PCB Mass Loading from Hazardous Substance Release Sites to Surface Waters of the Christina River Basin

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Site Investigation & Restoration Branch
Division of Air and Waste Management
Department of Natural Resources &
Environmental Control
391 Lukens Drive
New Castle, Delaware 19720

And

Watershed Assessment Branch
Division of Water Resources
Department of Natural Resources &
Environmental Control
820 Silver Lake Boulevard, Suite 200
Dover, Delaware 19904

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Prepared By:

BrightFields, Inc.
Environmental Services

801 Industrial Street, Suite 1
Wilmington, Delaware 19801
(302) 656-9600

File # 0985.26.51

BrightFields, Inc.

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1.0 INTRODUCTION

BrightFields, Inc. (BrightFields) was retained by the Delaware Department of Natural Resources and Environmental Control - Site Investigation and Restoration Branch (DNREC-SIRB) to assess the mass loading of polychlorinated biphenyls (PCBs) from various Delaware Hazardous Substance Control Act (HSCA) sites to the surface waters of the Christina River Basin and adjacent areas. The purpose of this assessment was to evaluate existing information from a total of 32 currently known PCB-contaminated Delaware HSCA sites pre-identified by DNREC-SIRB, in order to evaluate the relative impact of PCBs transported from these sites by overland flow of surface water and through the discharge of PCB-contaminated groundwater into the surface water bodies.

1.1 Project Background

The Christina River Basin (Basin) lies within the greater Delaware River Basin and consists of the Brandywine Creek, the White Clay Creek, the Red Clay Creek, and the Christina River Watersheds. These four major streams drain a 565 square mile area, one-third of which is situated in northern Delaware. The Basin provides more than 100 million gallons of water a day for over 500,000 people. The Christina River Basin streams and wells provide 70% of the water supply for residents in New Castle County, Delaware, and up to 40% of the water supply for residents in Chester County, Pennsylvania. The basin provides the only source of public surface water supply in Delaware, and the Brandywine Creek is the source of Wilmington's drinking water (DRBC, 2008).

In 1999 DNREC performed a water quality assessment of the portion of the Christina River Basin that falls within Delaware. This study identified elevated concentrations of PCB in fish tissue. Due to this problem and many other environmental issues associated with the Christina River Basin, portions of the Basin were included in the State of Delaware's Clean Water Act Section 303(d) list of impaired waters. This listing required the state of Delaware to develop a Total Maximum Daily Load (TMDL) for PCBs for the affected waters. The PCB TMDL for the

Delaware portion of the Christina Basin is expected to be completed by the end of the calendar year 2009. In order for the State of Delaware to develop regulations pertaining to the TMDL for PCBs, a current estimate of the mass (loading) of PCBs entering the Basin from discrete sources via overland runoff and groundwater transport needed to be generated.

The State of Delaware contains numerous sites where previous or current operations have impacted the soil or groundwater with PCBs. Some of these sites are located in the vicinity of surface water bodies. Rain falling on exposed surfaces at these sites can cause erosion of soil containing contaminants and/or dissolve site contaminants, resulting in discharge of impacted runoff to a surface water body. In addition to overland flow, contaminated groundwater can also discharge into a surface water body. The specific objective of this project was to develop PCB mass loading estimates for PCBs released from Delaware HSCA sites to surface waters of the Christina Basin. By evaluating all of the sites consistently, the relative contribution from each site can be estimated and compared.

1.2 Background of Polychlorinated Biphenyls (PCBs)

PCBs are synthetic chlorinated biphenyls. The biphenyl structure consists of two connected benzene rings with up to 10 chlorines. PCBs are not a single chemical compound but, based on the number of chlorines and their placement, comprise 209 related chemicals known as congeners. The congeners can be subdivided into groups that contain the same number of chlorine atoms, with each of the 10 groups (e.g., the trichlorinated biphenyls) referred to as homologs. Because the analyses quantify the mass of the individual components, when samples are analyzed for congeners (e.g., using EPA Method 1668a), the sum of the congeners equals the "total PCB" content. The same situation also applies to samples analyzed for the 10 homologs.

The most common commercial PCB mixtures manufactured in the U.S. had the trade name Aroclor, of which there were different formulations based upon the overall percent chlorine in the mixture. With the exception of Aroclor 1016, the first two digits refer to the number of carbon atoms, and the last two digits refer to the percentage of chlorine (for example Aroclor 1260 has 12 carbon atoms and contains 60% chlorine by mass). PCBs can be analyzed for Aroclor content through pattern matching to standards (e.g., using EPA Method 8082 or earlier methods such as 8080A).

Because Aroclors are multi-component mixtures, a higher level of analyst expertise is required to attain acceptable qualitative and quantitative analysis when samples contain more than one Aroclor. The same is also true of Aroclors that have been weathered or degraded by long exposure in the environment. Such weathered mixtures may have significant differences in peak patterns than those of Aroclor standards. In addition, due to this uncertainty and other factors, a summation of the detected Aroclors does not necessarily equal the "total PCBs" present.

Based upon evidence that PCBs bioaccumulate in food chains and can cause harmful effects in animals, they have not been produced commercially in the United States since October 1977. They are considered to be probable human carcinogens by the EPA (Class B2).

The environmental fate of PCBs is generally related to the degree of chlorination. Each of the 209 possible PCB congeners has their own physical and chemical properties and potential for biodegradation. In general, those with fewer chlorine atoms tend to be more readily subject to microbial degradation under aerobic conditions and the higher chlorinated congeners are more subjected to dechlorination under anaerobic conditions. The potential for biodegradation is a function of the number of chlorine atoms on a PCB congener and also the structural placement of the chlorines. PCB congeners with the chlorine atoms on the ortho carbons (the ring position closest to the bond connecting the two rings) tend to be more difficult to biotransform than those with the chlorine atom in the meta or para positions, the positions farther away from the connecting bond. Aerobic processes oxidize PCBs, breaking open the carbon ring and destroying the compounds, but only can degrade less chlorinated congeners. Anaerobic processes leave the biphenyl rings intact while removing the chlorines. This anaerobic dechlorination degrades highly chlorinated compounds into less chlorinated derivatives (Erickson, 1997).

If released to soil, PCBs adsorb strongly to soil particles and the sorption generally increases with the degree of chlorination of the PCB. The log of the sorption coefficients (Log Koc) values for the various Aroclors range from approximately 2.44 for Aroclor 1221 to 6.42 for Aroclor 1260 (Montgomery, 1991). Due to adsorption, PCBs generally do not leach significantly in aqueous soil systems and, due to lower solubility, the higher chlorinated congeners have a lower tendency to leach than the lesser chlorinated congeners. However, in the presence of organic solvents (such as petroleum hydrocarbons), PCBs may leach quite rapidly through soil, due to co-solvency.

If released to water, adsorption to sediment and suspended matter is an important process. Although adsorption can immobilize PCBs (especially the higher chlorinated congeners) for relatively long periods of time, eventual re-solution into the water column has been shown to occur. The PCB composition in the water will be enriched by lower chlorinated PCBs because of their greater water solubility while the higher chlorinated PCBs will remain adsorbed to sediment and suspended particles.

Once the contaminated media is exposed to receptors (people and animals) the PCBs will tend to bind to fatty tissues. PCBs are stored in the fatty tissue and then released to into bloodstream slowly. Even at low exposure levels, the concentration of PCBs in fatty tissue can accumulate to a high level. In addition, PCBs accumulate in the fatty tissue of organisms low in the food chain and then become "magnified" when consumed by animals at a higher level of the chain.

PCBs continue to be a major environmental problem in the U.S. and abroad based upon their persistence. Their tendency to persist in the environment, bioaccumulate in food chains, and their toxicity, places them in a group of chemicals referred to as Persistent Bioaccumulative and Toxic substances (PBTs).

1.3 Objective

The specific objective of this project was to develop PCB mass loading estimates for the amount of PCBs currently being released from a pre-identified list of 32 Delaware HSCA sites (Figure 1) to surface waters of the Christina River Basin. This was assessed through two transport mechanisms:

1. Erosion and overland flow of surface water contaminated by PCB-impacted surface soil; and

2. Subsurface (groundwater) flow and transport of dissolved phase PCBs.

2.0 PROCEDURES

This section describes the procedures that were developed to estimate the quantity of PCBs currently being released to surface waters of the Christina River Basin through overland flow and groundwater transport. A site specific appendix was developed for each of the 32 sites. Each appendix includes a summary of the site location, site historical usage, previous investigations, PCB remediation (if performed), current regulatory status, concentrations of PCBs remaining on site, summary of overland flow and/or groundwater transport variables for the site, uncertainty evaluation and estimated mass loading to the Christina Basin. Supporting tables and figures are also included in each site specific appendix.

2.1 Data Compilation

Each individual site was researched by contacting DNREC and submitting a "Freedom of Information Act" (FOIA) request. Once the FOIA request was processed, BrightFields personnel examined the files and identified which files had information pertaining to this study. All of the files of interest were segregated by using a tagging system; the files were then copied by the DNREC office. In some instances where files were missing data, BrightFields contacted the project manager of that job at DNREC to request individual files.

In one case (Diamond State Salvage), BrightFields personnel had to contact the United States Environmental Protection Agency Region 4 office to request a FOIA review for files that DNREC did not have.

BrightFields developed a master spreadsheet that was filled out for all individual sites and allowed personnel reviewing the files to sort out pertinent information. The master spreadsheet is in the format used in ArcGIS. Data was collected from all existing reports that could be found in DNREC's files pertaining to the site soil and groundwater PCB contamination. Information was also collected on sediment and surface water data although it was not specifically evaluated. The parameters recorded included: sample identification, sample depth, sampling company, report date, figure names, presence of descriptive logs, sample type, sample date, type of sample (e.g. surface or subsurface), total concentration of PCBs, individual Aroclor concentrations, congener analysis, depth to groundwater, saturation definition, sample method, and result type (e.g. laboratory result or screening result).

Once the data was tabulated, the spreadsheets were reviewed for errors and all of the data was entered into the GIS database files.

2.2 Mapping Protocol

Once the data was compiled a series of six or seven maps were created for each site as listed below:

1. Historic Sample Locations and Aerial Photograph
2. PCB Distribution in Surface Soil
3. PCB Distribution in Subsurface Unsaturated Soil
4. PCB Distribution in Subsurface Saturated Soil
5. PCB Distribution in Groundwater,
6. Overland Flow Map (may not be present for some sites), and/or the
7. Groundwater Discharge area (may not be present for some sites).

For each site, all existing report figures that showed sample locations were georeferenced using the georeferencing tool in ArcGIS 9.3. Each sample on the map was then digitized and stored as a location in the GIS database. In some instances sample location information was obtained from georeferencing CAD files and/or GIS shapefiles where the sample would be directly digitized and stored into the GIS database.

Each sample was assigned a status based on any known site remedial activities conducted since the sample was collected and categorized as to whether it was covered by at least 2 feet of fill, removed (e.g., excavated), or unchanged. Samples that were given a status of filled were treated as subsurface samples even if the original sampling depth was less than 2 feet (i.e., a surface sample). Samples in areas that had been remediated are still shown on the appropriate map; however, the total PCB concentration and the depth were not posted on the map and the concentrations of the removed samples were not included in the estimated PCB distribution area. The individual legend shown on each map explains where these samples are located for each site.

The Historic Sample Locations and Aerial Photograph shows the locations of all samples as well as a 2007 aerial photograph underlay from the Delaware DataMIL. The PCB Distribution in Surface Soil map shows those locations that have PCB data from depths of 0 to 2 feet below ground surface (bgs) (surface soil). The PCB Distribution in Subsurface Unsaturated Soil map shows sample locations that have that have PCB data at depths greater than 2 feet bgs and are also located above the water table. The PCB Distribution in Subsurface Saturated Soil map shows sample locations that have PCB data at depths greater than 2 feet bgs and are also located below the water table (saturated). The PCB Distribution in Groundwater map shows the locations where groundwater samples were analyzed for PCBs.

The PCB Distribution Maps depict the concentrations of total PCBs. Concentrations derived from commercial laboratory analysis are shown in plain text with the sample depth in parentheses. PCB concentrations measured using screening methods (e.g., immunoassay) are italicized and shown in parentheses. All maps also show existing and historic buildings, water bodies, and roads.

The PCB Distribution in Surface Soil, PCB Distribution in Subsurface Unsaturated Soil, PCB Distribution in Subsurface Saturated Soil, and PCB Distribution in Groundwater maps include a polygon showing estimated PCB distribution areas. The boundary of this polygon for each map was typically drawn using the midway point between samples that have PCB concentrations above the detection limit and those samples whose PCB concentrations are considered not detected. In areas where the edge of the polygon was estimated, the edge is dashed. The polygon encompassing those samples with concentrations above the detection limit is considered the estimated PCB distribution area.

The Overland Flow Map shows sampling locations with erodable surface soil, overland flow direction to the nearest water body, and site surface topographic elevations (where available). The estimated PCB distribution area for the Overland Flow Map is the same as the PCB Distribution in Surface Soil map; however, it has been modified to exclude all impervious surfaces such as buildings and parking lot. The overland flow direction on the Overland Flow map was assessed by calculating the centroid (the geometric center of the polygon) of each PCB distribution area and drawing the shortest downhill path from the centroid to the nearest surface water body. A site visit was then performed in order to confirm the most likely overland flow path. Modifications were made to the figure based on field conditions.

The Groundwater Discharge map shows the projected PCB-impacted groundwater discharge distance in feet. The Groundwater Discharge distance(s) was calculated by assessing the groundwater flow direction and drawing a line perpendicular to the flow direction across the PCB distribution area. At some sites with limited groundwater elevation data, the groundwater flow direction was estimated from the topography (shallow groundwater flow frequently mimics topography).

In cases where none of the available data met the criteria for a specific map, that map was excluded from the figure series for that site. For example, if no surface soil samples were present, the Overland Flow map was not created and, if no soil samples had a depth greater than 2 feet, were located below the water table and no PCBs were detected in the groundwater, then the Groundwater Discharge map was not created.

2.3 Site Inspections

Site inspections were begun after the first set of maps were completed. Access to some sites was restricted and assumptions regarding site cover and topography had to be made using aerial photographs and observations from outside the property boundaries. BrightFields personnel inspected and evaluated the sites for specific features. These features included: presence of identifiable slopes, drainageways and stormwater discharge areas; types and thickness of ground cover, presence of buffer zones and sediment control features, and locations of impermeable surfaces and discharge points (e.g., stormwater drains). All site inspections were performed by the same individual in order to maintain consistency throughout the project. Observations were documented with photographs that are included in the site specific appendices.

2.4 Mass Loading Calculations

After the figures were completed for each individual site, BrightFields reviewed the data and the concentrations associated with each zone of interest, primarily the surface soil and subsurface soil where PCBs were in contact with the groundwater table (saturated).

The analytical protocol used for the available data varied from immunoassay screening to EPA Method 8082 to PCB Homolog to PCB Congener (EPA Method 1668a) in order of least to most stringent. In order to evaluate the screening data in a quantitative manner, BrightFields utilized half of the detected range in the calculations. For example, if the screening data reported a value of greater than 0.5 mg/kg but less than 1 mg/kg a quantitative concentration of 0.75 mg/kg was assigned to the sample point. This was necessary in order to evaluate the detection in a manner consistent with the quantitative laboratory data. For areas where laboratory data and screening data were available the laboratory data was used.

The concentrations observed in these zones were then evaluated using statistical methods to develop estimated site "average" concentrations to be used in the loading calculations.

The statistical method used for the surface soil was the 95% upper confidence level (UCL) of the mean of the total PCBs concentrations. Where PCBs were detected in a sufficient number of samples at a concentration above the laboratory detection limit, the 95% UCL was calculated using the EPA software ProUCL Version 4.0. If the number of detections was insufficient for the software to calculate the 95% UCL (normally four or less detections) or the calculated 95% UCL was higher than the maximum detected concentration due to elevated sample quantification limits (SQL) for the non-detects, the maximum concentration was used.

The EPA has issued guidance for calculating the UCL of an unknown population mean for hazardous waste sites and has developed software (ProUCL Version 4.0) that computes an appropriate 95% UCL of the unknown population mean. ProUCL tests the distribution of the data set to assess whether or not it fits a defined distribution (normal, log-normal, or gamma) and computes a conservative and stable 95% UCL of the unknown population mean using various methods developed for that distribution. ProUCL 4.0 was used to compute these limits based on full uncensored data sets, as well as left-censored data using non-detects (NDs) and/or multiple detection limits.

The number of detections in the subsurface saturated soil or the groundwater was low, generally less than four. Because of the low number of detections, more sophisticated statistical analysis was not possible. Therefore, simple arithmetic means were normally used to assess the estimated site "average" concentration.

For some sites, multiple areas of concern were identified. This occurred when areas of concern were segregated by large areas of soil that had no PCBs or where the PCBs where concentrated in a "hot spot" surrounded by considerably lower PCB concentrations. For this effort a "hot spot" was defined as an area of concentrations one order of a magnitude higher than the remainder of the site. The overall site contribution was then summed for the individual areas. Once the site contribution concentration(s) were calculated, the mass loading of PCBs to the surface waters of the Christina River Basin were evaluated for erosion and overland flow and subsurface (groundwater) flow and transport of dissolved phase PCB, where applicable.

2.4.1 Overland Flow

Based on research conducted at the Soil Loss Data Center at Purdue University and prior studies, Wischmeier, Smith, and others (Wischmeier and Smith, 1978) developed the empirical Universal Soil Loss Equation (USLE). An Agriculture Handbook (No. 537) describing USLE was originally published in 1965 and was revised in 1978. The USLE estimates soil loss from erosion caused by rainfall. It does this by accounting for specified soil types, rainfall patterns, topography, vegetative ground cover and canopy, and sediment and erosion control practices. With a widespread acceptance, the USLE became the major soil conservation planning tool and is used in the United States and other countries. This equation follows the general form:

A = (R)(K)(L)(S)(C)(P), where:

A = annual soil loss (ton/acre/year)

R = rainfall/erodibility index (100 ft tonf in/acre year)

K = soil erodibility (ton acre h/100 acre ft-tonf in)

L = Slope Length factor (unitless)

S = Slope steepness factor (unitless)

C = cover/management factor (unitless)

P = support practice factor (unitless)

As additional research, experiments, data, and resources became available, research scientists continued to improve the USLE, which led to the development of the Revised Universal Soil Loss Equation (RUSLE). The RUSLE retains the same general factors as USLE.

The main difference established for RUSLE is that each factor has been either updated with recent information, or new factor relationships have been derived based on modern erosion theory and data. RUSLE also has several improvements in assessing factors. These include revised isoerodent maps and erodibility index (R) distributions for some areas, a time-varying approach for the soil erodibility (K) that reflects freeze-thaw; new equations to reflect slope length and steepness, a subfactor approach for evaluating the cover-management factor (C), and new conservation-practice values (P) (Renard, et al., 1997). A new Agriculture Handbook (No. 703) describing RUSLE was published in 1997 by the U.S. Department of Agriculture.

RUSLE2 (version 1.26.6.4, November 2006) is a windows based program that allows the user to input specific parameters about the site. This program provides estimates of long-term average annual soil erosion for use in conservation planning based on the RUSLE equation.

The RUSLE2 program was used to estimate mass loading of each site in terms of tons/acre lost per year. The factors used in the RUSLE are based on long-term averages. The following is a brief description of each of the factors used in RUSLE2 compiled from the Field Office Technical Guide (USDA NRCS, 2001) and how it was estimated in this study.

RAINFALL-RUNOFF INTENSITY EROSIVITY INDEX (R)

A long gentle rain may have the same total energy as a short intense rain. Because raindrop erosion increases with the intensity of the rain, total energy of the rainfall alone is not a good indicator of erosive potential. However, when energy is combined with rainfall intensity the result (EI-Energy/lntensity) is a good predictor of erosive potential. The term includes particle detachment combined with transport capacity (the soil erosion process). The sum of EI's for an average year for a particular locality is the Rainfall Erosion Index - “R” for that location. The “R” values for Delaware counties range from 170 (New Castle County) to 200 (Sussex County). The higher the “R” value, the higher the erosion potential.

Intense rainfall on slopes less than approximately 1% causes water to pond, and the ponding reduces the erosivity of raindrop impact. The RUSLE2 program computes the effect of ponding on erosivity of both flat and ridged surfaces by reduction of R values.

For the purposes of this study, BrightFields used the lower end of this range (170) because all of the sites fell within New Castle County.

SOIL ERODIBILITY (K)

Soil erodibility is a function of chemical and physical properties of the soil. Soil erodibility is the ease with which soil is detached by raindrop splash during rainfall and/or surface flow. Soil erodibility is a combination of the effect of rainfall, runoff, and infiltration and the soil erodibility factor (K) is the soil loss rate for a specified soil. The "K" represents both the susceptibility of the soil to erode and the rate of runoff. Soil generally becomes easier to erode with an increase in the silt fraction regardless of the clay or sand fraction. Infiltration rates are much higher and there is less surface runoff in sand than clay. In addition to these factors, an increase in organic matter produces an increased resistance to detachment due to aggregation and the resultant larger particle size.

RUSLE2 adjusts the "K" factor based on seasonal variability related to freeze/thaw and soil moisture during the year. “K” factors were generally assigned using surface soil descriptions from soil logs to assess the soil composition and equate them to a corresponding generic soil type and organic material content within the RUSLE program. This was completed by looking at the boring logs for the boring with the detected concentration, boring on the property, or boring that was located on a neighboring parcel (Salvage Yards). The top two feet of the log (“surface soil”) was reviewed to make a determination of the soil description. Once the soil description was made it was compared to the RUSLE program generic soil types and a soil type closest to the observed soil matrix was chosen.

LENGTH AND SLOPE FACTORS (LS)

The length and slope factors used in RUSLE account for the effect of topography on erosion. Erosion increases as the slope length increases. The slope-length factor (L) is defined as the horizontal distance from the origin of flow to the point where either the slope decreases enough to allow deposition to begin or the runoff becomes concentrated in a defined channel. The slope steepness factor (S) reflects the influence of the slope angle on erosion. Erosion potential increases with the steepness of the slope.

The combined LS factor in RUSLE represents the ratio of soil loss on a given slope length and steepness referenced to a value of 1.0 from a 72.6 foot slope length with a 9% steepness. The shape and makeup of a slope must be accounted for when assigning its LS value. Uniform slopes are slopes that are generally uniform over the entire length. Irregular or complex slopes have slope changes along the measured slope length.

Calculation of LS values is not a straight forward multiplication because RUSLE2 calculates LS values differently depending on the site susceptibility to rill or interill erosion. RUSLE2 adjusts LS values based on three typical situations (a fourth factor is only applicable for the pacific northwest).

1. Where most erosion is sheet (interill) versus rill erosion.

2. Where the ratio of rill to interill erosion is moderate.

3. Where the ratio of rill to interill is high and the soil has a strong tendency to form rills (typically sites with relatively loose disturbed soil).

BrightFields normally utilized the Delaware DataMIL for contour data pertaining to the site. Once the contour information was plotted (overland flow map) the elevation change over the amount of feet change to the discharge point was calculated to provide slope steepness (%). The slope length factor and slope steepness were entered into the RUSLE2 program to asses the erosion type (rill vs. interill) based on a multiple factors, including soil type.

COVER MANAGEMENT FACTOR (C)

The cover-management factor (C) reflects the effect of management practices on erosion rates. The "C" Factor measures how soil loss potential will be distributed in time during management schemes. The "C" factor represents the effect of plants, soil cover, soil biomass (roots and other organic residue), and soil-disturbing activities on soil loss. RUSLE2 assesses the impact of crops and management procedures based on several sub-factors. It assesses the impacts from previous crop and management procedures (prior land use), the protection offered the soil surface by a vegetative canopy (canopy cover), the reduction in erosion due to surface cover, and the reduction in erosion due to surface roughness. The following is a brief description of the impact of these subfactors on the "C" factor.

1. Prior Land Use (PLU) - evaluates the effects of subsurface biomass (roots and residue buried in the top 4 inches) to resist erosion.

2. Canopy Cover (CC) - expresses the effectiveness of a vegetative canopy in reducing the energy of rainfall striking the soil surface.

3. Surface Cover (SC) - affects erosion by reducing the transport capacity of runoff water, by causing deposition in ponded areas, and by decreasing the surface area susceptible to raindrop impact. RUSLE2 also assesses the percentage of rocks on the surface as a part of surface cover.

4. Surface Roughness (SR) - surface roughness directly effects soil erosion. A rough surface has many depressions and barriers. During a rainfall event, these trap water and sediment causing rough surfaces to erode at lower rates than do smooth surfaces under similar conditions. Rougher soil generally has higher infiltration rates due to soil sealing by raindrop impact.

BrightFields assigned a cover management factor by first attempting to complete a site visit to evaluate the current site conditions. Once on site the same BrightFields field scientist evaluated the site cover for percentage of vegetation, vegetation type, impervious surfaces, gravel thickness, etc. After the cover management was described appropriately, BrightFields created a profile of the cover using the built-in functions of the RUSLE program.

If the site had restricted access then BrightFields used aerial photography to assess the cover for the same characteristics. The profile was then created utilizing the information obtained from the aerial photography.

SUPPORT PRACTICE FACTOR (P)

The support practice factor "P" in RUSLE assesses the soil loss with specific support practices. The support practices principally affect erosion by modifying the flow pattern, grade, or direction of surface runoff. The P factor accounts for control practices that reduce the erosion potential of the runoff by their influence on drainage patterns, runoff concentration, runoff velocity, and hydraulic forces exerted by runoff on soil. There are two major approaches to erosion control. One approach is through on-site protection of the soil so that the long-term productivity of the land is maintained. The supporting mechanical practices include tillage (furrowing, soil replacement, seeding, etc.), strips of close-growing vegetation, deep ripping, terraces, diversions, and other soil-management practices.

The other approach is sediment control so that off-site resources are protected. These practices include buffer strips of close-growing vegetation, stiff grass hedges, straw-bale barriers, gravel filters, sand bags, silt fences, continuous berms, and rock check-dams. Sediment-control barriers and structures cause ponding of water and sediment deposition on the upslope side. The effectiveness of a barrier or basin is directly related to the length and volume of ponded water. This length and volume increases as hillslope gradients increase, unless the sediment control fails or is overwhelmed.

BrightFields used historical information and site visits to determine the extent of sediment and erosion controls. The information was directly entered into the RUSLE2 program. In some cases the type of sediment and erosion controls being used were not listed in the program. In these instances BrightFields evaluated the site utilizing the most similar sediment and erosion control within the program.

The source of all information used for assessing K, LS, C, and P for each site is documented in the site specific appendices. Once annual soil loss was estimated for each site, PCB mass loading to surface water via overland flow was calculated as the product of soil loss, the area of PCB contamination, and the 95% Upper Confidence Limit (UCL) of the mean PCB concentration in the erodible surface soil on the site or the maximum total PCB concentration detected, if the 95% UCL of the mean could not be calculated.

2.4.2 Groundwater Mass Loading

The estimate of the rate of a mass (mass/time) of contaminants entering a surface water body (mass loading) is the product of groundwater discharge (units of volume/time) and groundwater concentration (units of mass/volume). PCB mass loading to a surface water body via groundwater transport was estimated by multiplying the measured (or predicted) dissolved phase PCB concentration in the groundwater beneath the site by the volume of groundwater discharge from the site to surface water.

PCBs are not often detected in groundwater. Their low aqueous solubility (1.45 mg/L for PCB-1232 to 14.4 µg/L for Aroclor 1260) and their tendency to bind to organic carbon and clay limit their mobility. Also, the typically used analytical method (EPA Method 8082) has a fairly high detection limit, with the method detection limits (MDLs) for Aroclors, according to the method document, in the range of 0.054 to 0.90 µg/L in water.

2.4.2.1 Groundwater Concentrations

For sites where PCBs have not been detected in groundwater and are not present in subsurface soil that is in contact with groundwater, PCB mass loading via groundwater discharge was assumed to be negligible. In situations where PCBs have not been detected in the groundwater, but are present in subsurface soil that is in contact with groundwater, a calculated dissolved phase PCB concentration in the pore water was estimated using an equilibrium partitioning equation (Schwarzenbach, et.al., 2003), except for the Howard Street site where a site derived leaching factor was used to estimate the groundwater concentration. It was then assumed that the groundwater is in equilibrium with the pore water. The equilibrium partitioning equation is:

[PCB]w = [PCB]s/(foc x Koc), where:

[PCB]w is the concentration of PCBs dissolved in the pore water;

[PCB]s is the PCB concentration in subsurface soil in contact with groundwater;

foc is the fraction of naturally occurring organic carbon in the subsurface soil; and

Koc is the soil/sediment partition or sorption coefficient.

The Koc is defined as the ratio of adsorbed chemical per unit weight of organic carbon to the aqueous solute concentration. It is an indication of the tendency of a chemical to partition between pore water and organic carbon. Total organic carbon (TOC) data for the subsurface soil was not available for most of the sites investigated, therefore, foc was assumed to be somewhere between 0.01 and 0.05 kilograms organic carbon per kilogram of dry soil. Finally, Koc was estimated using the following linear free energy relationship (LFER) from Schwarzenbach (2003):

Log Koc = 0.74 Log Kow + 0.15, where:

Kow is the octanol-water partition coefficient. Kow values for PCBs are available in the literature for each homolog (Mackay et.al., 1992; ATSDR, 2000; Hawker and Connell, 1988; and Erickson, 1997). The Kow values presented below are a weighted average based on homolog content of the Aroclors and the Kow values of each of the homologs, as presented by Erickson.

The majority of PCBs detected during this investigation were PCB-1248, -1254, or -1260. The Log Koc for PCB-1254 (4.96) was used in the calculations to represent the typical value.

Aroclor	1242	1248	1254	1260
Log Kow	5.58	5.99	6.50	6.87
Log Koc	4.28	4.58	4.96	5.24

Once a measured (or estimated) PCB concentration in the groundwater is obtained, that concentration is multiplied by the groundwater discharge from the site to the surface water body (Section 2.4.2.3). Note that this calculation assumes that PCBs are only sorbed by organic carbon and that grain size is not a significant factor (i.e., no additional sorption to silt and clay). This method would underestimate the PCB concentration in fine grained sediment.

2.4.2.2 Groundwater Discharge

The groundwater discharge is a function of the hydraulic conductivity of the saturated soil, the horizontal groundwater gradient (hydraulic head), and the cross-sectional area of the aquifer.

Groundwater discharge was calculated using the general form of the Darcy equation:

$$Q = KiA$$

where:

Q = groundwater discharge (cubic feet/day)

K = hydraulic conductivity (ft/day)

i = groundwater gradient (ft/ft)

A = cross sectional area through which flow occurs (square feet)

<u>HYDRAULIC CONDUCTIVITY</u>

Hydraulic conductivity describes the ease which groundwater can flow through pore spaces or fractures. The hydraulic conductivity is best estimated through aquifer testing. Aquifer testing is performed to assess the hydraulic properties of a water-bearing unit. There are two general types of aquifer tests, pumping tests and slug tests. In pumping tests, groundwater is pumped from a well and water levels are typically measured in one or more observation wells. In slug tests, the groundwater level in a well is abruptly raised or lowered and water levels are measured following the initial change. Pumping tests sample a much larger volume of soil and provide more representative estimates of large scale hydraulic properties in heterogeneous systems than slug tests, especially if the hydraulic conductivity is high or quite variable. Variable conductivity is frequently found in areas that have been filled with soil from various areas and/or contain debris. Slug testing results are very useful, but may be somewhat less representative of the entire area.

Aquifer testing was not performed at many of the sites; therefore hydraulic conductivity was estimated by using correlations between hydraulic conductivity and effective grain size measurements. The best grain size measurements are obtained by a sieve analysis. If sieve data was not available, then grain size was estimated from soil descriptions. These estimates are entirely dependent on the quality of the soil descriptions and can results in a wide variation in "typical" grain size. However, estimates of the hydraulic conductivity from a sieve analysis of even well sorted soil can have variable conductivity ranges that exceed an order of magnitude.

HYDRAULIC GRADIENT

The groundwater gradient was calculated from groundwater elevations measured in monitoring wells. The accuracy of this measurement is dependent upon the accuracy of the vertical surveying, the density of monitoring wells, the complexity of the flow pattern, and whether the measurements made during limited testing are indicative of the typical flow pattern. Sites located near tidal rivers may have wide ranges of gradients and variable direction if the groundwater has a strong tidal influence. Also, sites with complex flow patterns need considerably more wells to fully assess the flow.

At sites where no monitoring wells were installed or no groundwater elevations were measured, the gradient was estimated by assuming that it paralleled the ground surface. In this case, estimates of groundwater flow are dependent on quality of the topographic survey and on contour interval. The gradient is also difficult to assess if the ground surface is irregular.

CROSS-SECTIONAL AREA

The cross-sectional discharge area is based on a vertical measurement (the thickness of the saturated zone) and a horizontal measurement (the width of the PCB impacted area measured perpendicular to the groundwater flow direction). The thickness of the saturated zone was based on interpretation of borehole logs and on well measurements. Saturated thicknesses were found to be variable across most sites and were difficult to accurately estimate if: 1) a lower confining unit was not encountered, 2) the borehole logs did not indicate the saturated interval, and/or 3) the water bearing zone is confined. Estimates of saturated thickness using groundwater elevations are only applicable if the water bearing unit is unconfined. In heterogeneous material, such as fill, the groundwater is typically confined to some extent and therefore use of groundwater elevation measurements would over estimate the saturated thickness.

Assessment of the areal extent of PCB impacted soil or groundwater is dependent on the sample density. The extent of contamination can only be accurately assessed if there are enough samples to delineate the edge of the contamination and to delineate any "hot spots." Also, to estimate the area where groundwater flows through PCB-impacted soil, the width of this zone must be measured perpendicular to the groundwater flow direction. Therefore, the cross-sectional area estimates are also dependent upon the quality of groundwater flow measurements.

2.4.2.3 Mass Loading Calculations

After the volume of groundwater discharging to the surface water body and the PCB concentrations in groundwater have been estimated, the mass of material introduced to the water body in a given time (mass loading) is estimated.

Estimates of the potential PCB mass loading to a water body was calculated using:

Mass Loading = Q x GW concentration x 0.001 g/µg

where: Mass Loading = estimate of daily PCB load to the water body (grams/year)

Q = Discharge (L/day)

GW Concentration = Measured or Calculated groundwater PCB concentration (µg/L)

The resulting measurement assumes that there is no degradation or sorption of the PCBs between the source and the water body and that any groundwater dispersion conserves the mass balance (i.e., all PCBs leaving the site end up in surface water). As such, the farther the site is from the water body (flow distance), the higher the uncertainty of the PCB mass loading calculations.

2.5 Uncertainty Evaluation

This section describes the procedures used to evaluate the level of uncertainty associated with estimated quantity of PCBs currently being released to surface waters of the Christina River Basin through overland flow and groundwater transport. A summary of the degree of uncertainty associated with each site is included in Table 1 and supporting information is included in each site specific appendix.

2.5.1 Overland Flow Mass Loading Uncertainty Approach

The input for each of the factors in the RUSLE equation was selected based on site specific information and each of the seven factors has a degree of uncertainty. The parameters are presented below in a matrix that shows the various degrees of certainty associated with each parameter. Using the parameters, BrightFields has ranked the uncertainty associated with the overland flow calculations, based on the criteria outlined below. The criteria have been assigned values from the lowest uncertainty (1) to the highest uncertainty (5). Intermediate numbers were assigned if the factor fell between criteria. Each of these factors was also assigned a weight based on its impact on the output of the calculation. Using the weighting of each of these factors, an overall uncertainty value was assigned to each of the sites.

Criterion Used to Evaluate Uncertainty in the Overland Flow Mass Loading Estimates

Overland Flow Mass Loading Factor	**Uncertainty Criteria**		
	Low (1)	Moderate (3)	High (5)
Chemical Data Quality	Soil concentration based on congener analyses	Soil concentration based on Aroclor data	Soil concentration based on screening data
Topography (LS)	Estimated on site survey data	Estimated using topographic map	Estimated based on site visit observations
Soil Type (K)	Detailed logs from the area of concern	Moderately detailed logs from the area of concern	Based on logs from off-site borings
Site Coverage	Based on a thorough site assessment	Based on a site assessment	Based on aerial photography
Distance to Discharge Point	0 to 50 feet to discharge point	150 to 250 feet to discharge point	> 350 feet to discharge point
Sample Density	Greater than six samples per acre	two to four samples per acre	Less than 0.75 samples per acre
Map Quality	Surveyed coordinates for sample locations	Scaled map	Hand drawing

2.5.2 Groundwater Mass Loading Uncertainty Approach

As with the overland flow calculations, each of the factors in the discharge estimate also have a degree of certainty associated with them. Using the factors discussed below, BrightFields has ranked the uncertainty associated with the groundwater discharge calculations, based on the criteria below. The matrix below shows the various degrees of uncertainty associated with each factor. The criteria have assigned values from the least uncertainty (1) to the highest uncertainty (5). Intermediate numbers were assigned if the factor fell between criteria. Each of these factors was also assigned a weight based on its impact on the output of the calculation. Using the weighting of each of these factors, an overall uncertainty value was assigned to each of the sites.

Criterion Used to Evaluate Uncertainty in the Groundwater Mass Loading Estimates

Groundwater Transport Mass Loading Factor	**Uncertainty Criteria**		
	Low (1)	Moderate (3)	High (5)
Groundwater PCB Concentration	Groundwater concentration based on groundwater congener analyses	Groundwater concentration based on Aroclor data in saturated soil	Groundwater concentration based on screening data in saturated soil
Sampling Density	PCB distribution adequately defined	Multiple samples but possible data gaps	Single sample or very few widely spaced
Hydraulic Conductivity	Conductivity based on Aquifer Testing	Conductivity based on good quality logs or geotechnical logs	Conductivity based on poor quality logs
Horizontal Gradient	Gradient based on multiple professionally surveyed wells	Gradient based on few professionally surveyed wells and/or tidal influenced wells	Gradient based on low quality topography
Saturated Thickness	High quality logs with consistent saturated thickness	Few logs, inconsistent saturated thickness	No or poor quality boring logs
Lateral discharge distance	High sample control/ quality, good ground-water flow data	Average sample control/ quality, acceptable ground-water flow data	Poor sample control/ quality, poor ground-water flow data
Distance to discharge point	Discharge point adjacent to site	Discharge point not adjacent, but < 200 feet	Discharge point >200 feet and/or not apparent

3.0 SUMMARY OF FINDINGS

As part of this study BrightFields evaluated existing information from a total of 32 Delaware HSCA sites (pre-identified by DNREC) to estimate PCB mass loading from the sites to the surface waters of the Christina River Basin. The sites ranged in size from 0.3 to 66 acres, where between 8 and 1,550 soil samples and between 0 and 51 groundwater samples had been collected per site. The quality of existing data varied from immunoassay screening (lowest quality) to EPA Method 8082 to PCB Homolog to PCB Congener (EPA Method 1668a, highest quality). Approximately half of the sites had very little PCB data and the most intensively investigated site had 1,550 soil samples and 51 groundwater samples collected.

3.1 Mass Loading Results

Table 1 summarizes the analytical method, PCB concentrations used in the mass loading calculations, estimated mass loading from overland flow and groundwater discharge (grams/year), and associated uncertainty for each site. This table shows that the estimated PCB mass loading via overland flow from the 32 evaluated sites ranges from 0 to 10,000 grams per year and that the estimated PCB mass loading via groundwater transport from the evaluated sites ranges from 0 to 300 grams per year. The general level of uncertainty associated with both the overland flow calculations and the groundwater transport calculations is moderate. The mass loading results for each site are shown on Figure 2.

It is important to note when reviewing the results, that the mass loading calculations are based on the condition of the sites at the time the sampling data was collected, unless information was available in the DNREC site files regarding site remediation efforts after this sampling. Some of these sites may have subsequently been remediated through excavation or capping and therefore their PCB contributions may currently be lower. Conversely, some of the sites may have experienced soil disturbance for non-environmental reasons, and therefore, their PCB contributions may currently be higher. Some of the sites could have generated additional soil or groundwater data that was not available at the time of the file review, which could make the contributions lower or higher.

Overland Flow:

Of the 32 sites evaluated, 6 sites contribute the highest PCB mass via overland flow. Of these:

- 3 sites (Amtrak Refueling, Amtrak Maintenance Facility, and Amtrak West Yards) contribute more than 1,000 grams of total PCBs per year. Amtrak Refueling and Amtrak Maintenance Facility contribute 10,000 or more grams per year.
- 3 sites (American Scrap and Waste, Kreiger Finger Property and Adjacent Sites, and Former Carney Harris) contribute between 100 and 1,000 grams of total PCBs per year.
- 5 sites contribute between 1 and 100 grams per year.
- 21 sites contribute less than 1 gram per year.

Groundwater Transport:

Of the 32 sites evaluated:

- 2 sites (Kreiger Finger Property and Adjacent Sites and Former Carney Harris) contribute more than 100 grams/year of total PCBs via groundwater transport and discharge.
- 4 sites (Wilmington Coal Gas Site-North, Diamond State Salvage, Amtrak Maintenance Facility, and American Scrap and Waste) contribute 19 to 35 grams of total PCBs per year.
- 5 sites contribute between 1 and 7.5 grams per year.
- 21 sites contribute less than 1 gram per year.

This study indicates that overland flow of water/sediment generally transports significantly more PCB mass to waterways than does groundwater. This is not a surprising conclusion and it was expected; however, an interesting finding is that the relationship between the sites with the highest PCB concentrations and the sites that are contributors of the maximum loads are not always the same. The maximum load contributed by each site depends on a variety of site characteristics for both overland flow and groundwater discharge which may result in less load being discharged even though the source concentration is higher.

Another interesting finding is that the calculations of mass loading from overland flow and the calculations of mass loading from groundwater transport, at sites where both contributed load, do not always directly correlate. On sites where groundwater samples were not available and the subsurface saturated soil data was used to estimate pore water concentration, the mass loading through overland flow and groundwater transport correlate to a higher degree.

3.2 Evaluation of Methods

The procedures outlined in Section 2.0 yield conservative, yet reasonable estimates of the total mass of PCBs entering waterways of the Christina River Basin each year from the 32 sites. While there are sources of error in any evaluation, consistently evaluating sites using the same criteria allows the sites to be compared using a relative ranking system. This study provides a tool to prioritization the sites that contribute the highest PCB load to waterways.

One significant source of variability in mass loading via groundwater transport is that at sites where there are no PCBs detected in groundwater, the soil partitioning equation was used to estimate pore water concentration from subsurface saturated soil PCB concentrations. This concentration was then used in the transport calculations. The pore water concentrations estimated from the subsurface saturated soil are generally greater than observed groundwater concentrations. Therefore, this results in a higher estimate of mass loading via groundwater transport.

One significant source of variability in mass loading via overland flow is the site cover assessments. The site cover factor was assessed by a site visit, observation of the site from the street, or observation of aerial photographs of the site. The site cover factor assigned to the site could make the mass loading higher or lower depending on differences between the assumed cover and the actual cover. For example, if the site was assumed to be bare ground from aerial photographs or a site observation through a fence, and it actually had a gravel cover, the mass loading would actually be lower than estimated in this study. It would also have been beneficial to observe each site during or immediately following a rainfall event in order to observe the exact overland flow pathway.

The loading estimates generated during this study may be off by an order of magnitude or more, especially in cases where the uncertainty is higher; however, since the same methodologies were used in this study the ranking of the sites in relation to each other is valuable. The sites listed above were the highest contributing sites in this study based on the data available and conditions of the time of the assessment. There are also likely to be more Hazardous Substance Clean-up Act (HSCA) sites as well as non-HSCA sites that are not part of this study that are also contributing to the PCB loading to the Christina River Basin.

3.3 Recommendations

Based on the information available to be reviewed for these sites, we recommend that a combination of more sampling to better define the extent and magnitude of PCB impact, and PCB remediation or interim remedial actions to limit the migration of PCBs via overland flow and/or groundwater transport.

Additional sampling and/or other testing and/or surveying would help to better define some of the assumptions made in the calculations, thereby reducing the level of uncertainty. It would be important to use a consistent sampling approach to collect the new data. Samples from additional soil and groundwater locations would help to better define the extent of PCB impact as well as provide more sample values to be used in statistical evaluation.

Sediment results, where available, are posted on the surface soil maps; however, this study did not specifically evaluate sediment results or the relationship between surface soil PCB concentrations, predicted mass loading via overland flow, and sediment data. Evaluation of the sediment data and collection of sediment samples would help to document whether there is an actual impact, and if so, to quantify, to the affected surface water body.

Additional groundwater samples, especially use of Congener or Homolog analyses, would allow use of actual groundwater concentrations instead of calculating pore water concentrations from partitioning calculations on some sites and actual groundwater concentrations on others.

In addition, because the groundwater seepage velocity has the most uncertainty, aquifer testing should be undertaken, if not already performed. This would remove much of the uncertainty regarding groundwater discharge volumes.

PCB remediation to remove the PCBs or to restrict the erosion of PCB impacted surface soil (e.g., capping) or to restrict the contact of PCBs the water table (groundwater or saturated soil) would reduce the loading of PCBs to the Christina River Basin. In lieu of, or prior to site remediation, interim measures such as stabilization of the surface or the installation of sediment and erosion control devices (i.e., silt fence, inlet protection, etc.), could be taken to limit the migration of PCBs via overland flow.

It would be prudent to further evaluate sites that appear to be the most significant contributors of PCBs to the Christina River Basin and to give highest priority for further evaluation to the sites with the highest PCB loading via overland flow.

In order to maintain a current priority ranking, sites should be re-evaluated, using the same methodology described in this report, as new data is collected, or remediation or interim measures occur and new sites should be added to the study as they are identified by DNREC as potential PCB contributors.

4.0 REFERENCES

Note: General references and references specifically referred to in the text above are included below. All site specific references are included in the site specific appendices.

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Figures

Table

Site Specific Appendices