoring equipment, appropriate to type of contaminant being investigated. For collection of volatile organic samples, refer to the work plan to ensure that 40 mL glass sample vials with Teflon lined septa are ordered and in sufficient numbers. Check sampling supplies: field kit for chlorine, preservatives, parafilm, foam sleeves, and coolers. Due to extreme trace levels at which volatile organics are detectable, cross contamination and introduction of contaminants must be avoided. Trip blanks are incorporated into the shipment package to provide a check against cross-contamination.
3. Decontaminate or pre-clean equipment, and ensure that it is in working order.
4. Prepare scheduling and coordinate with staff, clients, and regulatory agency, if appropriate.
5. Perform a general site survey prior to site entry in accordance with the site specific health and safety plan.
6. Identify and mark all sampling locations.

Field Preparation:

1. Start at the least contaminated well, if known.
2. Lay plastic sheeting around the well to minimize likelihood of contamination of equipment from soil adjacent to the well.
3. Remove locking well cap, note location, time of day, and date in field notebook or appropriate log form.
4. Remove well casing cap.
5. Screen headspace of well with an appropriate monitoring instrument to determine the presence of volatile organic compounds and record in site logbook.
6. Lower water level measuring device or equivalent (i.e., permanently installed transducers or airline) into well until water surface is encountered.
7. Measure distance from water surface to reference measuring point on well casing or protective barrier post and record in site logbook. Alternatively, if no reference point, note that water level measurement is from top of steel casing, top of PVC riser pipe, from ground surface, or some other position on the well head. If floating organics are of concern, this can be determined by measuring the water level with an oil/water interface probe that measures floating organics.
8. Measure total depth of well (at least twice to confirm measurement) and record in site logbook or on field data sheet.
9. Calculate the volume of water in the well and the volume to be purged using the calculations near the end of this SOP.
10. Select the appropriate purging and sampling equipment.
11. If residual chlorine is suspected, use the Hach Field Test Kit for chlorine to determine if there is residual chlorine in the water to be sampled. If there is, treat the sample vial with a crystal of sodium thiosulfate prior to sample collection.

Purging: The amount of flushing a well receives prior to sample collection depends on the intent of the monitoring program and the hydrogeologic conditions. Programs where overall quality determination of water resources are involved may require long pumping periods to obtain a sample that is representative of a large volume of that aquifer. The pumped volume can be determined prior to sampling so that the sample is collected after a known volume of the water is

evacuated from the aquifer, or the well can be pumped until the stabilization of parameters such as temperature, electrical conductance, pH, or turbidity has occurred.

However, monitoring to define a contaminant plume requires a representative sample of a small volume of the aquifer. These circumstances require that the well be pumped enough to remove the stagnant water but not enough to induce flow from surrounding areas. Generally, three well volumes are considered effective, or calculations can be made to determine, on the basis of the aquifer parameters and well dimensions, the appropriate volume to remove prior to sampling.

During purging, water level measurements may be taken regularly at 15-30 second intervals. These data may be used to compute aquifer transmissivity and other hydraulic characteristics. The following well evacuation devices are most commonly used. Other evacuation devices are available, but have been omitted in this discussion due to their limited use.

Bailers: Bailers are the simplest purging device used and have many advantages. They generally consist of a rigid length of tube, usually with a ball check-valve at the bottom. A line is used to lower the bailer into the well and retrieve a volume of water. The three most common types of bailer are PVC, Teflon, and stainless steel.

This manual method of purging is best suited to shallow or narrow diameter wells. For deep, larger diameter wells which require evacuation of large volumes of water, other mechanical devices may be more appropriate.

Operation: Equipment needed will include a clean decontaminated bailer, Teflon or nylon line, a sharp knife, and plastic sheeting.

1. Determine the volume of water to be purged as described in the calculations near the end of this SOP.
2. Lay plastic sheeting around the well to prevent contamination of the bailer line with foreign materials.
3. Attach the line to the bailer and slowly lower until the bailer is completely submerged, being careful not to drop the bailer to the water, causing turbulence and the possible loss of volatile organic contaminants.
4. Pull bailer out ensuring that the line either falls onto a clean area of plastic sheeting or never touches the ground.
5. Empty the bailer into a pail until full to determine the number of bails necessary to achieve the required purge volume.
6. Thereafter, pour the water into a container and dispose of purge waters as specified in the site-specific sampling plan.

Submersible Pumps: The use of submersible pumps for sample collection is permissible provided they are constructed of suitable non-contaminating materials. The chief drawback, however, is the difficulty avoiding cross-contamination between wells. Although some units can be disassembled easily to allow surfaces contacted by contaminants to be cleaned, field decontamination may be difficult and require solvents that can affect sample analysis. The use of submersible pumps in multiple well-sampling programs, therefore, should be carefully

considered against other sampling mechanisms (bailers, bladder pumps). In most cases, a submersible pump, however, may be the only practical sampling device for extremely deep wells (greater than 91 meters of water). Under those conditions, dedicated pump systems should be installed to eliminate the potential for cross-contamination. A sample can be collected by bailer after purging.

Submersible pumps generally use one of two types of power supplies, either electric or compressed gas or air. Electric powered pumps can run off a 12 volt DC rechargeable battery, or a 110 or 220 volt AC power supply. Those units powered by compressed air normally use a small electric or gas-powered air compressor. They may also utilize compressed gas (i.e., nitrogen) from bottles. Different size pumps are available for different depth or diameter monitoring wells.

Operation:

1. Determine the volume of water to be purged as described in near the end of this SOP.
2. Lay plastic sheeting around the well to prevent contamination of pumps, hoses or lines with foreign materials.
3. Assemble pump, hoses and safety cable, and lower the pump into the well. Make sure the pump is deep enough so all the water is not evacuated. (Running the pump without water may cause damage.)
4. Attach flow meter to the outlet hose to measure the volume of water purged.
5. Use a ground fault circuit interrupter (GFCI) or ground the generator to avoid possible electric shock.
6. Attach power supply, and purge the well until the specified volume of water has been evacuated (or until field parameters, such as temperature, pH, conductivity, etc., have stabilized). Do not allow the pump to run dry. If the pumping rate exceeds the well recharge rate, lower the pump further into the well, and continue pumping.
7. Collect and dispose of purge waters as specified in the site-specific sampling plan.

Non-Contact Gas Bladder Pumps: For this procedure, an all stainless-steel and Teflon Middleburg-squeeze bladder pump (e.g., IEA, TIMCO, Well Wizard, Geoguard, and others) is used to provide the least amount of material interference to the sample (Barcelona, 1985). Water comes into contact with the inside of the bladder (Teflon) and the sample tubing (also Teflon) which may be dedicated to each well. Some wells may have permanently installed bladder pumps, (i.e., Well Wizard, Geoguard), that will be used to sample for all parameters.

Operation:

1. Assemble Teflon tubing, pump, and charged control box.
2. Procedure for purging with a bladder pump is the same as for a submersible pump.
3. Be sure to adjust flow rate to prevent violent jolting of the hose as sample is drawn in.

Suction Pumps: There are many different types of suction pumps. They include: centrifugal, peristaltic, and diaphragm. Diaphragm pumps can be used for well evacuation at a fast pumping rate and sampling at a low pumping rate. The peristaltic pump is a low volume pump that uses

rollers to squeeze the flexible tubing thereby creating suction. This tubing can be dedicated to a well to prevent cross contamination. Peristaltic pumps, however, require a power source.

Operation:

1. Assembly of the pump, tubing, and power source if necessary.
2. Procedure for purging with a suction pump is exactly the same as for a submersible pump.

Inertia Pumps: Inertia pumps such as the WaTerra pump and piston pump, are manually operated. They are most appropriate to use when wells are too deep to bail by hand, or too shallow or narrow (or inaccessible) to warrant an automatic (submersible, etc.) pump. These pumps are made of plastic and may be either decontaminated or discarded.

Operation:

1. Determine the volume of water to be purged as described near the end of this SOP.
2. Lay plastic sheeting around the well to prevent contamination of pumps or hoses with foreign materials.
3. Assemble pump and lower to the appropriate depth in the well.
4. Begin pumping manually, discharging water into a 5 gallon bucket (or other graduated vessel). Purge until specified volume of water has been evacuated (or until field parameters such as temperature, pH, conductivity, etc. have stabilized).
5. Collect and dispose of purge waters as specified in the site specific project plan.

Sampling: Sample withdrawal methods require the use of pumps, compressed air, bailers, and samplers. Ideally, purging and sample withdrawal equipment should be completely inert, economical to manufacture, easily cleaned, sterilized, reusable, able to operate at remote sites in the absence of power resources, and capable of delivering variable rates for sample collection. There are several factors to take into consideration when choosing a sampling device. Care should be taken when reviewing the advantages or disadvantages of any one device. It may be appropriate to use a different device to sample than that which was used to purge. The most common example of this is the use of a submersible pump to purge and a bailer to sample.

Bailers: The positive-displacement volatile sampling bailer is perhaps the most appropriate for collection of water samples for volatile analysis. Other bailer types (messenger, bottom fill, etc.) are less desirable, but may be mandated by cost and site conditions.

Operation:

1. Surround the monitor well with clean plastic sheeting. If using the GPI bailer, insert a vial into the claim and assemble the unit.
2. Attach a line to a clean decontaminated bailer.
3. Lower the bailer slowly and gently into the well, taking care not to shake the casing sides or to splash the bailer into the water. Stop lowering at a point adjacent to the screen.
4. Allow bailer to fill and then slowly and gently retrieve the bailer from the well avoiding contact with the casing, so as not to knock flakes of rust or other foreign

materials into the bailer. If using the GPI bailer for collecting volatile organic samples, once at the surface, remove the bailer from and remove the vial. Begin slowly pouring from the bailer, and collect the duplicate the cable. Carefully open the GPI bailer unit samples from the midstream sample.

5. Remove the cap from the sample container and place it on the plastic sheet or in a location where it won't become contaminated.
6. Begin slowly pouring from the bailer.
7. Filter and preserve samples as required by sampling plan.
8. Cap the sample container tightly and place prelabeled sample container in a carrier.
9. Replace the well cap.
10. Log all samples in the site logbook and on field data sheets and label all samples.
11. Package samples and complete necessary paperwork.
12. Transport sample to decontamination zone for preparation for transport to analytical laboratory.

Submersible Pumps: Although it is recommended that samples not be collected with a submersible pump for the reasons stated earlier, there are some situations where they may be used.

Operation:

1. Allow the monitor well to recharge after purging, keeping the pump just above screened section.
2. Attach gate valve to hose (if not already fitted), and reduce flow of water to a manageable sampling rate.
3. Assemble the appropriate bottles.
4. If no gate valve is available, run the water down the side of a clean jar and fill the sample bottles from the jar.
5. Cap the sample container tightly and place prelabeled sample container in a carrier.
6. Replace the well cap.
7. Log all samples in the site logbook and on the field data sheets and label all samples.
8. Package samples and complete necessary paperwork.
9. Transport sample to decontamination zone for preparation for transport to the analytical laboratory.
10. Upon completion, remove pump and assembly and fully decontaminate prior to setting into the next sample well. Dedicate the tubing to the hole.

Non-Contact Gas Bladder Pumps: The use of a non-contact gas positive displacement bladder pump is often mandated by the use of dedicated pumps installed in wells. These pumps are also suitable for shallow (less than 30.5 meters) wells. They are somewhat difficult to clean, but may be used with dedicated sample tubing to avoid cleaning. These pumps require a power supply and a compressed gas supply (or compressor). They may be operated at variable flow and pressure rates making them ideal for both purging and sampling.

Barcelona (1984) and Nielsen (1985) report that the non-contact gas positive displacement pumps cause the least amount of alteration in sample integrity as compared to other sample retrieval methods.

Operation:

1. Allow well to recharge after purging.
2. Assemble the appropriate bottles.
3. Turn pump on, increase the cycle time and reduce the pressure to the minimum that will allow the sample to come to the surface.
4. Cap the sample container tightly and place prelabeled sample container in a carrier.
5. Replace the well cap.
6. Log all samples in the site logbook and on field data sheets and label all samples.
7. Package samples and complete necessary paperwork.
8. Transport sample to decontamination zone for preparation for transport to analytical laboratory.
9. On completion, remove the tubing from the well and either replace the Teflon tubing and bladder with new dedicated tubing and bladder or rigorously decontaminate the existing materials.
10. Nonfiltered samples shall be collected directly from the outlet tubing into the sample bottle.
11. For filtered samples, connect the pump outlet tubing directly to the filter unit. The pump pressure should remain decreased so that the pressure build up on the filter does not blow out the pump bladder or displace the filter. For the Geotech barrel filter, no actual connections are necessary so this is not a concern.

Suction Pumps: In view of the limitations of these type pumps, they are not recommended for sampling purposes.

Inertia Pumps: Inertia pumps may be used to collect samples. It is more common, however, to purge with these pumps and sample with a bailer.

Operation:

1. Following well evacuation, allow the well to recharge.
2. Assemble the appropriate bottles.
3. Since these pumps are manually operated, the flow rate may be regulated by the sampler. The sample may be discharged from the pump outlet directly into the appropriate sample container.
4. Cap the sample container tightly and place prelabeled sample container in a carrier.
5. Replace the well cap.
6. Log all samples in the site logbook and on field data sheets and label all samples.
7. Package samples and complete necessary paperwork.
8. Transport sample to decontamination zone for preparation for transport to the analytical laboratory.
9. Upon completion, remove pump and decontaminate or discard, as appropriate.

Sample Retrieval – Syringe: A limited number of commercial syringe type samplers are available (IEA, TIMCO, etc.) and some are homemade devices. These devices are claimed to provide good quality samples for volatile analysis, but are severely limited in sample volume and are specific to sampling for volatiles. Essentially, they are operated with an evacuated chamber that is lowered down the well, and allowed to fill with the pressure of the water. The entire mechanism is then brought to the surface with the sample. The sample may then be transferred to a sample vial, or the entire unit may be sent as the sample container.

1. Evacuate the syringe if necessary, and lower the sampling device to just below the well screen.
2. Remove the constriction from the device and allow the sample to fill the syringe, apply slight suction as necessary.
3. Bring unit to the surface. If necessary, transfer the sample to vials, as outlined in steps 2 through 7 above.

Filtering: For samples requiring filtering, such as total metals analysis, the filter must be decontaminated prior to and between uses. Filters work by two methods. A barrel filter such as the “Geotech” filter works with a bicycle pump, used to build up positive pressure in the chamber containing the sample which is then forced through the filter paper (minimum size 0.45 μm) into a jar placed underneath. The barrel itself is filled manually from the bailer or directly via the hose of the sampling pump. The pressure must be maintained up 0.0202 kg/mm^2 by periodic pumping.

A vacuum type filter involves two chambers; the upper chamber contains the sample and a filter (minimum size 0.45 μm) divides the chambers. Using a hand pump or a Gilian type pump, air is withdrawn from the lower chamber, creating a vacuum and thus causing the sample to move through the filter into the lower chamber where it is drained into a sample jar. Repeated pumping may be required to drain all the sample into the lower chamber. If preservation of the sample is necessary, this should be done after filtering.

Post Operation: After all samples are collected and preserved, the sampling equipment should be decontaminated prior to sampling another well to prevent cross-contamination of equipment and monitor wells between locations.

1. Decontaminate all equipment.
2. Replace sampling equipment in storage containers.
3. Prepare and transport groundwater samples to the laboratory. Check sample documentation and make sure samples are properly packed for shipment.

Special Considerations for Volatile Organic Analysis (VOA) Sampling: The proper collection of a sample for volatile organics requires minimal disturbance of the sample to limit volatilization and therefore a loss of volatiles from the sample.

Sample retrieval systems suitable for the valid collection of volatile organic samples are: positive displacement bladder pumps, gear driven submersible pumps, syringe samplers, and bailers

(Barcelona, 1984; Nielsen, 1985). Field conditions and other constraints will limit the choice of appropriate systems. The focus of concern must be to provide a valid sample for analysis, one which has been subjected to the least amount of turbulence possible.

The following procedures should be followed:

1. Open the vial, set cap in a clean place, and collect the sample during the middle of the cycle. When collecting duplicates, collect both samples at the same time.
2. Fill the vial to just overflowing. Do not rinse the vial, nor excessively overflow it. There should be a convex meniscus on the top of the vial.
3. Check that the cap has not been contaminated (splashed) and carefully cap the vial. Place the cap directly over the top and screw down firmly. Do not overtighten and break the cap.
4. Invert the vial and tap gently. Observe vial for at least ten seconds. If an air bubble appears, discard the sample and begin again. It is imperative that no entrapped air is in the sample vial.
5. Immediately place the vial in the protective foam sleeve and place into the cooler, oriented so that it is lying on its side, not straight up.
6. The holding time for VOAs is seven days. Samples should be shipped or delivered to the laboratory daily so as not to exceed the holding time. Ensure that the samples remain at 4°C, but do not allow them to freeze.

Calculations: If it is necessary to calculate the volume of the well, utilize the following equation:

Well volume $\pi r^2 h (cf)$ [Equation 1]:

$\pi = 3.14$

r = radius of monitoring well (meters)

h = height of the water column (meters) [This may be determined by subtracting the depth to water from the total depth of the well as measured from the same reference point.]

cf = conversion factor (L/m^3) = 1,000 L/m^3

[In this equation, 1,000 L/m^3 is the necessary conversion factor.]

$\pi r^2 (cf)$ [Equation 2]

Monitor well diameters are typically 50.8mm, 76.2mm, 101.6mm, or 152.4mm. Knowing the diameter of the monitor well, there are a number of standard conversion factors which can be used to simplify the equation above.

The volume, in gallons per linear foot, for various standard monitor well diameters can be calculated as follows:

$\pi = 3.14$

r = radius of monitoring well (m)

cf = conversion factor (1,000 L/m^3)

For a 50.8mm diameter well, the volume per linear foot can be calculated as follows:

vol/linear meter $\pi r^2 (cf)$ [Equation 3]

$3.14 (0.0254m)^2 1,000 L/m^3$

2.03 L/m

Remember that if you have a 50.8mm diameter well, you must convert this to the radius in feet to be able to use the equation.

The conversion factors for the common size monitor wells are as follows:

Well diameter (mm)	50.8	76.2	101.6	152.4
Volume (L/m.)	2.027	4.560	8.107	18.24

If you utilize the conversion factors above, the equation should be modified as follows:

Well volume (h)(cf) [Equation 4]

h = height of water column (meters)

cf = the conversion factor calculated from Equation 2

The well volume is typically tripled to determine the volume to be purged.

QA/QC: There are no specific QA activities which apply to the implementation of these procedures. However, the following general QA procedures apply:

1. All data must be documented on field data sheets or within site logbooks.
2. All instrumentation must be operated in accordance with operating instructions as supplied by the manufacturer, unless otherwise specified in the work plan. Equipment checkout and calibration activities must occur prior to sampling/operation and they must be documented.
3. The collection of rinsate blanks is recommended to evaluate potential for cross contamination from the purging and/or sampling equipment.
4. Trip blanks are required if analytical parameters include VOAs.

Data Validation: This section is not applicable to this SOP.

Health and Safety: When working with potentially hazardous materials, follow U.S. EPA, OSHA or REAC health and safety guidelines. More specifically, depending upon the site specific contaminants, various protective programs must be implemented prior to sampling the first well. The site health and safety plan should be reviewed with specific emphasis placed on the protection program planned for the well sampling tasks. Standard safe operating practices should be followed such as minimizing contact with potential contaminants in both the vapor phase and liquid matrix through the use of respirators and disposable clothing.

When working around volatile organic contaminants:

1. Avoid breathing constituents venting from the well.
2. Pre-survey the well head-space with flame ionization/photoionization prior to sampling.
3. If monitoring results indicate organic constituents, sampling activities may be conducted in Level C protection. At a minimum, skin protection will be afforded by disposable protective clothing.

Physical hazards associated with well sampling:

1. Lifting injuries associated with pump and bailers retrieval; moving equipment.
2. Use of pocket knives for cutting discharge hose.

3. Heat/cold stress as a result of exposure to extreme temperatures and protective clothing.
4. Slip, trip, and fall conditions as a result of pump discharge.
5. Restricted mobility due to the wearing of protective clothing.
6. Electrical shock associated with use of submersible pumps is possible. Use a GFCI or a copper grounding stake to avoid this problem.

1.3.6 Sediment Sampling (USEPA- Environmental Response Team)

SOP#: 2016

DATE: 11/17/94

REV. #: 0.0

Scope and Application: This SOP is applicable to the collection of representative sediment samples. Sediments may be analyzed for biological, chemical, or physical characteristics to determine the following:

- Toxicity
- Biological availability and effects of contaminants
- Benthic biota
- Extent and magnitude of contamination
- Contaminant migration pathways and source
- Fate of contaminants
- Grain size distribution

The methodologies discussed in this SOP are applicable to the sampling of sediment in both flowing and standing water. They are generic in nature and may be modified in whole or part to meet the handling and analytical requirements of the contaminants of concern, as well as the constraints presented by site conditions and equipment limitations. However, if modifications occur, they should be documented in a site or personal logbook and discussed in reports summarizing field activities and analytical results.

For the purposes of this procedure, sediments are those mineral and organic materials situated beneath an aqueous layer. The aqueous layer may be either static (lakes, ponds, and impoundments) or flowing (rivers and streams).

Mention of trade names or commercial products does not constitute USEPA endorsement or recommendation for use.

Method Summary: Sediment samples may be collected using a variety of methods and equipment, depending on the depth of the aqueous layer, the portion of the sediment profile required (surface vs. subsurface), the type of sample required (disturbed vs. undisturbed), contaminants present, and sediment type.

Sediment is collected from beneath an aqueous layer either directly (using a hand held device such as a shovel, trowel, or auger) or indirectly (using a remotely activated device such as an Ekman or Ponar dredge). Following collection, sediment is transferred from the sampling device to a sample container of appropriate size and construction for the analyses requested. If

composite sampling techniques are employed, multiple grabs are placed into a container constructed of inert material, homogenized, and transferred to sample containers appropriate for the analyses requested. The homogenization procedure should not be used if sample analysis includes volatile organics; in this case, sediment, or multiple grabs of sediment, should be transferred directly from the sample collection device or homogenization container to the sample container.

Sample Preservation, Containers, Handling, and Storage:

1. Chemical preservation of solids is generally not recommended. Cooling to 4°C is usually the best approach, supplemented by the appropriate holding time for the analyses requested.
2. Wide mouth glass containers with Teflon-lined caps are utilized for sediment samples. The sample volume is a function of the analytical requirements and will be specified in the work plan.
3. If analysis of sediment from a discrete depth or location is desired, sediment is transferred directly from the sampling device to a labeled sample container(s) of appropriate size and construction for the analyses requested. Transfer is accomplished with a stainless steel or plastic lab spoon or equivalent.
4. If composite sampling techniques or multiple grabs are employed, equal portions of sediment from each location are deposited into a stainless steel, plastic, or other appropriate composition (e.g., Teflon) containers. The sediment is homogenized thoroughly to obtain a composite representative of the area sampled. The composite sediment sample is transferred to a labeled container(s) of appropriate size and construction for the analyses requested. Transfer of sediment is accomplished with a stainless steel or plastic lab spoon or equivalent. Samples for volatile organic analysis must be transferred directly from the sample collection device or pooled from multiple areas in the homogenization container prior to mixing. This is done to minimize loss of contaminant due to volatilization during homogenization.
5. All sampling devices should be decontaminated, then wrapped in aluminum foil. The sampling device should remain in this wrapping until it is needed. Each sampling device should be used for only one sample. Disposable sampling devices for sediment are generally impractical due to cost and the large number of sediment samples that may be required. Sampling devices should be cleaned in the field using the decontamination procedure described in the Sampling Equipment Decontamination SOP.

Interferences and Potential Problems: Substrate particle size and organic matter content are a direct consequence of the flow characteristics of a waterbody. Contaminants are more likely to be concentrated in sediments typified by fine particle size and a high organic matter content. This type of sediment is most likely to be collected from depositional zones. In contrast, coarse sediments with low organic matter content do not typically concentrate pollutants and are generally found in erosional zones. The selection of a sampling location can, therefore, greatly influence the analytical results and should be justified and specified in the Work Plan.

Equipment/Apparatus: Equipment needed for collection of sediment samples may include:

- Maps/plot plan

- Safety equipment
- Compass
- Tape measure
- Survey stakes, flags, or buoys and anchors
- Camera and film
- Stainless steel, plastic, or other appropriate composition bucket
- 4-oz., 8-oz., and 1 liter, wide mouth jars with Teflon-lined lids
- Ziploc plastic bags
- Logbook
- Sample jar labels
- Chain of custody records, field data sheets
- Cooler(s)
- Ice
- Decontamination supplies/equipment
- Spade or shovel
- Spatula
- Scoop
- Trowel
- Bucket auger
- Tube auger
- Extension rods
- “T” handle
- Sediment coring device (tube, drive head, eggshell check valve, nosecone, acetate tube, extension rods, “T” handle)
- Ponar dredge
- Ekman dredge
- Nylon rope or steel cable
- Messenger device

Reagents: Reagents are not used for preservation of sediment samples. Decontamination solutions are specified in the Sampling Equipment Decontamination SOP.

Procedures: *Preparation:*

1. Determine the objective(s) and extent of the sampling effort. The sampling methods to be employed, and the types and amounts of equipment and supplies required will be a function of site characteristics and objectives of the study.
2. Obtain the necessary sampling and monitoring equipment.
3. Prepare schedules and coordinate with staff, client, and regulatory agencies, if appropriate.
4. Decontaminate or pre-clean equipment, and ensure that it is in working order.
5. Perform a general site survey prior to site entry in accordance with the site specific health and safety plan.
6. Use stakes, flagging, or buoys to identify and mark all sampling locations. Specific site factors including flow regime, basin morphometry, sediment characteristics, depth of overlying aqueous layer, contaminant source, and extent and nature of contamination

should be considered when selecting sample locations. If required, the proposed locations may be adjusted based on site access, property boundaries, and surface obstructions.

Sample Collection: Selection of a sampling device is most often contingent upon: (1) the depth of water at the sampling location, and (2) the physical characteristics of the sediment to be sampled. The following procedures may be utilized:

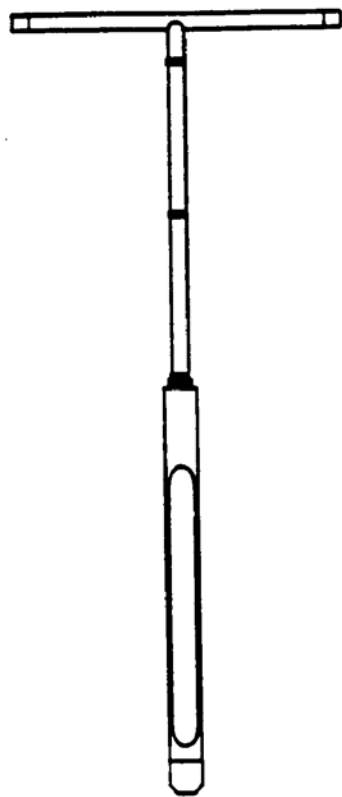
Sampling Surface Sediment with a Trowel or Scoop from Beneath a Shallow Aqueous Layer: For the purpose of this method, surface sediment is considered to range from zero to 152.5 millimeters in depth and a shallow aqueous layer is considered to range from zero to 305 millimeters in depth. Collection of surface sediment from beneath a shallow aqueous layer can be accomplished with tools such as spades, shovels, trowels, and scoops. Although this method can be used to collect both unconsolidated/consolidated sediment, it is limited somewhat by the depth and movement of the aqueous layer. Deep and rapidly flowing water render this method less accurate than others discussed below. However, representative samples can be collected with this procedure in shallow sluggish water provided care is demonstrated by the sample team member. A stainless steel or plastic sampling implement will suffice in most applications. Care should be exercised to avoid the use of devices plated with chrome or other materials; plating is particularly common with garden trowels.

The following procedure will be used to collect sediment with a scoop, shovel, or trowel:

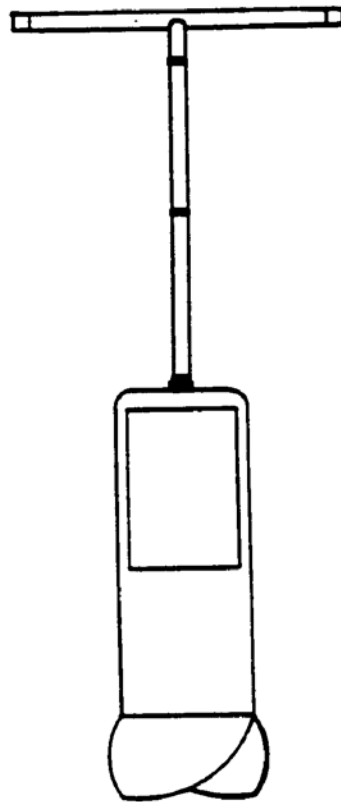
1. Using a decontaminated sampling implement, remove the desired thickness and volume of sediment from the sampling area.
2. Transfer the sample into an appropriate sample or homogenization container. Ensure that non-dedicated containers have been adequately decontaminated.
3. Surface water should be decanted from the sample or homogenization container prior to sealing or transfer; care should be taken to retain the fine sediment fraction during this procedure.

Sampling Surface Sediment with a Bucket Auger or Tube Auger from Beneath a Shallow Aqueous Layer: For the purpose of this method, surface sediment is considered to range from zero to 152.5 in depth and a shallow aqueous layer is considered to range from zero to 610 millimeters in depth. Collection of surface sediment from beneath a shallow aqueous layer can be accomplished with a system consisting of bucket auger or tube auger, a series of extensions, and a “T” handle (Figure 6). The use of additional extensions in conjunction with a bucket auger can increase the depth of water from which sediment can be collected from 610 millimeters to three meters or more. However, sample handling and manipulation increases in difficulty with increasing depth of water. The bucket auger or tube auger is driven into the sediment and used to extract a core. The various depths represented by the core are homogenized or a subsample of the core is taken from the appropriate depth.

The following procedure will be used to collect sediment samples with a bucket auger or tube auger:



TUBE
AUGER



BUCKET
AUGER

Figure 6. Sampling Augers.

1. An acetate core may be inserted into the bucket auger or tube auger prior to sampling if characteristics of the sediments or waterbody warrant. By using this technique, an intact core can be extracted.
2. Attach the auger head to the required length of extensions, then attach the “T” handle to the upper extension.
3. Clear the area to be sampled of any surface debris.
4. Insert the bucket auger or tube auger into the sediment at a 0 to 20° angle from vertical. This orientation minimizes spillage of the sample from the sampler upon extraction from the sediment and water.
5. Rotate the auger to cut a core of sediment.
6. Slowly withdraw the auger; if using a tube auger, make sure that the slot is facing upward.
7. Transfer the sample or a specified aliquot of sample into an appropriate sample or homogenization container. Ensure that non-dedicated containers have been adequately decontaminated.

Sampling Deep Sediment with a Bucket Auger or Tube Auger from Beneath a Shallow Aqueous Layer: For the purpose of this method, deep sediment is considered to range from 152.5 to greater than 457 millimeters in depth and a shallow aqueous layer is considered to range from zero to 610 millimeters. Collection of deep sediment from beneath a shallow aqueous layer can be accomplished with a system consisting of a bucket auger, a tube auger, a series of extensions and a “T” handle. The use of additional extensions can increase the depth of water from which sediment can be collected from 610 millimeters to 1.5 meters or more. However, water clarity must be high enough to permit the sampler to directly observe the sampling operation. In addition, sample handling and manipulation increases in difficulty with increasing depth of water. The bucket auger is used to bore a hole to the upper range of the desired sampling depth and then withdrawn. The tube auger is then lowered down the borehole, and driven into the sediment to the lower range of the desired sampling depth. The tube is then withdrawn and the sample recovered from the tube. This method can be used to collect firmly consolidated sediments, but is somewhat limited by the depth of the aqueous layer, and the integrity of the initial borehole.

The following procedure will be used to collect deep sediment samples with a bucket auger and a tube auger:

1. Attach the bucket auger bit to the required lengths of extensions, then attach the “T” handle to the upper extension.
2. Clear the area to be sampled of any surface debris.
3. Begin augering, periodically removing any the auger bucket. Cuttings should be disposed far enough from the sampling area to minimize cross contamination of accumulated sediment (i.e., cuttings) from various depths.
4. After reaching the upper range of the desired depth, slowly and carefully remove bucket auger from the boring.
5. Attach the tube auger bit to the required lengths of extensions, then attach the “T” handle to the upper extension.

6. Carefully lower the tube auger down borehole using care to avoid making contact with the borehole sides and, thus, cross-contaminating the sample. Gradually force the tube auger into sediment to the lower range of the desired sampling depth. Hammering of the tube auger to facilitate coring should be avoided as the vibrations may cause the boring walls to collapse.
7. Remove the tube auger from the borehole, again taking care to avoid contact with the borehole sides and, thus, cross-contaminating the sample.
8. Discard the top of core (approximately 25.5 mm); as this represents material collected by the tube auger before penetration to the layer of concern.
9. Transfer sample into an appropriate sample or homogenization container. Ensure that non-dedicated containers have been adequately decontaminated.

Sampling Surface Sediment with an Ekman or Ponar Dredge from Beneath a Shallow or Deep Aqueous Layer: For the purpose of this method, surface sediment is considered to range from zero to 152.5 millimeters in depth. Collection of surface sediment can be accomplished with a system consisting of a remotely activated device (dredge) and a deployment system. This technique consists of lowering a sampling device (dredge) to the surface of the sediment by use of a rope, cable, or extended handle. The mechanism is activated, and the device entraps sediment in spring loaded or lever operated jaws. An Ekman dredge is a lightweight sediment sampling device with spring activated jaws. It is used to collect moderately consolidated, fine textured sediment. The following procedure will be used for collecting sediment with an Ekman dredge (Figure 7):

1. Attach a sturdy nylon rope or stainless steel cable through the hole on the top of the bracket, or secure the extension handle to the bracket with machine bolts.
2. Attach springs to both sides of the jaws. Fix the jaws so that they are in open position by placing trip cables over the release studs. Ensure that the hinged doors on the dredge top are free to open.
3. Lower the sampler to a point 102 to 152.5 millimeters above the sediment surface.
4. Drop the sampler to the sediment.
5. Trigger the jaw release mechanism by lowering a messenger down the line, or by depressing the button on the upper end of the extension handle.
6. Raise the sampler and slowly decant any free liquid through the top of the sampler. Care should be taken to retain the fine sediment fraction during this procedure.
7. Open the dredge jaws and transfer the sample into a stainless steel, plastic or other appropriate composition (e.g., Teflon) container. Ensure that non-dedicated containers have been adequately decontaminated. If necessary, continue to collect additional sediment grabs until sufficient material has been secured to fulfill analytical requirements. Thoroughly homogenize and then transfer sediment to sample containers appropriate for the analyses requested. Samples for volatile organic analysis must be collected directly from the bucket before homogenization to minimize volatilization of contaminants.

A Ponar dredge is a heavyweight sediment sampling device with weighted jaws that are lever or spring activated. It is used to collect consolidated fine to coarse textured sediment. The following procedure will be used for collecting sediment with a Ponar dredge (Figure 8):

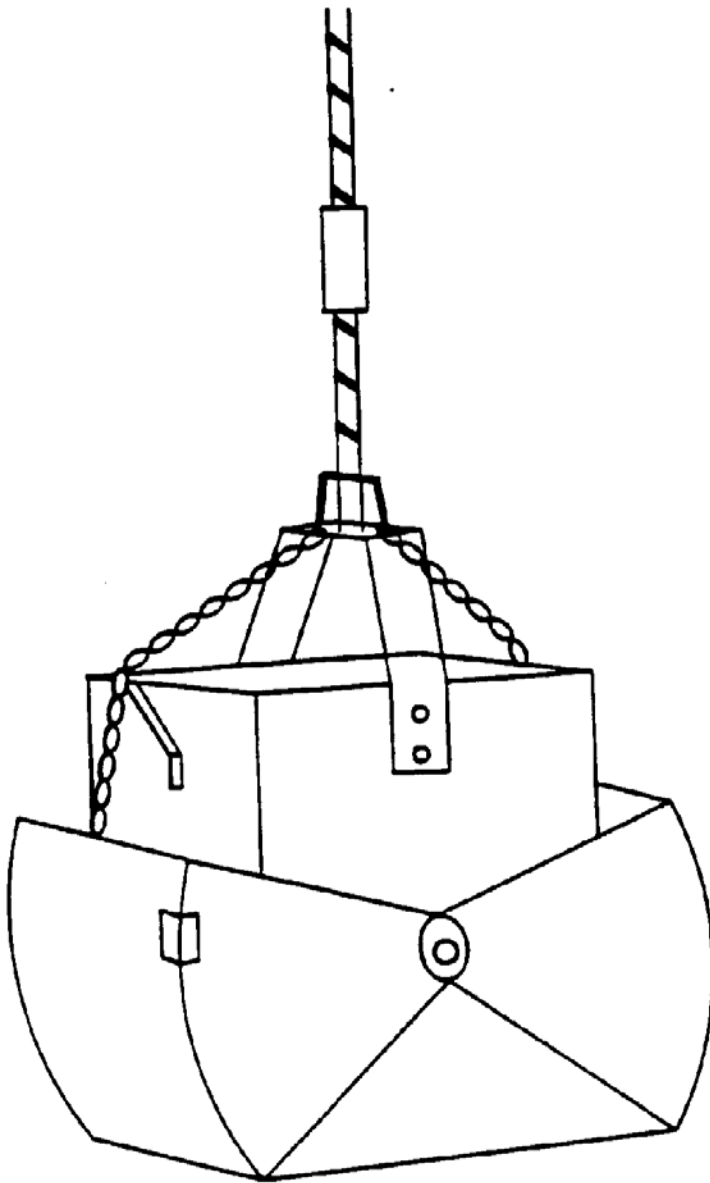


Figure 7. Ekman Dredge.

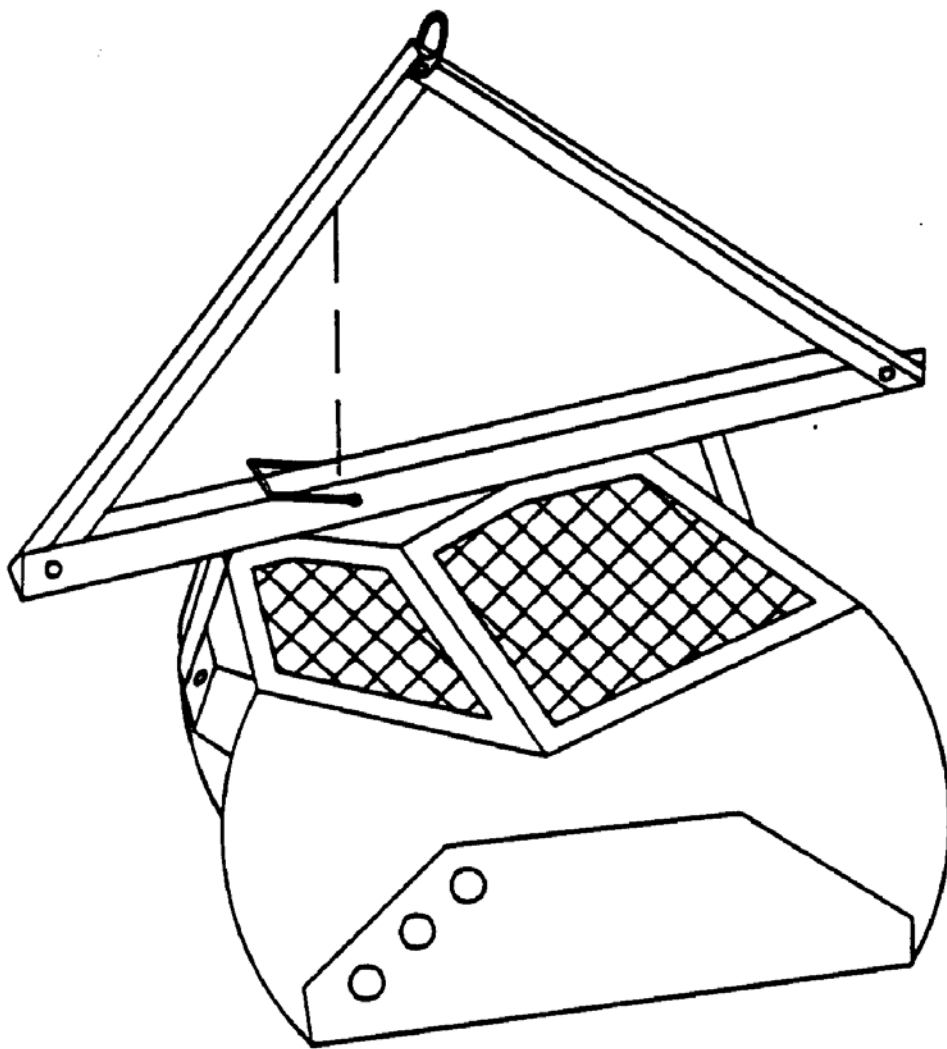


Figure 8. Ponar Dredge.

1. Attach a sturdy nylon rope or steel cable to the ring provided on top of the dredge.
2. Arrange the Ponar dredge with the jaws in the open position, setting the trip bar so the sampler remains open when lifted from the top. If the dredge is so equipped, place the spring loaded pin into the aligned holes in the trip bar.
3. Slowly lower the sampler to a point approximately 51 millimeters above the sediment.
4. Drop the sampler to the sediment. Slack on the line will release the trip bar or spring loaded pin; pull up sharply on the line closing the dredge.
5. Raise the dredge to the surface and slowly decant any free liquid through the screens on top of the dredge. Care should be taken to retain the fine sediment fraction during this operation.
6. Open the dredge and transfer the sediment to a stainless steel, plastic or other appropriate composition (e.g., Teflon) container. Ensure that non-dedicated containers have been adequately decontaminated. If necessary, continue to collect additional sediment until sufficient material has been secured to fulfill analytical requirements. Thoroughly homogenized and then transfer sediment to sample containers appropriate for the analyses requested. Samples for volatile organic analysis must be collected directly from the bucket before homogenization to minimize volatilization of contaminants.

Sampling Subsurface Sediment with a Coring Device from Beneath a Shallow Aqueous

Layer: For purposes of this method, subsurface sediment is considered to range from 152.5 to 610 millimeters in depth and a shallow aqueous layer is considered to range from zero to 610 millimeters in depth. Collection of subsurface sediment from beneath a shallow aqueous layer can be accomplished with a system consisting of a tube sampler, acetate tube, eggshell check valve, nosecone, extensions, and “T” handle, or drivehead. The use of additional extensions can increase the depth of water from which sediment can be collected from 610 millimeters to three meters or more. This sampler may be used with either a drive hammer for firm sediment, or a “T” handle for soft sediment. However, sample handling and manipulation increases in difficulty with increasing depth of water.

The following procedure describes the use of a sample coring device (Figure 9) used to collect subsurface sediments.

1. Assemble the coring device by inserting the acetate core into the sampling tube.
2. Insert the “egg shell” check valve into the lower end of the sampling tube with the convex surface positioned inside the acetate core.
3. Screw the nosecone onto the lower end of the sampling tube, securing the acetate tube and eggshell check valve.
4. Screw the handle onto the upper end of the sampling tube and add extension rods as needed.
5. Place the sampler in a perpendicular position on the sediment to be sampled.
6. If the “T” handle is used, place downward pressure on the device until the desired depth is reached. After the desired depth is reached, rotate the sampler to shear off the core at the bottom. Slowly withdraw the sampler from the sediment and proceed to Step 15.

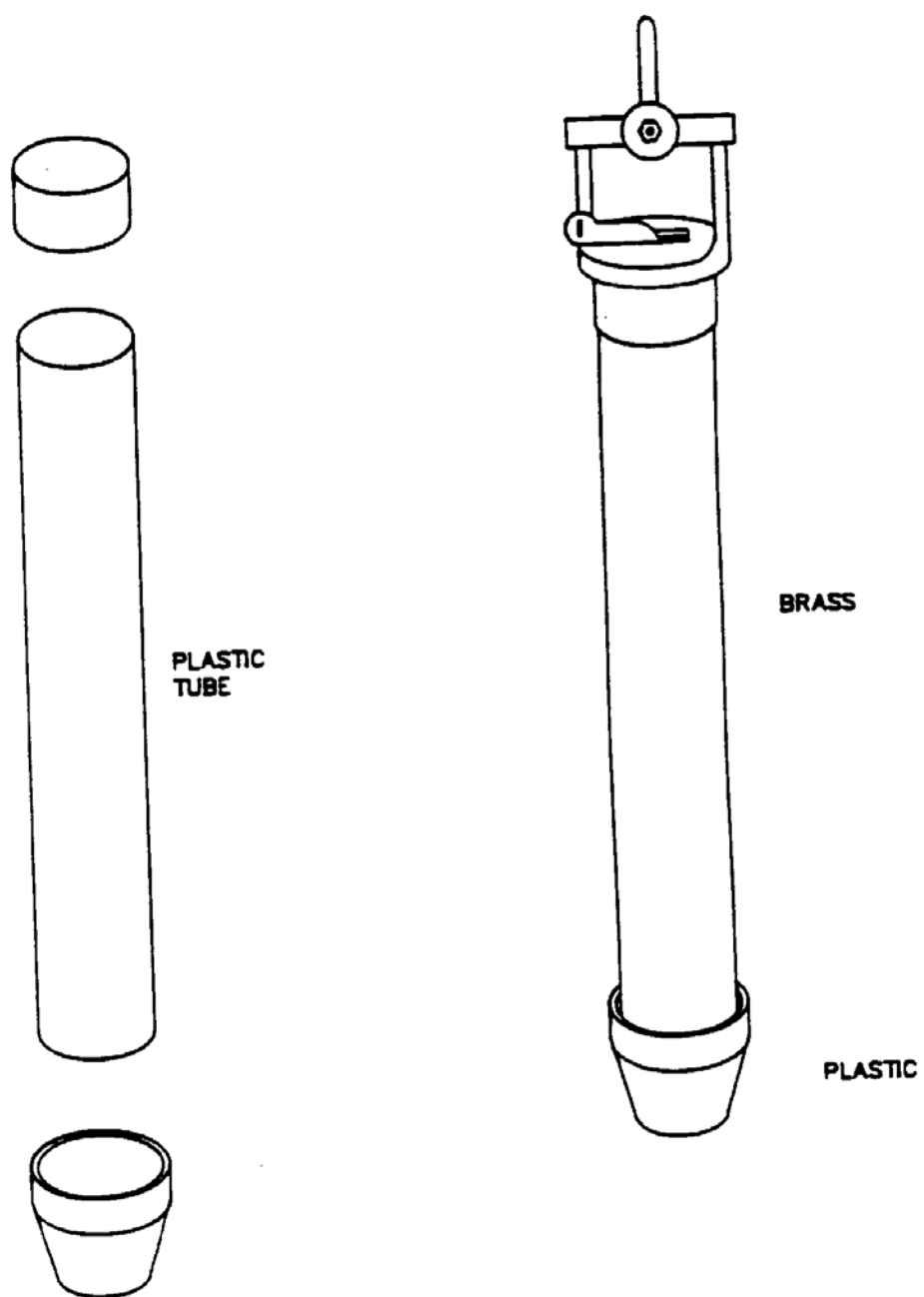


Figure 9. Sample Coring Device.

7. If the drive hammer is selected, insert the tapered handle (drive head) of the drive hammer through the drive head.
8. Drive the sampler into the sediment to the desired depth.
9. Record the length of the tube that penetrated the sample material, and the number of blows required to obtain this depth.
10. Remove the drive hammer and fit the keyhole-like opening on the flat side of the hammer onto the drive head. In this position, the hammer serves as a handle for the sampler.
11. Rotate the sampler to shear off the core at the bottom.
12. Lower the sampler handle (hammer) until it just clears the two ear-like protrusions on the drive head, and rotate about 90°.
13. Slowly withdraw the sampler from the sediment. If the drivehead was used, pull the hammer upwards and dislodge the sampler from the sediment.
14. Carefully remove the coring device from the water.
15. Unscrew the nosecone and remove the eggshell check valve.
16. Slide the acetate core out of the sampler tube. Decant surface water, using care to retain the fine sediment fraction. If head space is present in the upper end, a hacksaw may be used to shear the acetate tube off at the sediment surface. The acetate core may then be capped at both ends. Indicate on the acetate tube the appropriate orientation of the sediment core using a waterproof marker. The sample may be used in this fashion, or the contents transferred to a sample or homogenization container.
17. Open the acetate tube and transfer the sediment to a stainless steel, plastic or other appropriate composition (e.g., Teflon) container. Ensure that non-dedicated containers have been adequately decontaminated. If necessary, continue to collect additional sediment until sufficient material has been secured to fulfill analytical requirements. Thoroughly homogenize and then transfer sediment to sample containers appropriate for the analyses requested. Samples for volatile organic analysis must be collected directly from the bucket before homogenization to minimize volatilization of contaminants.

Calculations: This section is not applicable to this SOP.

QA/QC: There are no specific QA activities that apply to the implementation of these procedures. However, the following QA procedures apply:

1. All data must be documented on field data sheets or within site logbooks.
2. All instrumentation must be operated in accordance with operating instructions as supplied by the manufacturer, unless otherwise specified in the work plan. Equipment checkout and calibration activities must occur prior to sampling/operation, and they must be documented.

Data Validation: This section is not applicable to this SOP.

Health and Safety: When working with potentially hazardous materials, follow USEPA/OSHA and corporate health and safety procedures.

More specifically, when sampling sediment from waterbodies, physical hazards must be identified and adequate precautions must be taken to ensure the safety of the sampling team. The team member collecting the sample should not get too close to the edge of the waterbody, where bank failure may cause loss of balance. To prevent this, the person performing the sampling should be on a lifeline, and be wearing adequate protective equipment. If sampling from a vessel is determined to be necessary, appropriate protective measures must be implemented.

1.3.7 Soil Sampling (USEPA- Environmental Response Team)

SOP: 2012

PAGE: 1 of 13

REV: 0.0

Scope and Application: The purpose of this SOP is to describe the procedures for the collection of representative soil samples. Sampling depths are assumed to be those that can be reached without the use of a drill rig, direct-push, or other mechanized equipment (except for a backhoe). Analysis of soil samples may determine whether concentrations of specific pollutants exceed established action levels, or if the concentrations of pollutants present a risk to public health, welfare, or the environment. These are standard (i.e., typically applicable) operating procedures that may be varied or changed as required, depending on site conditions, equipment limitations or limitations imposed by the procedure. In all instances, the actual procedures used should be documented and described in an appropriate site report. Mention of trade names or commercial products does not constitute USEPA endorsement or recommendation for use.

Method Summary: Soil samples may be collected using a variety of methods and equipment depending on the depth of the desired sample, the type of sample required (disturbed vs. undisturbed), and the soil type. Near-surface soils may be easily sampled using a spade, trowel, and scoop. Sampling at greater depths may be performed using a hand auger, continuous flight auger, a trier, a split-spoon, or, if required, a backhoe.

Sample Preservation, Containers, Handling, and Storage: Chemical preservation of solids is not generally recommended. Samples should, however, be cooled and protected from sunlight to minimize any potential reaction. The amount of sample to be collected and proper sample container type are discussed in ERT/REAC SOP #2003 Rev. 0.0 08/11/94, Sample Storage, Preservation and Handling.

Interferences and Potential Problems: There are two primary potential problems associated with soil sampling - cross contamination of samples and improper sample collection. Cross contamination problems can be eliminated or minimized through the use of dedicated sampling equipment. If this is not possible or practical, then decontamination of sampling equipment is necessary. Improper sample collection can involve using contaminated equipment, disturbance of the matrix resulting in compaction of the sample, or inadequate homogenization of the samples where required, resulting in variable, non-representative results.

Equipment: Soil sampling equipment includes the following:

- Maps/plot plan
- Safety equipment, as specified in the site-specific health and safety plan
- Survey equipment or global positioning system (GPS) to locate sampling points
- Tape measure
- Survey stakes or flags
- Camera and film
- Stainless steel, plastic, or other appropriate homogenization bucket, bowl or pan
- Appropriate size sample containers
- Ziploc plastic bags
- Logbook
- Labels
- Chain of custody records and custody seals
- Field data sheets and sample labels
- Cooler(s)
- Ice
- Vermiculite
- Decontamination supplies/equipment
- Canvas or plastic sheet
- Spade or shovel
- Spatula
- Scoop
- Plastic or stainless steel spoons
- Trowel(s)
- Continuous flight (screw) auger
- Bucket auger
- Post hole auger
- Extension rods
- T-handle
- Sampling trier
- Thin wall tube sampler
- Split spoons
- Vehimeyer soil sampler outfit
- Tubes
- Points
- Drive head
- Drop hammer
- Puller jack and grip
- Backhoe

Reagents: Reagents are not used for the preservation of soil samples. Decontamination solutions are specified in ERT/REAC SOP #2006 Rev. 0.0 08/11/94, Sampling Equipment Decontamination, and the site specific work plan.

Procedures: *Preparation:*

1. Determine the extent of the sampling effort, the sampling methods to be employed, and the types and amounts of equipment and supplies required.
2. Obtain necessary sampling and monitoring equipment.
3. Decontaminate or pre-clean equipment, and ensure that it is in working order.
4. Prepare schedules and coordinate with staff, client, and regulatory agencies, if appropriate.
5. Perform a general site survey prior to site entry in accordance with the site specific health and safety plan.
6. Use stakes, flagging, or buoys to identify and mark all sampling locations. Specific site factors, including extent and nature of contaminant, should be considered when selecting sample location. If required, the proposed locations may be adjusted based on site access, property boundaries, and surface obstructions. All staked locations should be utility-cleared by the property owner or the on-scene-coordinator prior to soil sampling; and utility clearance should always be confirmed before beginning work.

Sample Collection:

Surface Soil Samples: Collection of samples from near-surface soil can be accomplished with tools such as spades, shovels, trowels, and scoops. Surface material is removed to the required depth and a stainless steel or plastic scoop is then used to collect the sample.

This method can be used in most soil types but is limited to sampling at or near the ground surface. Accurate, representative samples can be collected with this procedure depending on the care and precision demonstrated by the sample team member. A flat, pointed mason trowel to cut a block of the desired soil is helpful when undisturbed profiles are required. Tools plated with chrome or other materials should not be used. Plating is particularly common with garden implements such as potting trowels. The following procedure is used to collect surface soil samples:

1. Carefully remove the top layer of soil or debris to the desired sample depth with a pre-cleaned spade.
2. Using a pre-cleaned, stainless steel scoop, plastic spoon, or trowel, remove and discard a thin layer of soil from the area that came in contact with the spade.
3. If volatile organic analysis is to be performed, transfer the sample directly into an appropriate, labeled sample container with a stainless steel lab spoon, or equivalent and secure the cap tightly. Place the remainder of the sample into a stainless steel, plastic, or other appropriate homogenization container, and mix thoroughly to obtain a homogenous sample representative of the entire sampling interval. Then, either place the sample into appropriate, labeled containers and secure the caps tightly; or, if composite samples are to be collected, place a sample from another sampling interval or location into the homogenization container and mix thoroughly. When compositing is complete, place the sample into appropriate, labeled containers and secure the caps tightly.

Sampling at Depth with Augers and Thin Wall Tube Samplers: This system consists of an auger, or a thin-wall tube sampler, a series of extensions, and a “T” handle (Figure 6). The auger is used to bore a hole to a desired sampling depth, and is then withdrawn. The sample may be collected directly from the auger. If a core sample is to be collected, the auger tip is then replaced with a thin wall tube sampler. The system is then lowered down the borehole, and driven into the soil to the completion depth. The system is withdrawn and the core is collected from the thin wall tube sampler.

Several types of augers are available; these include: bucket type, continuous flight (screw), and post-hole augers. Bucket type augers are better for direct sample recovery because they provide a large volume of sample in a short time. When continuous flight augers are used, the sample can be collected directly from the flights. The continuous flight augers are satisfactory when a composite of the complete soil column is desired. Post-hole augers have limited utility for sample collection as they are designed to cut through fibrous, rooted, swampy soil and cannot be used below a depth of approximately one meter.

The following procedure is used for collecting soil samples with the auger:

1. Attach the auger bit to a drill rod extension, and attach the “T” handle to the drill rod.
2. Clear the area to be sampled of any surface debris (e.g., twigs, rocks, litter). It may be advisable to remove the first 76 to 152.5 millimeters of surface soil for an area approximately 152.5 in radius around the drilling location.
3. Begin augering, periodically removing and depositing accumulated soils onto a plastic sheet spread near the hole. This prevents accidental brushing of loose material back down the borehole when removing the auger or adding drill rods. It also facilitates refilling the hole, and avoids possible contamination of the surrounding area.
4. After reaching the desired depth, slowly and carefully remove the auger from the hole. When sampling directly from the auger, collect the sample after the auger is removed from the hole and proceed to Step 10.
5. Remove auger tip from the extension rods and replace with a pre-cleaned thin wall tube sampler. Install the proper cutting tip.
6. Carefully lower the tube sampler down the borehole. Gradually force the tube sampler into the soil. Do not scrape the borehole sides. Avoid hammering the rods as the vibrations may cause the boring walls to collapse.
7. Remove the tube sampler, and unscrew the drill rods.
8. Remove the cutting tip and the core from the device.
9. Discard the top of the core (approximately 25.5mm), as this possibly represents material collected before penetration of the layer of concern. Place the remaining core into the appropriate labeled sample container. Sample homogenization is not required.
10. If volatile organic analysis is to be performed, transfer the sample into an appropriate, labeled sample container with a stainless steel lab spoon, or equivalent and secure the cap tightly. Place the remainder of the sample into a stainless steel, plastic, or other appropriate homogenization container, and mix thoroughly to obtain a homogenous sample representative of the entire sampling interval. Then, either place the sample into appropriate, labeled containers and secure the caps tightly, or if composite samples are to be collected, place a sample from another sampling interval into the homogenization

container and mix thoroughly. When compositing is complete, place the sample into appropriate, labeled containers and secure the caps tightly.

11. If another sample is to be collected in the same hole, but at a greater depth, reattach the auger bit to the drill and assembly, and follow steps 3 through 11, making sure to decontaminate the auger and tube sampler between samples.
12. Abandon the hole according to applicable state regulations. Generally, shallow holes can simply be backfilled with the removed soil material.

Sampling with a Trier: The system consists of a trier and a “T” handle. The auger is driven into the soil to be sampled and used to extract a core sample from the appropriate depth.

The following procedure is used to collect soil samples with a sampling trier:

1. Insert the trier (Figure 10) into the material to be sampled at a 0° to 45° angle from horizontal. This orientation minimizes the spillage of sample.
2. Rotate the trier once or twice to cut a core of material.
3. Slowly withdraw the trier, making sure that the slot is facing upward.
4. If volatile organic analyses are required, transfer the sample into an appropriate, labeled sample container with a stainless steel lab spoon, or equivalent and secure the cap tightly. Place the remainder of the sample into a stainless steel, plastic, or other appropriate homogenization container, and mix thoroughly to obtain a homogenous sample representative of the entire sampling interval. Then, either place the sample into appropriate, labeled containers and secure the caps tightly, or if composite samples are to be collected, place a sample from another sampling interval into the homogenization container and mix thoroughly. When compositing is complete, place the sample into appropriate, labeled containers and secure the caps tightly.

Sampling at Depth with a Split Spoon (Barrel) Sampler: Split spoon sampling is generally used to collect undisturbed soil cores of 457 or 610 millimeters in length. A series of consecutive cores may be extracted with a split spoon sampler to give a complete soil column profile, or an auger may be used to drill down to the desired depth for sampling. The split spoon is then driven to its sampling depth through the bottom of the augured hole and the core extracted.

When split spoon sampling is performed to gain geologic information, all work should be performed in accordance with ASTM D1586-98, Standard Test Method for Penetration Test and Split-Barrel Sampling of Soils.

The following procedures are used for collecting soil samples with a split spoon:

1. Assemble the sampler by aligning both sides of barrel and then screwing the drive shoe on the bottom and the head piece on top.
2. Place the sampler in a perpendicular position on the sample material.
3. Using a well ring, drive the tube. Do not drive past the bottom of the head piece or compression of the sample will result.

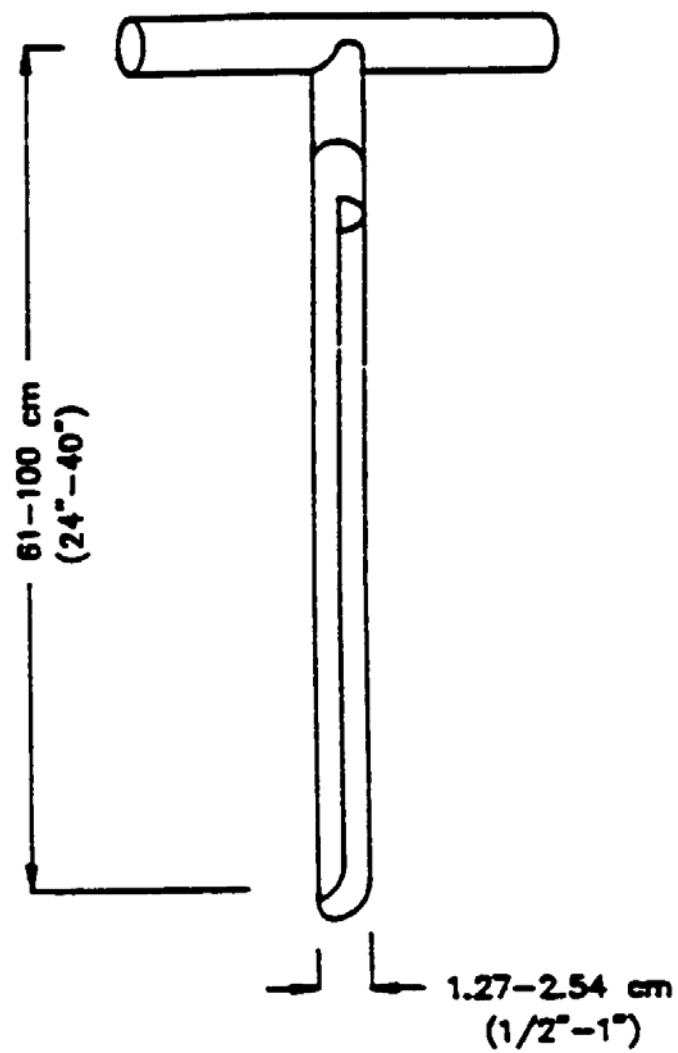


Figure 10. Sampling Trier.

4. Record in the site logbook or on field data sheets the length of the tube used to penetrate the material being sampled, and the number of blows required to obtain this depth.
5. Withdraw the sampler, and open by unscrewing the bit and head and splitting the barrel. The amount of recovery and soil type should be recorded on the boring log. If a split sample is desired, a cleaned, stainless steel knife should be used to divide the tube contents in half, longitudinally. This sampler is typically available in 51 and 89 millimeter diameters. A larger barrel may be necessary to obtain the required sample volume.
6. Without disturbing the core, transfer it to appropriate labeled sample container(s) and seal tightly.

Test Pit/Trench Excavation: A backhoe can be used to remove sections of soil, when detailed examination of soil characteristics are required. This is probably the most expensive sampling method because of the relatively high cost of backhoe operation.

The following procedures are used for collecting soil samples from test pits or trenches:

1. Prior to any excavation with a backhoe, it is important to ensure that all sampling locations are clear of overhead and buried utilities.
2. Review the site specific health and safety plan and ensure that all safety precautions including appropriate monitoring equipment are installed as required.
3. Using the backhoe, excavate a trench approximately one meter wide and approximately 305 millimeters deep below the cleared sampling location. Place excavated soils on plastic sheets. Trenches greater than 1.5 meters deep must be sloped or protected by a shoring system, as required by OSHA regulations.
4. A shovel is used to remove a 25.5 to 51 millimeter layer of soil from the vertical face of the pit where sampling is to be done.
5. Samples are taken using a trowel, scoop, or coring device at the desired intervals. Be sure to scrape the vertical face at the point of sampling to remove any soil that may have fallen from above, and to expose fresh soil for sampling. In many instances, samples can be collected directly from the backhoe bucket.
6. If volatile organic analyses are required, transfer the sample into an appropriate, labeled sample container with a stainless steel lab spoon, or equivalent and secure the cap tightly. Place the remainder of the sample into a stainless steel, plastic, or other appropriate homogenization container, and mix thoroughly to obtain a homogenous sample representative of the entire sampling interval. Then, either place the sample into appropriate, labeled containers and secure the caps tightly, or if composite samples are to be collected, place a sample from another sampling interval into the homogenization container and mix thoroughly. When compositing is complete, place the sample into appropriate, labeled containers and secure the caps tightly.
7. Abandon the pit or excavation according to applicable state regulations. Generally, shallow excavations can simply be backfilled with the removed soil material.

Calculations: This section is not applicable to this SOP.

QA/QC: There are no specific QA activities which apply to the implementation of these procedures. However, the following QA procedures apply:

1. All data must be documented on field data sheets or within site logbooks.
2. All instrumentation must be operated in accordance with operating instructions as supplied by the manufacturer, unless otherwise specified in the work plan. Equipment checkout and calibration activities must occur prior to sampling/operation, and they must be documented.

Data Validation: This section is not applicable to this SOP.

Health and Safety: When working with potentially hazardous materials, follow USEPA, OSHA, and corporate health and safety procedures, in addition to the procedures specified in the site specific health and safety plan.

1.3.8 Survey of Environmental Contaminants National Park Service

- Dedicated to improving the health of diverse populations -

165

1	What park are you reporting on? What is your position at the park? Do you have a WWTP or WTP operation within your park?	 Neither v
2	Does your waste go to a municipal waste facility or do you have septic systems or both?	Waste v
3	How large a janitorial staff do you have?	
4	Have you converted to "green" products? What products are used?	No v
5	Do you have a paint shop? What type of products are used?	No v
6	Do you have an autoshop?	No v
7	Do you recycle oil or antifreeze?	Neither v
8	What is your vehicle fleet size?	
9	Do you use diesel or gas or both? Underground storage tanks? Have the tanks been recently replaced?	Neither v No v No v
10	Do you have a hazardous waste storage area? What types of wastes are stored?	No v

11	Have you had a spill, if so what/when/where?	No
12	Do you have a lab? If so what is its primary use? What chemicals do you routinely use. How much waste is generated per year roughly from lab activities?	No
13	Do you have a landfill in close proximity (either historic or currently used)? If so, name the facility.	No
14	Do you have boat operations? If so, estimate the fleet size.	No
15	Do you have marina?	No
16	Does illegal dumping occur within your park? Is one particular area targeted?	No
17	Is there a hazardous waste site within or near your boundaries? If so where and name the site.	No
18	What contaminant threats pose the greatest concern to you from outside the boundaries?	
19	What contaminant threats pose the greatest concern to you from inside the boundaries?	

20	Do you salt your roads, if so what is sand/salt ratio? Is it under cover?	No 
21	Are there any historic practices that existed in the park that you would now consider a contaminant problem (i.e., oiling sand roads with used motor oil)?	No  
22	Do you fertilize lawns? Do you use pesticides? What types? With what frequency does your use of pesticides need to be supplemented?	No  No  Infrequently 
23	Do you flush wells? If so what is technique?	No 
24	Do you use pressure treated wood? Creosote or CCA treated?	No  Both 
25	Do you do prescribed fires? How many acres per year?	No 
26	Have you burned buildings for demolition or training historically? Currently?	No  No 
27	Do you store batteries for recycling?	No 
28	Do you have a photo lab?	No 

29	Do you own buildings which are being renovated? (concern associated with Hg, PCB)?	No v No v
30	Do you have a waste oil furnace?	No v
31	Do you ave buildings with asbestos tiles or lead paint?	No v
32	Are your pipes covered in asbestos wraps?	No v
33	Do you have termites? If so how are they treated?	No v
34	Are any of your facilities formerly used Defense Sites?	No v
35	Do you know of any unexploded ordnance issues?	No v
36	Do you have old transformers?	No v
37	How do you deal with refrigerant coolants?	
38	Do you have any incinerators?	No v
39	How do you store and dispose of tires?	

Natural Resource Assessment Questions (to establish setting and exposure pathways)

40	Do you have any T&E species present in your boundaries?	No 
41	What do you consider as your most sensitive habitats?	
42	What type of water resources do you have?	
43	What other threats (other than contaminants) exist within your park?	

Please provide a recent copy of your General Management Plan and an old Resource Management Plan (if available).

Submit

The Department of the Interior protects and manages the nation's natural resources and cultural heritage; provides scientific and other information about those resources; and honors its special responsibilities to American Indians, Alaska Natives, and affiliated Island Communities.

NPS 419/104175, June 2010

National Park Service
U.S. Department of the Interior



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