REPORT

Draft Remedial Action Work Plan

Georgia-Pacific Corporation Kalamazoo Mill Property and Former Hawthorne Mill Property

Allied Paper, Inc./Portage Creek/Kalamazoo River Superfund Site
Kalamazoo, Michigan

October 2005

BBL®
BLASLAND, BOUCK & LEE, INC.
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1. Introduction

1.1 General

This document presents a Removal Action Work Plan (Work Plan) for the removal of paper-making residuals (residuals) and soils that contain, or may potentially contain, polychlorinated biphenyls (PCB) from the Georgia-Pacific Corporation (Georgia-Pacific) Kalamazoo Mill Property (Kalamazoo Mill Property) and the former Hawthorne Mill Property (Hawthorne Mill Property). These two locations, collectively referred to as the Mill Properties, (Figure 1) are associated with the Allied Paper, Inc./Portage Creek/Kalamazoo River Superfund Site (Superfund Site). This Work Plan is being implemented in accordance with the Willow Boulevard/A-Site Operable Unit, Remedial Design/Remedial Action Administrative Order by Consent (WB/A-Site OU RD/RA AOC). Additional information on the Mill Properties is presented in the *Allied Paper, Inc./Portage Creek/Kalamazoo River Superfund Site Description of the Current Situation* (Blasland & Bouck Engineers, P.C. [BBEPC], 1993a).

The proposed activities outlined in this Work Plan include the removal activities proposed in the *Draft Work Plan for Residuals/Soil Removal in Support of NPL Delisting Petition for the Georgia-Pacific Kalamazoo Mill* (Blasland, Bouck & Lee [BBL], 2003a) at the Kalamazoo Mill Property and additional removal activities at the Hawthorne Mill Property. The goal of this Work Plan is to describe a removal action that meets the requirements of the National Contingency Plan (NCP).

1.2 Related Documentation

Several existing documents support the removal action activities discussed in this Work Plan, including:

- *Allied Paper, Inc./Portage Creek/Kalamazoo River Remedial Investigation/Feasibility Study – Field Sampling Plan* (FSP) (BBEPC, 1993b);

- *Allied Paper, Inc./Portage Creek/Kalamazoo River Remedial Investigation/Feasibility Study – Quality Assurance Project Plan* (QAPP) (BBEPC, 1993c);

- *Substantive Requirements Document – No. MIU990018 for Treated Wastewater Discharge from the Georgia-Pacific Corporation to the Kalamazoo River* (SRD) (Michigan Department of Environmental Quality [MDEQ], 1998);

- *Allied Paper, Inc./Portage Creek/Kalamazoo River Remedial Action Turbidity Monitoring Plan* (TMP) (BBL, 1999); and

- *Final King Highway Landfill Operable Unit Closure Erosion and Sedimentation Control Plan* (ESCP) (BBL, 2002).

1.3 Report Organization

The remainder of this report addresses the following:

- Section 2 presents background information related to previous investigations at the Mill Properties;
- Section 3 describes the proposed removal action activities;
- Section 4 presents proposed post-removal site control activities; and
- Section 5 presents references cited in this Work Plan.

2. Previous Activities

2.1 General

This section presents a summary of information related to previous investigations conducted at the Mill Properties. These investigation efforts included:

- Allied Paper, Inc./Portage Creek/Kalamazoo River Superfund Site – Remedial Investigation (RI) (1993);
- Refuse Area drum removal and sampling activities (1999);
- Focused Soil and Sediment Sampling Program (2000);
- Property Divestiture Study (2002);
- Sediment and Bank Soil sampling at the Oxbow Area (2004); and
- Supplemental soil investigation activities at the Hawthorne Mill Property (2005).

Highlights of the historical investigations at each of the Mill Properties are provided below. More detailed discussions of the investigations, including rationale, sampling approach, and results are included in various investigation-specific reports, as indicated.

2.2 Kalamazoo Mill Property

2.2.1 RI Activities

The Kalamazoo Mill Property was initially investigated to assess the nature and extent of PCB impacts associated with the Mill's five former onsite lagoons (Mill Lagoons #1 through #5), a former wastewater treatment system clarifier, and storm water runoff as part of the Superfund Site RI activities conducted in 1993. Results were presented in *Technical Memorandum 15 – Mill Investigation* (BBL, 1996). Follow up sampling was conducted in June 1996, and the results were reported in *Final Document in Support of King Highway Landfill Operable Unit RI/FS* (BBL, 1997). These activities were conducted consistent with the requirements prescribed in the AOC (Final Order No. DFO-ERD-91-001) issued by the Michigan Department of Natural Resources (MDNR) in 1991.

2.2.2 Discovery of the Refuse Area

Based on the findings of the RI, remedial actions at the five former Mill Lagoons commenced in 1999 as part of the King Highway Landfill Operable Unit 3 (KHL-OU) response activities. During work at the KHL-OU, which was conducted consistent with the requirements prescribed in the 1991 AOC, deteriorating metal drums were observed in the heavily vegetated area adjacent to the river to the south and west of Mill Lagoons #4 and #5. This area has since been referred to as the Refuse Area (see Figure 1). On June 11, 1999 seven solids samples collected from this area were analyzed for Toxicity Characteristic Leaching Procedure (TCLP) analytes and PCB. No PCB were detected in any of the samples. The only TCLP analyte detected was lead, which was identified in one sample at a concentration of 2.2 milligrams per liter (mg/L) (compared to the TCLP regulatory level of 5 mg/L). All other TCLP analysis results were non-detect. In the initial response at the Refuse Area in June 1999, one of the deteriorating drums was removed and disposed of at the EQ landfill in Detroit, Michigan. Additionally, approximately 10 cubic yards (cy) of material excavated from beneath and adjacent to the drums (e.g., drum remnants, soil, white crystals) were disposed in a local Type II landfill. This information is reported in the *Georgia-Pacific Corporation Kalamazoo Paper Mill Property Divestiture Study/Supporting Materials Report* (Property Divestiture Study; BBL, 2003b).

2.2.3 Kalamazoo Mill Property Divestiture Study

In the fall of 2002, as part of the Kalamazoo Mill Property Divestiture Study, soil and groundwater samples were collected from areas at the Kalamazoo Mill Property where available information suggested the potential for PCB-containing materials to be present.

Sampling activities are described in the Property Divestiture Study (BBL, 2003b). PCB were detected in the Refuse Area, in a wastewater pipeline, and in soils beneath an electrical transformer pad. These results are summarized below.

Refuse Area

During removal and disposal of the drums found in the Refuse Area in June of 1999, a variety of construction debris and scrap metal was observed in a number of locations, some of which were visible at the surface. As part of the Kalamazoo Mill Property Divestiture Study, this area was identified as a potential PCB-containing

area. In November and December 2002, two soil borings and seven test pits were installed in the Refuse Area (see Figure 1), and more than 30 soil samples were collected for PCB analysis.

The seven exploratory test pits were excavated to the depth of the water table. In all cases, the interface between disturbed soils/fill materials and undisturbed native soils was encountered above the groundwater table. Soil sample collection from the Refuse Area test pits was biased toward apparent residuals, if present. In several test pit locations, isolated pockets of residuals were found and discretely sampled. PCB concentrations in the test pit samples ranged from non-detect to a maximum of 330 milligrams per kilogram (mg/kg). The maximum result of 330 mg/kg was for a sample collected from an isolated deposit of residuals located 2.5 to 3 feet below ground surface (bgs). This sample was the only sample with a PCB concentration that exceeding Michigan's Part 201 Natural Resources and Environmental Protection Act (Part 201) Industrial PCB Cleanup Criterion of 16 mg/kg. The next highest sample PCB concentration was 9.7 mg/kg. PCB results for four samples collected between the surface and a depth of approximately 2 feet in this same test pit ranged from non-detect to 2.4 mg/kg, while results for three samples collected between 3 and 9.5 feet bgs ranged from non-detect to 0.81 mg/kg.

Additionally, in December 2002 groundwater samples were collected from two monitoring wells located within the Refuse Area. Neither sample contained detectable levels of PCB at the reporting limit of 0.05 micrograms per liter (µg/L). Additional information is available in the Property Divestiture Study (BBL, 2003b).

Wastewater Pipeline Residuals

The Kalamazoo Mill Property Divestiture Study also included collection of seven soil samples from a wastewater pipeline and a wet well located between the former Mill Lagoons and Mill #1 (Figure 1). The wet well is located near the former Mill Lagoons at the end of the wastewater pipeline, which runs northwest from Mill #1.

PCB concentrations in the seven samples associated with the wastewater pipeline and the wet well – which were biased toward apparent residuals where present – ranged from not detected to a maximum of 31.1 mg/kg in a sample of residuals, scraped from the inside of the wastewater pipeline. The average and median concentrations of these seven samples were 4.9 and 1.3 mg/kg, respectively. Additional information is provided in the Property Divestiture Study (BBL, 2003b).

Electrical Transformer Pad Soils

Soil samples were collected from a test pit excavated at the location of a former transformer pad at Mill #1 (Figure 1) where stained soils were observed. Four samples were collected between depths of 0 and 5 feet bgs. In the 0 to 1 foot bgs interval, PCB were detected at a concentration of 2.6 mg/kg. PCB were not detected in the other three samples. Additional information is provided in the Property Divestiture Study (BBL, 2003b).

2.3 Former Hawthorne Mill Property

2.3.1 Sampling in 2000 and 2002

During RI activities, residuals were observed in the Oxbow Area of the Hawthorne Mill Property. As a result, additional samples were collected from this area as part of the 2000 Focused Soil and Sediment Sampling Program conducted for the Superfund Site. PCB were detected in two samples in the 0.5- to 1-foot layers (220 mg/kg and 2.4 mg/kg). Based on this information, additional sampling was conducted as part of the Kalamazoo Mill Property Divestiture Study to further assess the nature and extent of PCB. Soil samples were collected from the Oxbow Area, former clarifier, and oxbow channel bank. The average bank soil PCB concentration was 0.49 mg/kg, with a maximum detection of 2.5 mg/kg; the maximum PCB concentration in the former clarifier was 0.52 mg/kg; and PCB concentrations in the Oxbow Area ranged from non-detect to 490 mg/kg (BBL, 2003b).

2.3.2 Oxbow Area Sampling

In 2004, at the request of the U.S. Environmental Protection Agency (USEPA), sediment and bank soil samples from the oxbow channel were collected in accordance with the USEPA-approved *Former Hawthorne Mill Oxbow Sediment Investigation Work Plan* (BBL, 2004a). The ranges in PCB results were non-detect to 3.4 mg/kg in the oxbow channel sediment, and non-detect to 1.4 mg/kg in bank soil samples. This information is described in greater detail in the *Former Hawthorne Mill Oxbow Sediment Investigation Report* (BBL, 2004b).

2.3.3 Supplemental Investigations

Pursuant to discussions held among the USEPA, the MDEQ, and Georgia-Pacific, additional focused soil sampling was conducted at the Hawthorne Mill Property on April 7, 2005. A total of six test pits were

excavated near the former Hawthorne Mill and clarifier located north of the oxbow, and three test pits were excavated within the Oxbow Area for waste characterization purposes. Three of the test pits were excavated to 6 feet bgs, with discrete samples collected at intervals of 2, 4, and 6 feet bgs. The three other test pits were excavated to a depth of 2.5 feet bgs. Test pits in the Oxbow Area were excavated to approximately 2 to 2.5 feet bgs, with samples collected from a layer of residuals at approximately 0.25 to 1 foot bgs. In addition, one sample was collected from an approximately 4-inch diameter steel pipe that was observed in the Oxbow Area. Lastly, five surface soil samples were collected near the Oxbow Area – two north of the oxbow channel and three south of the oxbow channel.

Some samples were analyzed just for PCB, while others were analyzed for Target Compound List/Target Analyte List (TCL/TAL) pesticides, PCB, semi-volatile organic compounds (SVOCs), metals, and volatile organic compounds (VOCs). PCB were detected in one sample collected from within the former Hawthorne Mill Building footprint at a concentration of 0.057 mg/kg. PCB concentrations in the Oxbow Area ranged from non-detect to 1.28 mg/kg. Additional information is provided in the *Former Hawthorne Mill Supplemental Soil Investigation Activities Summary* field memorandum (BBL, 2005).

3. Removal Action Activities

3.1 General

Removal action activities at the Mill Properties will consist of the excavation of materials from the Refuse Area, Transformer Pad Area, Wastewater Pipeline, and the Oxbow Area, and the subsequent consolidation of these excavated materials at either the A-Site disposal area or if appropriate a Type II landfill (excavation areas are shown on Figure 1 and the A-Site disposal area is shown on Figure 2). Georgia-Pacific will procure a removal action contractor (Contractor) to perform the removal action activities, and will provide an onsite representative throughout the removal action to observe and document the activities. Georgia-Pacific's onsite representative will also be present to coordinate and consult with the USEPA on-scene coordinator, as necessary. Information regarding the removal action activities is discussed below. A summary of activities associated with specific areas is provided in the following table:

Area	Removal Action
Refuse Area	Excavate PCB-containing material, dispose at A-Site
Transformer Pad Area	Excavate visibly-stained soil, dispose at A-Site or Type II Landfill as appropriate
Wastewater Pipeline Area	Excavate pipeline and wet well, dispose at A-Site
Oxbow Area	Excavate PCB-containing material, dispose at A-Site

3.2 Pre-Mobilization Activities

Given the nature of the proposed removal action, several pre-mobilization activities are anticipated to occur. These activities are briefly discussed below.

3.2.1 Permits and Approvals

As provided for by Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) Section 121(e)(1), State and Federal substantive permit requirements will be satisfied through the USEPA's review and approval of this Work Plan. A Substantive Requirements Document (SRD; MDEQ, 1998) exists that addresses the discharge of treated water from Georgia-Pacific property to the Kalamazoo River (see Appendix A). In addition, a Restoration Plan for the Refuse and Oxbow Areas has been developed and

incorporated into this Work Plan to address applicable permit requirements related to the disturbance of regulated wetlands.

All local permits and approvals required as part of the construction activities (e.g., Kalamazoo County Drainage Commission) will be procured by the Contractor.

3.2.2 Pre-Mobilization Submittals

Prior to onsite mobilization, the Contractor will prepare a limited number of submittals for Georgia-Pacific's review (e.g., site-specific Health and Safety Plan, Operations Plan, Project Schedule, Decontamination Plan, and Contingency Plan). If requested, Georgia-Pacific may provide the Contractor's submittals to the USEPA for information purposes. Additional requirements related to pre-mobilization submittals and review procedures shall be identified in the Construction Quality Assurance Plan (CQAP) that will be developed by Georgia-Pacific.

3.3 Mobilization/Site Preparation

Prior to initiating removal action construction, the Contractor will perform mobilization and site preparation activities. At a minimum, it is anticipated that the following site preparation activities will be performed:

- Verify existing site conditions;
- Identify the location of, and relocate as necessary, aboveground and underground utilities, equipment, and structures;
- Mobilize personnel, equipment, and materials to the site;
- Clear and grub areas as necessary to perform the removal action activities (e.g., tree removal in the Oxbow Area, removal of debris and miscellaneous aboveground appurtenances in the Refuse Area);
- Construct equipment and material staging/dewatering areas (as necessary);
- Prepare equipment and personnel decontamination areas;
- Establish erosion and sedimentation control measures (as discussed below);
- Construct temporary access roads (as needed) for ingress and egress of construction equipment as well as offsite transportation of excavated materials; and
- Install temporary fencing or barriers as necessary to protect and secure the work areas.

3.3.1 Erosion and Sedimentation Controls

This subsection describes structural controls to be installed before initiating earth-moving activities. In general, erosion and sedimentation controls will be implemented consistent with the ESCP (BBL, 2002), as applicable. The specific locations of erosion and sedimentation controls will be determined and/or modified in the field based on site-specific considerations related to drainage, topography, and work activities. The selection of specific erosion and sedimentation control measures (either land- or water-based) will be based on, but not limited to, the scope of removal activities, site topography, type of ground cover, anticipated run-off from the project area, and operational/maintenance considerations. Additionally, certain operational and best management practices (to be defined in the Contractor's site-specific plans) will be implemented throughout the project.

Throughout the duration of the project, erosion and sedimentation control devices will be inspected and maintained and/or modified, as necessary, based on site conditions and site activities. The erosion and sedimentation control devices will be maintained for the duration of the project until site restoration activities have provided a final surface cover (as appropriate).

3.4 Removal Activities

Removal activities at the Refuse Area, Transformer Pad Area, Wastewater Pipeline Area, and Oxbow Area are discussed in the following sections. Construction quality assurance requirements related to the proposed soil excavation and backfilling activities shall be identified in the CQAP.

3.4.1 Refuse Area

The initial extent of excavation in the Refuse Area will be determined based on visual criteria, and any additional removal will be completed as necessary to achieve Michigan's Part 201 Natural Resources and Environmental Protection Act (Part 201) Industrial PCB Cleanup Criterion of 16 mg/kg. Based on the results of the test pit and soil boring activities conducted in the Refuse Area, it is anticipated that approximately 30,000 cy will be excavated from the Refuse Area and consolidated at the A-Site.

The depth of excavation will extend to the approximate interface with native soils. This interface was identified during test pit construction, and it occurred above the groundwater table at all locations. Excavated materials from the Refuse Area will be disposed of at the A-Site as identified on Figure 2. The disposal area in the A-Site

was selected based on consideration of where additional material is needed to raise the site contours to grading design elevations.

In general, excavation activities will commence along the east side of the Refuse Area, directly west of former Mill Lagoon #5. The excavation operations will continue radially outward from the initial point. It is anticipated that excavation activities will be conducted in a staged approach to minimize sloughing and to provide a stable, clean excavation base from which to work. As the excavation activities approach the Kalamazoo River bank, a maximum 10-foot buffer will be left intact along the water's edge, assuming it consists of native material. If this buffer contains materials targeted for removal, a small temporary diversion berm, composed of certified clean fill, will be constructed in the river to isolate the excavation activities from river water prior to removing any buffer materials. Additional excavation in other areas beyond the initial limits may be performed based on visual observations during removal, as well as the results of post-excavation verification sampling.

Following post-excavation verification sampling and confirmation that the established cleanup criterion has been achieved, the excavation areas will be backfilled and restored in accordance with the Refuse Area Restoration Plan described in Section 3.6.1.

Materials excavated from the Refuse Area will be segregated during excavation activities. Excavated materials that are deemed unsuitable for placement at the A-Site (i.e., drums, drum remnants, or other questionable materials) will be segregated, characterized, and disposed of appropriately at an offsite disposal facility. Concrete and scrap metals will be segregated and temporarily staged on the foundation floor of the former Mill #5 (Figure 1). Depending on the quantity of materials recovered from the Refuse Area, scrap metals and concrete may be transported offsite for recycling or disposal in a Type II landfill, as appropriate. Other excavated materials (i.e., residuals and soils) will be transported directly to the A-Site and consolidated with existing materials. Excavated materials that contain free liquids will be placed in a temporary lined staging area and gravity dewatered prior to transport to the A-Site. An imported aggregate may be used to solidify excavated material, as necessary. The contractor will be responsible for conducting paint filter testing (USEPA Method 9095A as presented in Appendix B) to evaluate the presence of free liquids in representative samples of material subject to transportation to the A-Site.

3.4.2 Transformer Pad Area

Based on the test pit results at the location of a former electrical transformer, the A-Site or pad adjacent to Mill #1, visibly-stained soils beneath the transformer pad will be removed and disposed of in a licensed Type II landfill, as appropriate. Samples of excavated soil will be analyzed for Resource Conservation and Recovery Act (RCRA) hazardous waste characteristics, PCB, TCLP metals, VOCs, and SVOCs to obtain approval for disposal. Following excavation, the area will be backfilled with certified clean backfill material and restored to match surrounding conditions.

3.4.3 Wastewater Pipeline Area

As discussed in Section 2, a mill wastewater pipeline exists that runs between Mill #1 and a wet well near the former lagoon area. The residuals that accumulated on the pipe walls were sampled and found to contain PCB above the 16 mg/kg Part 201 criterion. To address the presence of PCB, the wastewater pipeline and the wet well will be excavated and disposed of at the A-Site. Following excavation, the area will be backfilled with certified clean backfill material and restored to match surrounding conditions.

3.4.4 Oxbow Area

The initial extent of excavation in the Oxbow Area will be determined based on visual criteria and any additional removal will be completed to achieve, at a minimum, a PCB concentration goal of 16 mg/kg. It should be noted that the excavation methods are expected to achieve substantially lower levels, which will be documented by verification sampling (see Section 3.9). Based on the results of the soil investigation activities conducted in the Oxbow Area, it is anticipated that approximately 5,000 cy of material will be excavated and consolidated at the A-Site (see Figure 2). Additional excavation may be performed based on visual observations during excavation as well as the results of post-excavation verification sampling.

In general, the removal effort will consist of a 2-foot-deep excavation that will be bounded to the south at the Hawthorne Mill Property line, along King Highway. As the excavation activities approach King Highway, existing trees will be protected to the extent practicable, so as to create a visual buffer between King Highway and the excavation area. Excavated materials will be transported to the A-Site and consolidated with existing materials. Trees cleared during excavation activities will be processed with an onsite wood chipper, and the resultant wood chips will be stockpiled onsite for potential reuse. Tree stumps and root systems will be

excavated and disposed of at the A-Site. It is anticipated that the excavation will not extend into the banks of the oxbow channel; this will be confirmed in the field by sampling.

Following post-excavation verification sampling and confirmation that the established cleanup criterion has been achieved, the excavation areas will be backfilled and restored as discussed in Section 3.6.2.

Materials excavated from the Oxbow Area will be transported to the A-Site and consolidated with existing materials. Excavated residuals observed to contain free liquids will be placed in a temporary lined staging area and gravity dewatered prior to transport to the A-Site. An imported aggregate may be used to solidify excavated material, as necessary. The contractor will be responsible for conducting paint filter testing (USEPA Method 9095A, as presented in Appendix B) to evaluate the presence of free liquids in representative samples of material subject to transportation to the A-Site.

3.5 Liquids Handling and Treatment

Water collected from temporary staging/dewatering areas, decontamination fluids, and other liquids generated during construction activities will be treated onsite at a temporary water treatment system. Water will be collected, handled, treated, monitored, and discharged to the Kalamazoo River consistent with the SRD (MDEQ, 1998) for discharge of treated water from Georgia-Pacific property to the Kalamazoo River (see Appendix A).

3.6 Refuse Area and Oxbow Area Restoration

3.6.1 Refuse Area Restoration Plan

Based on the collective recommendation of the USFWS and the MDNR, the intent of the restoration plan in the Refuse Area is to restore the area as a floodplain. Following excavation of the Refuse Area, an approximately 10-foot buffer zone, consisting of native material, is anticipated to remain along the river bank. For the purposes of this Work Plan, the buffer zone will be considered the area between the edge of the Refuse Area excavation and the river bank, at an elevation of 755 feet above mean sea level. Prior to disturbing this material, seven representative samples will be collected from the buffer zone and analyzed for PCB. If the analytical results confirm that PCB concentrations in the buffer zone are below 1 mg/kg, then the existing material will be used as backfill for the Refuse Area.

If during excavation the materials in the buffer zone are observed to contain residuals or are not native material, the buffer materials will be removed after construction of a small temporary diversion berm, as discussed in Section 3.4.1. The berm material will be analyzed prior to its use to confirm that it does not contain PCB concentrations greater than or equal to 1 mg/kg.

Following the completion of excavation activities in the Refuse Area, the native material in the buffer zone (or the imported material used to create a temporary diversion berm, if necessary) will be used to backfill the Refuse Area. Backfilling will be performed by creating a gradual inclining slope from the edge of the river back to the upland extent of the excavation. Once backfilling and grading activities are complete, the new floodplain will be vegetated and a 5-foot-wide, 6-inch-thick layer of riprap will be installed along the bank of the Kalamazoo River. For the purposes of establishing vegetation, material used to backfill the Refuse Area will be tested to confirm that the pH (between 5.5 and 7.5) and organic content (e.g., greater than 10%) are suitable for establishing vegetative growth. If, based on these criteria, the existing material is deemed unsuitable for establishing vegetative growth, the floodplain area will be covered with a 4- to 6-inch layer of topsoil and hydroseeded.

3.6.2 Oxbow Area Restoration

Following excavation of the upper 2 feet of material in the Oxbow Area, the excavated area will be backfilled with imported material. Similar to the Refuse Area restoration, backfill material will be tested to confirm that the pH (between 5.5 and 7.5) and organic content (e.g., greater than 10%) are suitable for establishing vegetative growth. The only restoration effort will take place along the bank of the Oxbow Channel, which will be vegetated with woody shrubs, as requested by U.S. Fish and Wildlife Service (USFWS) and MDNR.

3.7 Environmental Monitoring

Environmental monitoring will be conducted throughout the removal action construction activities. Environmental monitoring activities, described below, are anticipated to include dust monitoring, ambient air monitoring for PCB, and turbidity monitoring. Additional information regarding environmental monitoring activities shall be included in the CQAP.

3.7.1 Dust Monitoring

Dust monitoring will be conducted during removal action construction activities that may potentially generate dust. Monitoring will consist of both visible observations of airborne particulates as well as monitoring via a Mini-Ram particulate monitor. In accordance with National Ambient Air Quality Standards (NAAQS), if airborne particulate concentrations are measured at 150 $\mu g/m^3$ or above, appropriate dust suppression/control measures will be implemented.

3.7.2 Air Monitoring

PCB will be monitored in ambient air at two locations (Figure 3), with an action level set at 0.02 micrograms per cubic meter ($\mu g/m^3$). However, in accordance with Rule 225 (3) of Part 55, Act 451 as amended, a 10-fold increase in the secondary risk screening levels (SRSLs) is permitted if the ambient impact occurs on industrial property or public roadways. Given the nature of the physical settings of the removal activities, an action level of 0.2 $\mu g/m^3$ for the location shown on Figure 3 will be used. If an action level is exceeded, the USEPA will be notified and corrective actions will be taken to reduce emissions.

The air monitoring program will follow the procedures outlined by USEPA Method TO-4A from the *Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air* (USEPA, 1999) for sample collection and analysis (see Appendix C). Sampling will be conducted daily for 5 days during commencement of remediation activities at the Mill Properties. Samples will be collected during the entire work day. If the first week's data demonstrate that concentrations at the monitoring locations are below the action levels and similar activities are planned for subsequent weeks, the frequency of sampling may be reduced or terminated upon approval by the USEPA. Following a reduction in sampling frequency, if the nature of the work changes significantly, air monitoring may be resumed.

Meteorological data will be recorded during sampling days. Approximate wind direction, wind speed, and general weather conditions will be obtained from the Battle Creek/Kalamazoo International Airport.

Georgia-Pacific's onsite representative will perform and document the air monitoring activities. The ambient air PCB concentration data will be made available for USEPA review as soon as the data are received from the laboratory.

3.7.3 Turbidity Monitoring

Turbidity monitoring will be performed in the Kalamazoo River approximately 100 feet upstream and 100 feet downstream of excavation activities in the Refuse Area during periods of active work. Measurements of turbidity at the mid-depth point of the water column will be recorded daily (2 hours into the start of the work day). Turbidity monitoring will be conducted consistent with the TMP (BBL, 1999).

If excavation activities progress to within close proximity of the oxbow channel, turbidity monitoring may also be performed at appropriate upstream and downstream locations in the oxbow channel, if necessary.

3.8 Decontamination

Field personnel, vehicles, and equipment will be decontaminated before leaving the work area. All field staff will complete the following decontamination procedures prior to leaving the work area:

- Remove significant residual material from outer clothing and boots;
- Remove soiled outer garments and gloves, and deposit them in lined waste receptacles; and
- Decontaminate hard hats and boots with an aqueous solution of detergent or other appropriate cleaning solution, as necessary.

Vehicle or equipment decontamination will consist of cleaning tires and wheel wells. Significantly soiled equipment will be steam cleaned or pressure washed. Wash water will be collected, transported to the onsite treatment system, treated, and discharged to the Kalamazoo River consistent with the SRD (MDEQ, 1998).

3.9 Verification Sampling and Analysis

Verification sampling will be conducted on the floor and walls of the Refuse Area and Oxbow Area excavations to confirm that residual PCB concentrations in the remaining soil are at or below the 16 mg/kg criterion. Twenty percent of the verification samples will also be analyzed for TCL/TAL constituents and compared against the established criteria.

Verification sampling frequency and sampling locations will be determined based on the steps described in *Sampling Strategies and Statistics Training Materials for Part 201 Cleanup Criteria* (MDEQ, 2002). It is

anticipated that the sampling grid will be determined in the field for each excavation segment, and samples will be collected in consultation with the USEPA on-scene coordinator following excavation of visible residuals. However, based on the anticipated extent of excavation, proposed sampling grids have been developed as a reference. The anticipated sampling grids and associated calculations are included in Appendix D.

If the analytical results of post-excavation verification samples indicate that PCB are present in soil at concentrations greater than the established criteria, a 20-foot by 20-foot area around the sample location will be re-excavated. A verification sample will then be collected from the floor or wall of the new excavation area and compared to the appropriate criterion. This process will be repeated as necessary to achieve the appropriate cleanup criterion.

3.10 Consolidation of Materials at the A-Site

Prior to disposal of excavated residuals and soils, the area of the A-Site being used for consolidation of material will be cleared and grubbed. Existing access roads will be used, as appropriate. Figure 4 presents the anticipated route that trucks will travel between the Mill Properties and the A-Site disposal area.

An erosion control blanket will be placed on the consolidated residuals as a temporary erosion control measure until the cover material is placed. The beds of the trucks used to transport the materials from the Mill Properties to the A-Site will be lined and properly covered (e.g., tarp covers).

Once consolidation of materials at the A-Site is complete, a minimum of 12 inches of clean soil will be placed over the newly placed materials and graded to a slope of 4:1, followed by implementation of long-term erosion control measures. Consistent with the ESCP, long-term erosion control will consist of planting shallow-rooted grasses (e.g., a mixture of perennial rye, Kentucky blue, creeping red fescue, timothy, and orchard grass). This will serve as an interim cover until the WB/A-Site OU is closed.

3.11 Documentation

Actions undertaken as part of this Work Plan will be summarized on a monthly basis as part of the monthly reports prepared for the Allied Paper, Inc./Portage Creek/Kalamazoo River Superfund Site. Additionally, after completion of all construction activities prescribed in the WB/A-Site OU RD/RA AOC, a Completion of

Construction Report will be prepared and submitted to USEPA for approval. The WB/A-Site OU Completion of Construction Report will document the work completed at the Mill Properties and sample results.

4. Post-Removal Action Activities

4.1 General

Following completion of removal action construction activities at the Mill Properties, several post-removal action activities will be performed, as discussed below.

4.2 Post-Removal Site Control Plan

Following approval of the WB/A-Site OU Construction Completion Report, Georgia-Pacific will submit a Post-Removal Site Control Plan for USEPA approval, as required by the WB/A-Site OU RD/RA AOC. The Post-Removal Site Control Plan will be prepared consistent with Section 300.415(1) of the NCP and USEPA's Office of Solid Waste and Emergency Response (OSWER) Directive No. 9360.2-02, and will identify procedures for post-removal operations, maintenance activities, and institutional controls (e.g., deed restrictions), as appropriate. Requirements related to post-removal site controls to be implemented at the Mill Properties are currently identified in Section ___ of the WB/A-Site OU RD/RA AOC.

5. References

Blasland & Bouck Engineers, P.C. (BBEPC). 1993a. *Allied Paper, Inc./Portage Creek/Kalamazoo River Superfund Description of the Current Situation.* (Syracuse, NY: June 1993).

BBEPC. 1993b. *Allied Paper, Inc./Portage Creek/Kalamazoo River Superfund Site Remedial Investigation/ Feasibility Study – Field Sampling Plan.* (Syracuse, NY: June 1993).

BBEPC. 1993c *Allied Paper, Inc./Portage Creek/Kalamazoo River Superfund Site Remedial Investigation/ Feasibility Study – Quality Assurance Project Plan.* (Syracuse, NY: June 1993).

Blasland, Bouck & Lee, Inc. (BBL). 1996. *Allied Paper, Inc./Portage Creek/Kalamazoo River Superfund Site Remedial Investigation/Feasibility Study Technical Memorandum 15 – Mill Investigation.* Volume I of II. (Syrcause, NY: August 1996).

BBL. 1997. *Final Document in Support King Highway Landfill Operable Unit RI/FS* (Syracuse, NY: June 1997).

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BBL. 2003b. *Georgia Pacific Corporation Kalamazoo Paper Mill Property Divestiture Study/Supporting Materials.* (Syracuse, NY: March 4, 2003).

BBL. 2004a. *Former Hawthorne Mill Oxbow Sediment Investigation Work Plan* (Syracuse, NY: December 2004).

BBL. 2004b. *Former Hawthorne Mill Oxbow Sediment Investigation Report* (Syracuse, NY: December 2004).

BBL. 2005. *Former Hawthorne Mill Supplemental Soil Investigation Activities Summary* (Syracuse, NY: September 2005).

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MDEQ. 2002. *Sampling Strategies and Statistics Training Materials for Part 201 Cleanup Criteria.* MDEQ – Environmental Response Division (Lansing, MI: 2002).

USEPA. 1999. *Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air*, *Second Edition*, EPA/625/R-96/010b, January, 1999.

Figures

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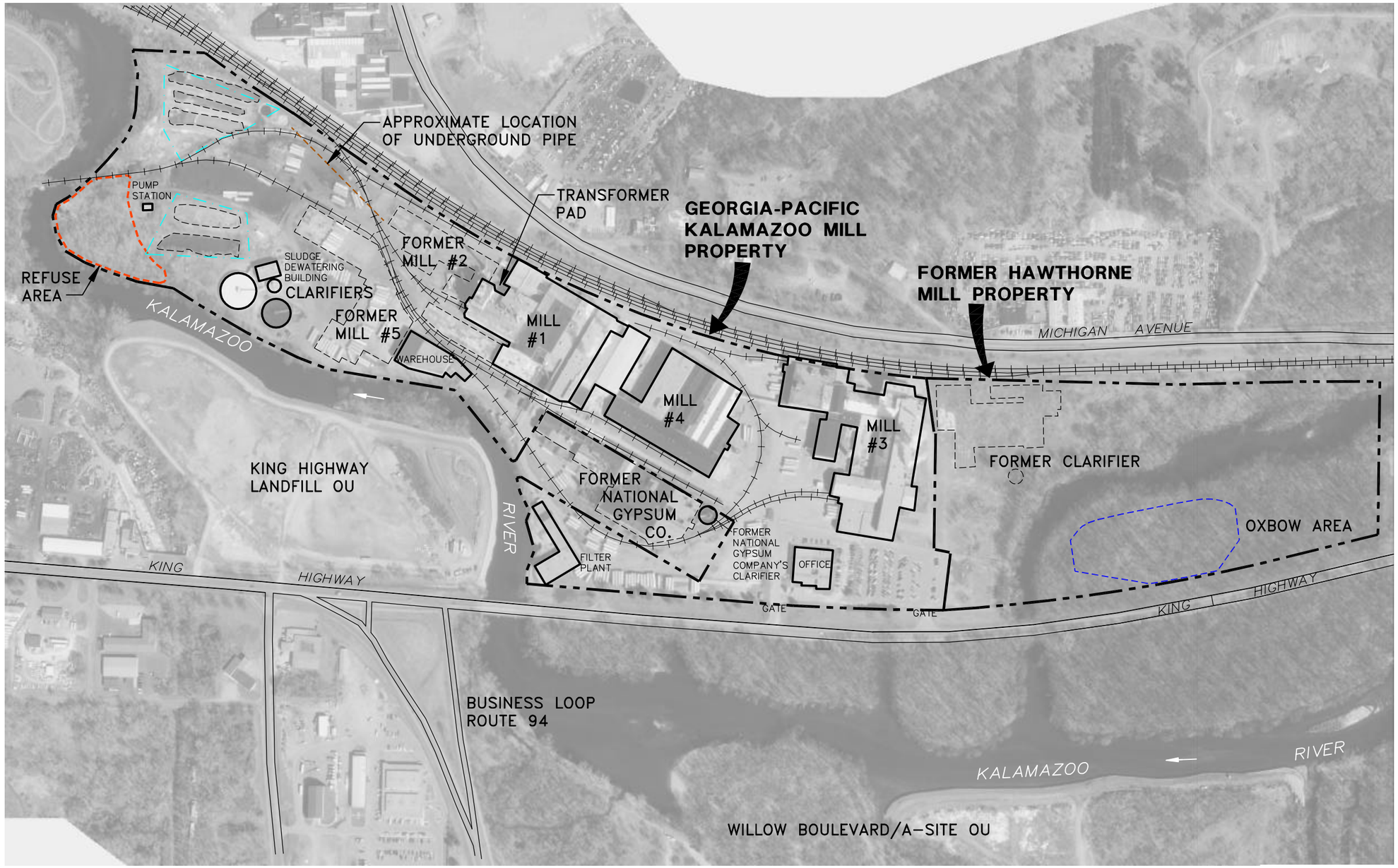

LEGEND:

- APPROXIMATE REFUSE AREA REMOVAL AREA
- APPROXIMATE OXBOW AREA REMOVAL AREA
- APPROXIMATE MILL LAGOON PROPERTY BOUNDARY
- APPROXIMATE BOUNDARY OF KALAMAZOO MILL AND HAWTHORNE MILL PROPERTIES
- APPROXIMATE BOUNDARY OF FORMER MILLS
- OUTLINE OF STANDING STRUCTURES

NOTES:

1. PLANIMETRIC MAPPING, INCLUDING PROPERTY BOUNDARIES, IS APPROXIMATE.
2. AERIAL IMAGE DERIVED FROM ORTHOPHOTOGRAPHIC DATA BY AIR LAND SURVEYS, INC., FLOWN 4/24/99.
3. FORMER MILL LAGOONS EXCAVATED PER KING HIGHWAY LANDFILL–OPERABLE UNIT AOC, 1999–2000.

0 400' 800'

GRAPHIC SCALE

DRAFT

GEORGIA–PACIFIC CORPORATION
KALAMAZOO MILL PROPERTY
REMOVAL ACTION WORK PLAN

GEORGIA-PACIFIC KALAMAZOO MILL AND HAWTHORNE MILL SITE PLAN

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FIGURE **1**

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NOTES:

1. PLANIMETRIC MAPPING, INCLUDING PROPERTY BOUNDARIES, IS APPROXIMATE.
2. AERIAL IMAGE DERIVED FROM ORTHOPHOTOGRAPHIC DATA BY AIR LAND SURVEYS, INC., FLOWN 4/24/99.

0 200' 400'

GRAPHIC SCALE

DRAFT

GEORGIA-PACIFIC CORPORATION
KALAMAZOO MILL PROPERTY
REMOVAL ACTION WORK PLAN

LOCATION OF A-SITE DISPOSAL AREA

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FIGURE
2

X: 64585X00, X01.DWG, 64585X02, X03.TIF
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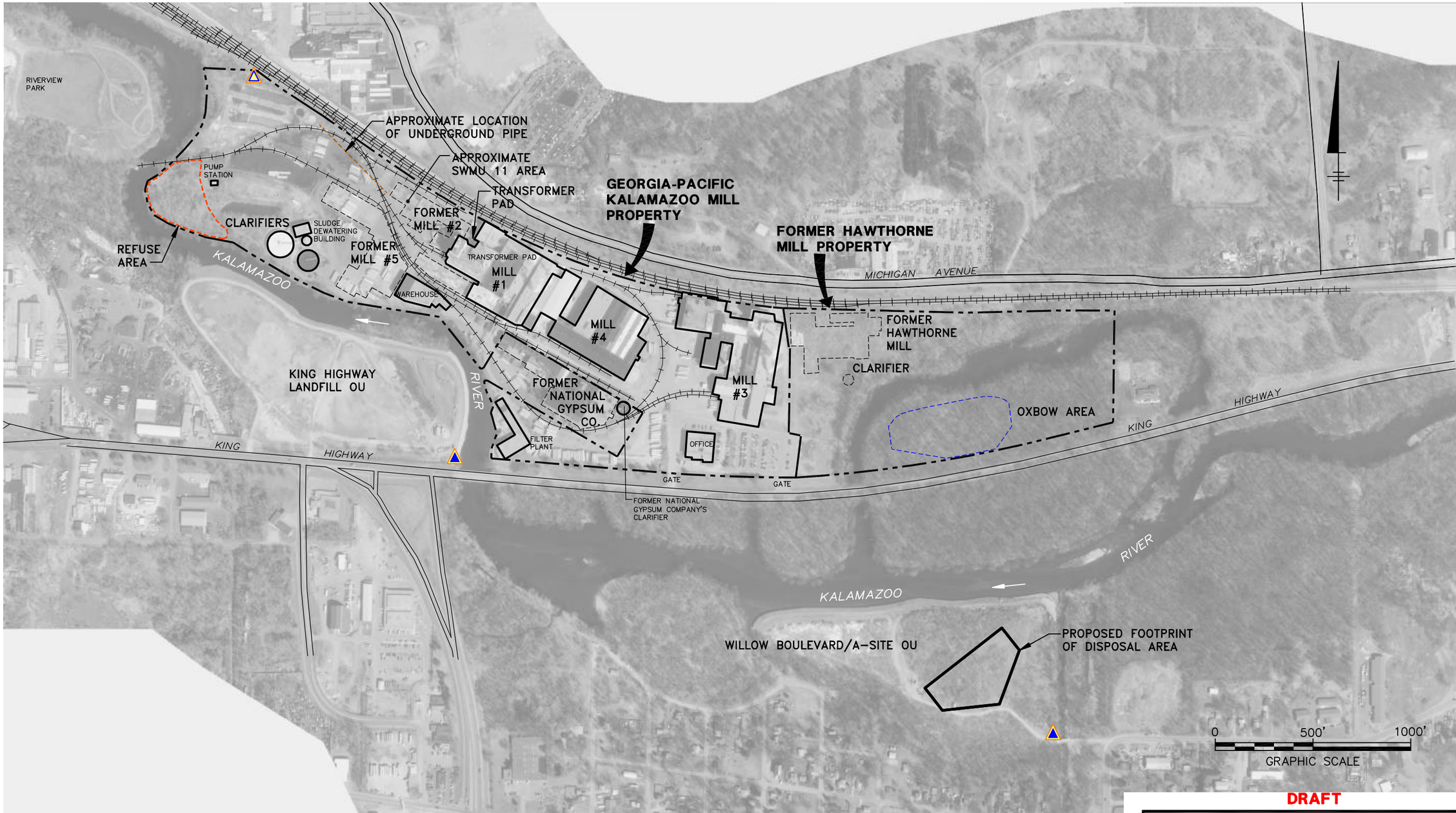

DRAFT

NOTES:

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2. AERIAL IMAGE DERIVED FROM ORTHOPHOTOGRAPHIC DATA BY AIR LAND SURVEYS, INC., FLOWN 4/24/99.
3. PROPOSED MONITORING LOCATIONS ARE APPROXIMATE, LOCATIONS MAY VARY BASED ON FIELD CONDITIONS ENCOUNTERED DURING THE REMOVAL ACTION.

LEGEND:

- APPROXIMATE REFUSE AREA REMOVAL AREA
- APPROXIMATE BOUNDARY OF KALAMAZOO MILL AND HAWTHORNE MILL PROPERTIES
- APPROXIMATE BOUNDARY OF FORMER MILLS
- APPROXIMATE OXBOW AREA REMOVAL AREA
- PROPOSED AIR MONITORING LOCATION AND PCB ACTION LEVEL
- PROPOSED AIR MONITORING LOCATION AND PCB ACTION LEVEL

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GEORGIA-PACIFIC CORPORATION
KALAMAZOO MILL PROPERTY
REMOVAL ACTION WORK PLAN

GEORGIA-PACIFIC KALAMAZOO MILL AND HAWTHORNE MILL ENVIRONMENTAL MONITORING LOCATIONS

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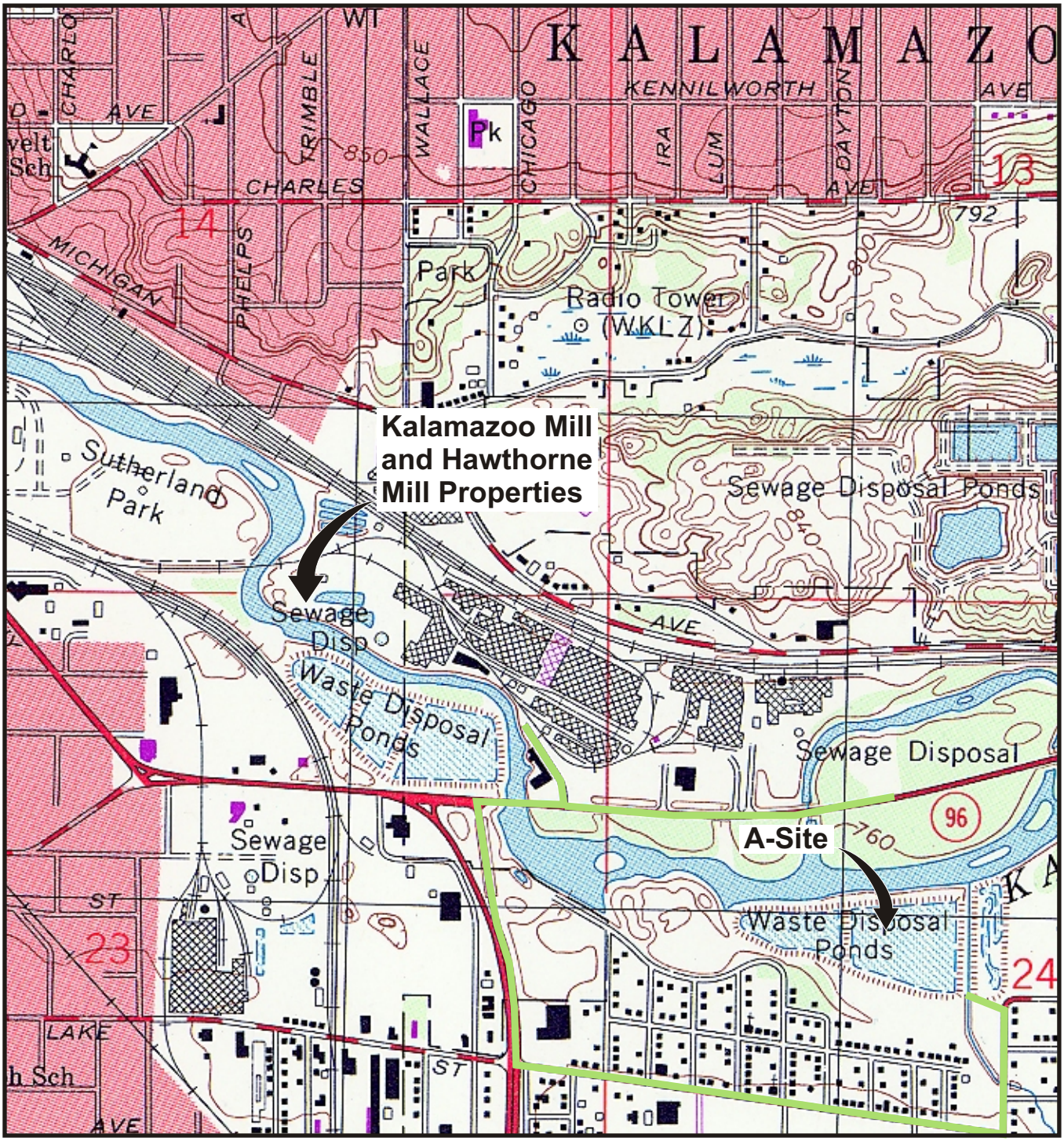
FIGURE **3**



REFERENCE: BASE MAP USGS 7.5 MIN. QUAD., KALAMAZOO, MI, 1995.

LEGEND

ROUTE TO DISPOSAL AREA

1000' 0 1000'

Approximate Scale: 1" = 1000'

DRAFT

Area Location

GEORGIA-PACIFIC CORPORATION
KALAMAZOO MILL PROPERTY
REMOVAL ACTION WORK PLAN

ROUTE TO DISPOSAL AREA

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FIGURE 4

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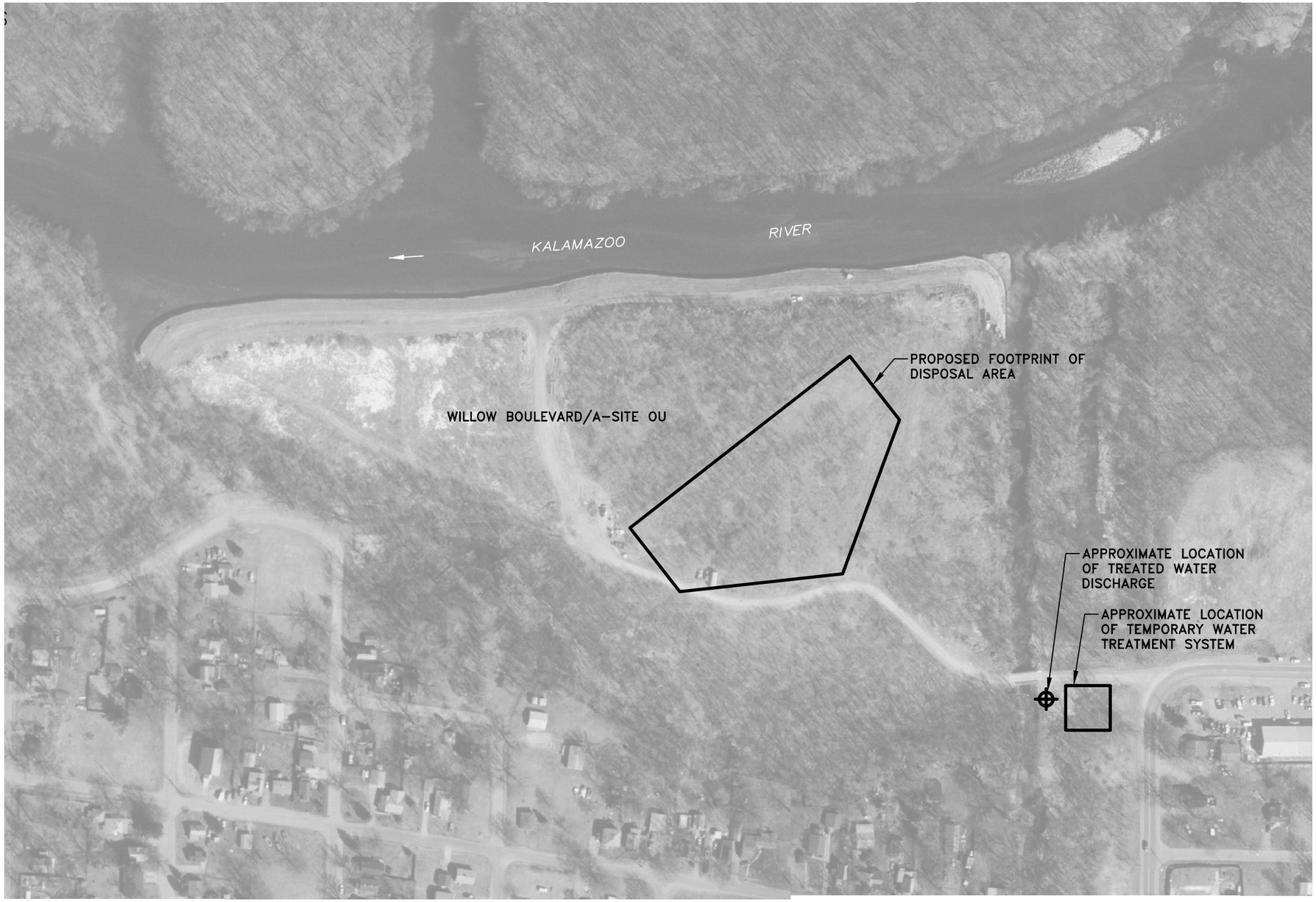

NOTES:

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2. AERIAL IMAGE DERIVED FROM ORTHOPHOTOGRAPHIC DATA BY AIR LAND SURVEYS, INC., FLOWN 4/24/99.

0 200' 400'

GRAPHIC SCALE

DRAFT

GEORGIA–PACIFIC CORPORATION
KALAMAZOO MILL PROPERTY
REMOVAL ACTION WORK PLAN

LOCATION OF A-SITE DISPOSAL AREA AND TEMPORARY WATER TREATMENT UNIT

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FIGURE
2

X: 64585X00, X01.DWG, 64585X02, X03.TIF
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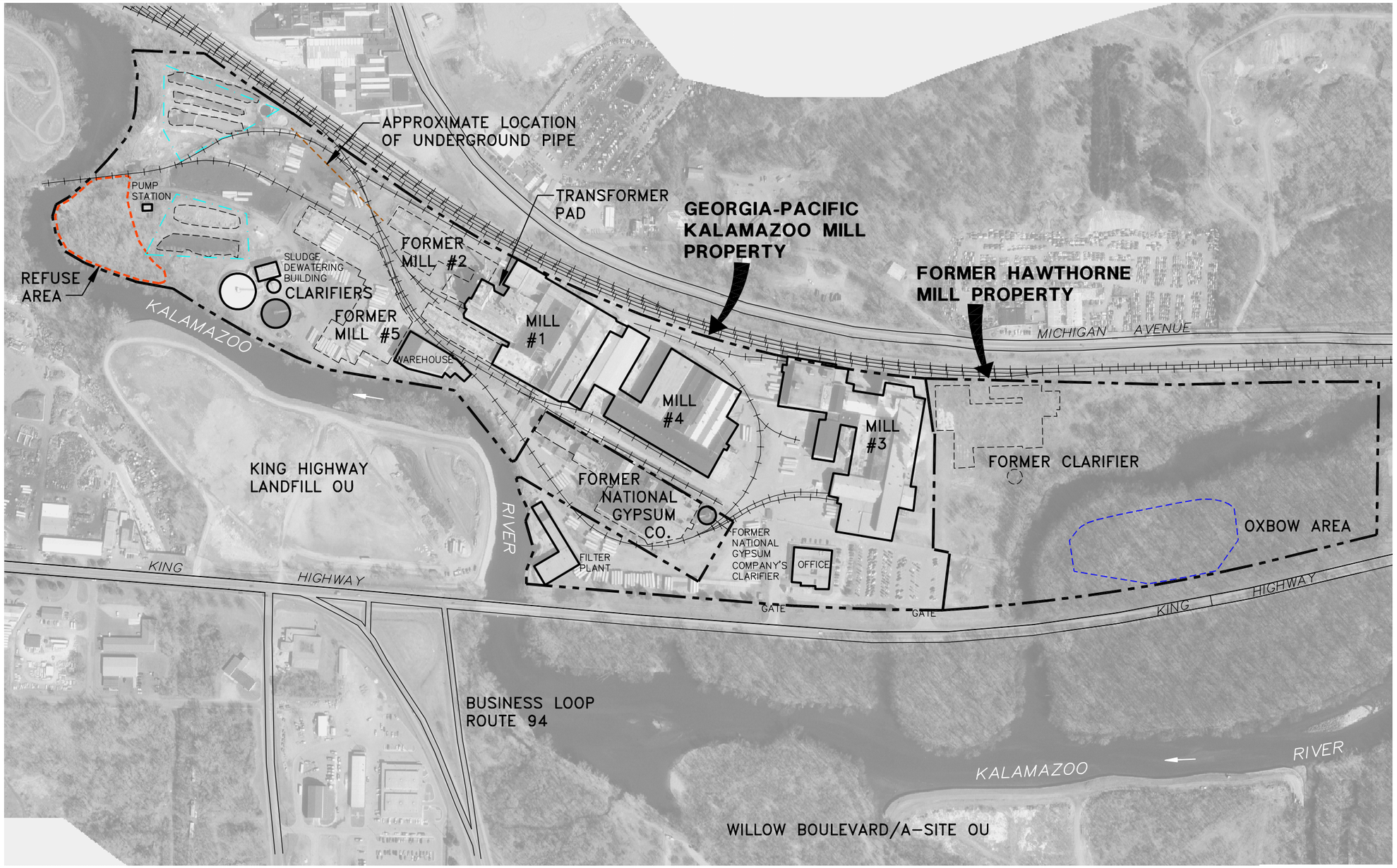

LEGEND:

- APPROXIMATE REFUSE AREA REMOVAL AREA
- APPROXIMATE OXBOW AREA REMOVAL AREA
- APPROXIMATE MILL LAGOON PROPERTY BOUNDARY
- APPROXIMATE BOUNDARY OF KALAMAZOO MILL AND HAWTHORNE MILL PROPERTIES
- APPROXIMATE BOUNDARY OF FORMER MILLS
- OUTLINE OF STANDING STRUCTURES

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1. PLANIMETRIC MAPPING, INCLUDING PROPERTY BOUNDARIES, IS APPROXIMATE.
2. AERIAL IMAGE DERIVED FROM ORTHOPHOTOGRAPHIC DATA BY AIR LAND SURVEYS, INC., FLOWN 4/24/99.
3. FORMER MILL LAGOONS EXCAVATED PER KING HIGHWAY LANDFILL–OPERABLE UNIT AOC, 1999–2000.

0 400' 800'

GRAPHIC SCALE

DRAFT

GEORGIA–PACIFIC CORPORATION
KALAMAZOO MILL PROPERTY
REMOVAL ACTION WORK PLAN

GEORGIA-PACIFIC KALAMAZOO MILL AND HAWTHORNE MILL SITE PLAN

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FIGURE **1**

X: 64585X01, X00.DWG, 64585X02, X03.TIF
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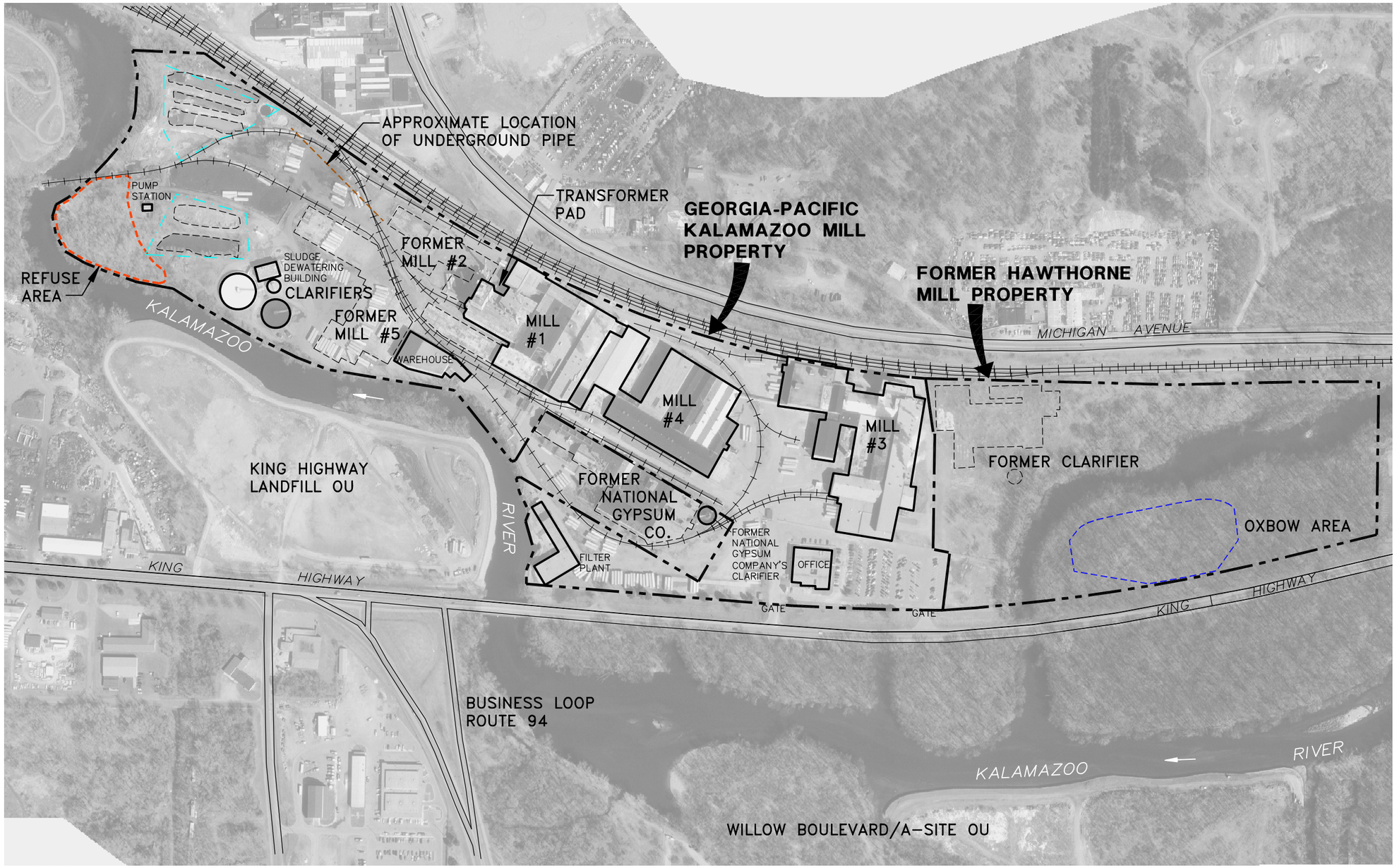

LEGEND:

- APPROXIMATE REFUSE AREA REMOVAL AREA
- APPROXIMATE OXBOW AREA REMOVAL AREA
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0 400' 800'

GRAPHIC SCALE

DRAFT

GEORGIA–PACIFIC CORPORATION
KALAMAZOO MILL PROPERTY
REMOVAL ACTION WORK PLAN

GEORGIA-PACIFIC KALAMAZOO MILL AND HAWTHORNE MILL SITE PLAN

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FIGURE **1**

X: 64585X01, X00.DWG, 64585X02, X03.TIF
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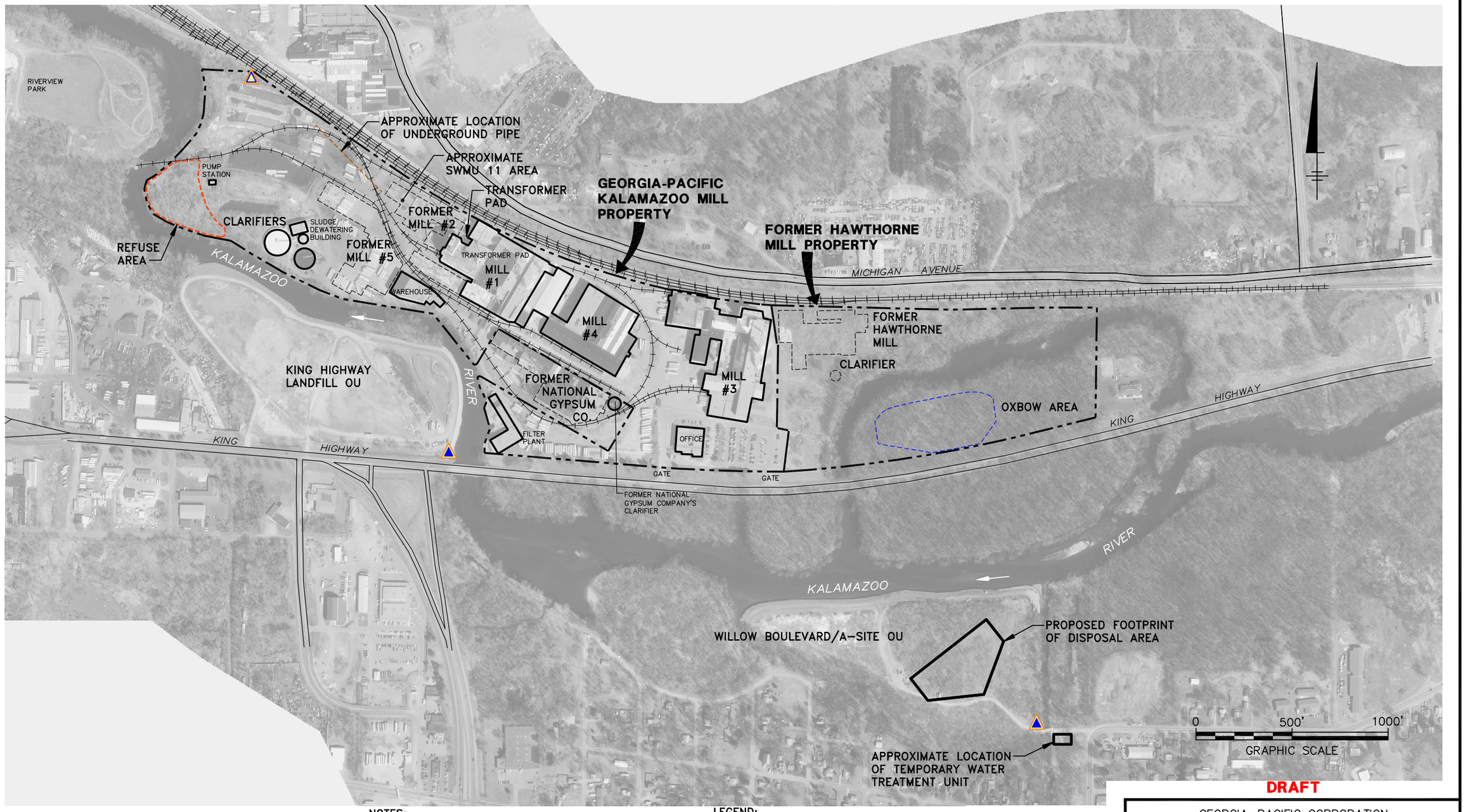

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3. PROPOSED MONITORING LOCATIONS ARE APPROXIMATE, LOCATIONS MAY VARY BASED ON FIELD CONDITIONS ENCOUNTERED DURING THE REMOVAL ACTION.

LEGEND:

- APPROXIMATE REFUSE AREA REMOVAL AREA
- APPROXIMATE BOUNDARY OF KALAMAZOO MILL AND HAWTHORNE MILL PROPERTIES
- APPROXIMATE BOUNDARY OF FORMER MILLS
- APPROXIMATE OXBOW AREA REMOVAL AREA
- PROPOSED AMBIENT AIR MONITORING LOCATION AND PCB ACTION LEVEL OF 0.2 ug/m3
- PROPOSED AMBIENT AIR MONITORING LOCATION AND PCB ACTION LEVEL OF 0.02 ug/m3

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GEORGIA-PACIFIC CORPORATION
KALAMAZOO MILL PROPERTY
REMOVAL ACTION WORK PLAN

GEORGIA-PACIFIC KALAMAZOO MILL AND HAWTHORNE MILL ENVIRONMENTAL MONITORING LOCATIONS

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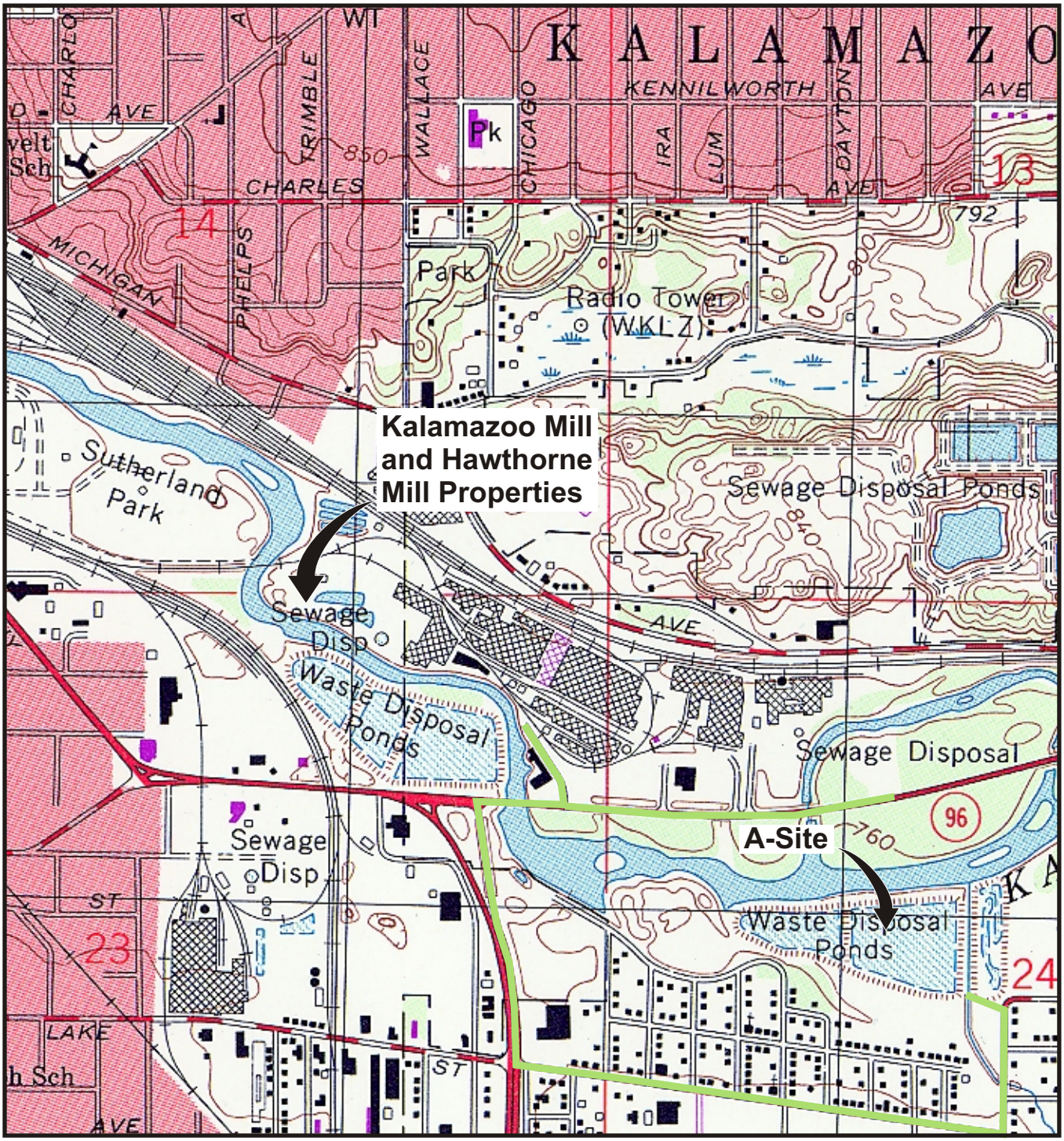
FIGURE **4**



REFERENCE: BASE MAP USGS 7.5 MIN. QUAD., KALAMAZOO, MI, 1995.

LEGEND

ROUTE TO DISPOSAL AREA

1000' 0 1000'

Approximate Scale: 1" = 1000'

DRAFT

Area Location

GEORGIA-PACIFIC CORPORATION
KALAMAZOO MILL PROPERTY
REMOVAL ACTION WORK PLAN

ROUTE TO DISPOSAL AREA

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FIGURE 5

05/15/06 SYR-D85-DJH
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Appendices

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Appendix A

Substantive Requirements Document

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STATE OF MICHIGAN

JOHN ENGLER, Governor

DEPARTMENT OF ENVIRONMENTAL QUALITY

"Better Service for a Better Environment"

HOLLISTER BUILDING, PO BOX 30473, LANSING MI 48909-7973

INTERNET: www.deq.state.mi.us

RUSSELL J. HARDING, Director

REPLY TO:

SURFACE WATER QUALITY DIVISION
KNAPPS CENTRE
PO BOX 30273
LANSING MI 48909-7773

July 27, 1998

CERTIFIED MAIL -- P 257 551 524

Georgia-Pacific Corporation
2425 King Highway
Kalamazoo, Michigan 49001

Dear Sir or Madam:

SUBJECT: Substantive Requirements Document -- No. MIU990018
Georgia Pacific-King Hwy SF, King Highway/M-96, Kalamazoo -- Superfund Site

The application for substantive requirements for wastewater discharge from the Georgia-Pacific Corporation has been processed in accordance with our Divisional Procedures. The enclosed Substantive Requirements Document (SRD) contains the requirements necessary for compliance with state and federal water pollution control laws.

Please review the requirements in the SRD, including the monitoring and reporting responsibilities. Discharge Monitoring Report forms will be transmitted to you in the near future. These reports are to be submitted as required by the SRD.

Any report, notifications, or questions regarding the enclosed SRD programs should be directed to the following address:

Mr. Fred Morley, District Supervisor
Plainwell District Office, SWQD, DEQ
1342 SR-89 W, Suite B
Plainwell, Michigan 49080-1915
Telephone: 616-692-2120

Questions about the basis for the SRD requirements may be directed to Ms. Camille Parker of the Permits Section at 517-335-4115.

Sincerely,

William E. McCracken

William E. McCracken
Chief, Permits Section
Surface Water Quality Division
517-373-8088

Attachment: Substantive Requirements Document
cc: Mr. Fred Morley, Plainwell District Supervisor, SWQD (2)
Ms. Camille Parker, Permits Section, SWQD
PCS Unit, SWQD
Superfund Section, ERD
Files

MIU990018

MICHIGAN DEPARTMENT OF ENVIRONMENTAL QUALITY

SUBSTANTIVE REQUIREMENTS DOCUMENT FOR THE GEORGIA PACIFIC CERCLA OUTFALL SITE

Authorization to (hereinafter referred to as the "discharger"):

Georgia-Pacific Corporation
2425 King Highway
Kalamazoo, Michigan 49001

is authorized to discharge from the King Highway Landfill located at

King Highway/M-96
Kalamazoo, Michigan 49001

designated as Georgia Pacific-King Hwy SF

In accordance with Section 121(d) of the Comprehensive Environmental Response, Compensation, and Liability Act (42 U.S.C. 9601 et seq; "CERCLA") and the Superfund Amendments and Reauthorization Act (Public Law No. 99-499, "SARA"), the Surface Water Quality Division of the Michigan Department of Environmental Quality, in compliance with the provisions of the Federal Water Pollution Control Act, as amended (33 U.S.C. 1251 et seq; the "Federal Act"), Michigan Act 451, Public Acts of 1994, as amended (the "Michigan Act"), Parts 31 and 41, and Michigan Executive Orders 1991-31, 1995-4 and 1995-18, which are legally applicable or relevant and appropriate requirements (ARARs), herein establishes substantive requirements for a discharge of treated excavation water, ponded water, washwater and stormwater runoff from the Georgia Pacific CERCLA Outfall Site to the Kalamazoo River in Section 23, T2S, R11W, Kalamazoo Township, Kalamazoo County.

These substantive requirements are based on information (hereinafter referred to as the "application") received on February 6, 1998, from Georgia-Pacific Corporation, which provided a description of the wastewater characteristics and proposed treatment. If new information is received subsequent to the effective date of this document, these substantive requirements may be revised if necessary to protect the receiving waters consistent with the Act and the Michigan Act.

This document is not a National Pollutant Discharge Elimination System (NPDES) permit. A NPDES permit is not required for this on-site remedial action associated with a CERCLA cleanup, however, a NPDES permit shall be required to authorize any discharges from this site under any circumstances not exempted by CERCLA Section 121(e)(1).

Effective Date: July 23, 1998.

William E. McCracken
Chief, Permits Section
Surface Water Quality Division

PART I

Section A. Limitations And Monitoring Requirements

1. Final Effluent Limitations, Outfall 001

This document is based on the discharge of a maximum of two hundred eighty-eight thousand (288,000) gallons per day of treated excavation water, ponded water, washwater and stormwater runoff through outfall 001 to the Kalamazoo River. Such discharge shall be limited and monitored by the discharger as specified below:

Parameter	Maximum Limits for Quantity or Loading			Maximum Limits for Quality or Concentration			Frequency of Analysis	Sample Type
	Monthly	Daily	Units	Monthly	Daily	Units		
INFLUENT MONITORING AND REPORTING								
Polychlorinated Biphenyls (PCBs)	---	---	---	(report)	(report)	µg/l	Weekly	Grab
Total Suspended Solids	---	---	---	(report)	(report)	mg/l	Weekly	Grab
INTERMEDIATE STAGE MONITORING AND REPORTING								
PCBs	---	---	---	(report)	(report)	µg/l	Weekly	Grab
DISCHARGE LIMITATIONS, MONITORING AND REPORTING								
	(report)	(report)	MGD	---	---	---	Daily During Discharge	Report Total Daily Flow
PCBs	6.248×10^{-8}	---	lbs/day	2.6×10^{-5}	---	µg/l	Daily During Discharge	3-Portion Composite
Total Suspended Solids	---	---	---	30	45	mg/l	Daily During Discharge	3-Portion Composite
Equipment Inspection	(report)	---	---	---	---	---	3X/Week	Visual
Outfall Observation	(report)	---	---	---	---	---	Daily	Visual

a. Limits Below Level of Detection

The sampling procedures, preservation and handling, and analytical protocol for compliance monitoring for PCBs shall be in accordance with EPA Method 608. The quantification level shall not exceed 0.1 µg/l, unless higher levels are appropriate because of sample matrix interference. Other analytical methods may be used upon approval of the Plainwell District Supervisor of the Surface Water Quality Division.

The water quality-based effluent limitations for PCBs are less than the level of detection using the specified analytical methods. Any discharge of PCBs at or above the level of detection is a specific violation of this document. If all the samples in any monthly reporting period are less than the level of detection, the Michigan Department of Environmental Quality will consider the discharger to be in compliance with the final effluent limitations for these pollutants for that reporting period. This paragraph does not authorize the discharge of PCBs at levels which are injurious to the designated uses of the waters of the state or which constitute a threat to the public health or welfare. Total PCBs shall be defined as the sum of Aroclors 1242, 1248, 1254, and 1260. In addition, any detected Aroclor-specific measurements shall be reported.

PART I

Section A. Limitations And Monitoring Requirements

b. BAT Treatment
This document is based on the discharger providing filtration and liquid-phase granular two-stage activated carbon. If treatment other than filtration and liquid-phase granular two-stage activated carbon is proposed, the discharger shall amend the application received on February 6, 1998. The document may then be modified to include additional effluent limitations to protect water quality in accordance with applicable rules and regulations.

c. Narrative Standard
The receiving water shall contain no unnatural turbidity, color, oil films, floating solids, foams, settleable solids, or deposits as a result of this discharge.

d. Monitoring Locations
Samples, measurements, and observations taken in compliance with the monitoring requirements above shall be taken prior to treatment for all influent monitoring, between the carbon stages for intermediate stage monitoring, and after treatment but prior to mixing with any other waste stream for all effluent monitoring.

e. Monitoring Frequency
Upon initiation of discharge, the influent, the intermediate stage, and the effluent shall be monitored and sampled at the frequency indicated in Part I.A.1. of this document. After three (3) months, and if steady state conditions have been achieved, the discharger may request a reduction in monitoring frequency. This request shall be submitted to the Plainwell District Supervisor of the Surface Water Quality Division. Upon receipt of written approval and consistent with such approval, the discharger may reduce the monitoring frequency indicated in Part I.A.1. of this document. The monitoring frequency shall not be reduced to less than once per month. The Plainwell District Supervisor may revoke the approval for reduced monitoring at any time upon notification to the discharger.

f. Analytical Testing
The discharger shall store the treated wastewater until sampling and analysis confirms that the discharge limitations have been achieved prior to discharging the wastewater to the Kalamazoo River.

g. Proper Operation and Maintenance
The discharger shall operate the two-stage activated carbon treatment system so that rotation and replacement of the carbon tanks shall occur immediately upon detection of PCBs at the intermediate stage.

h. Outfall Observation
Any unusual characteristics of the discharge (i.e., unnatural turbidity, color, oil film, floating solids, foams, settleable solids, suspended solids, or deposits) shall be reported within 24 hours to the Plainwell District Supervisor of the Surface Water Quality Division followed with a written report within five (5) days detailing the findings of the investigation and the steps taken to correct the condition.

PART I

Section A. Limitations And Monitoring Requirements

i. Water Treatment Additives

This document does not authorize the discharge of water additives without approval from the Department. Water additives include any material that is added to water used at the facility or to a wastewater generated by the facility to condition or treat the water. In the event a discharger proposes to discharge water additives, the discharger shall submit a request to the Department for approval. Such requests shall be sent to the Great Lakes and Environmental Assessment Section, Surface Water Quality Division, Department of Environmental Quality, P.O. Box 30273, Lansing, Michigan 48909, with a copy of the request to the District Supervisor. Instructions may be obtained via the internet at *http://www.deq.state.mi.us/swq/gleas/docs/wta/wtamemo.htm* to submit a request electronically. Written approval from the Department to discharge such additives at specified levels shall be obtained prior to discharge by the discharger. Additional monitoring and reporting may be required as a condition for the approval to discharge the additive.

A request to discharge water additives shall include all of the following water additive usage and discharge information:

1) Material Safety Data Sheet;

2) the proposed water additive discharge concentration;

3) the discharge frequency (i.e., number of hours per day and number of days per year);

4) the outfall from which the product is to be discharged;

5) the type of removal treatment, if any, that the water additive receives prior to discharge;

6) product function (i.e. microbiocide, flocculant, etc.);

7) a 48-hour LC_{50} or EC_{50} for a North American freshwater planktonic crustacean (either *Ceriodaphnia sp., Daphnia sp., or Simocephalus sp.*); and

8) the results of a toxicity test for one other North American freshwater aquatic species (other than a planktonic crustacean) that meets a minimum requirement of Rule 323.1057(2) of the Water Quality Standards.

Prior to submitting the request, the discharger may contact the Great Lakes and Environmental Assessment Section by telephone at 517-335-4184 or via the internet at *http://www.deq.state.mi.us/swqd/gleas/docs/wta/wtalist.htm* to determine if the Department has the product toxicity data required by items 7) and 8). If the Department has the data, the discharger will not need to submit product toxicity data.

PART II

Section A. Definitions

This list of definitions may include terms not applicable to this document.

Acute toxic unit (TU_a) means $100/LC_{50}$ where the LC_{50} is determined from a whole effluent toxicity (WET) test which produces a result that is statistically or graphically estimated to be lethal to 50% of the test organisms.

Bioaccumulative chemical of concern (BCC) means a chemical which, upon entering the surface waters, by itself or as its toxic transformation product, accumulates in aquatic organisms by a human health bioaccumulation factor of more than 1000 after considering metabolism and other physiochemical properties that might enhance or inhibit bioaccumulation. The human health bioaccumulation factor shall be derived according to R 323.1057(5). Chemicals with half-lives of less than 8 weeks in the water column, sediment, and biota are not BCCs. The minimum bioaccumulation concentration factor (BAF) information needed to define an organic chemical as a BCC is either a field-measured BAF or a BAF derived using the biota-sediment accumulation factor (BSAF) methodology. The minimum BAF information needed to define an inorganic chemical as a BCC, including an organometal, is either a field-measured BAF or a laboratory-measured bioconcentration factor (BCF). The BCCs to which these rules apply are identified in Table 5 of R 323.1057 of the Water Quality Standards.

Chronic toxic unit (TU_c) means 100/MATC or $100/IC_{25}$, where the maximum acceptable toxicant concentration (MATC) and IC_{25} are expressed as a percent effluent in the test medium.

Daily concentration is the sum of the concentrations of the individual samples of a parameter divided by the number of samples taken during any calendar day. If the parameter concentration in any sample is less than the quantification limit, regard that value as zero when calculating the daily concentration. The daily concentration will be used to determine compliance with any maximum and minimum daily concentration limitations (except for pH and dissolved oxygen). When required by the document, report the maximum calculated daily concentration for the month in the "MAXIMUM" column under "QUALITY OR CONCENTRATION" on the Discharge Monitoring Reports (DMRs).

For pH, report the maximum value of any individual sample taken during the month in the "MAXIMUM" column under "QUALITY OR CONCENTRATION" on the DMRs and the minimum value of any individual sample taken during the month in the "MINIMUM" column under "QUALITY OR CONCENTRATION" on the DMRs. For dissolved oxygen, report the minimum concentration of any individual sample in the "MINIMUM" column under "QUALITY OR CONCENTRATION" on the DMRs.

Daily loading is the total discharge by weight of a parameter discharged during any calendar day. This value is calculated by multiplying the daily concentration by the total daily flow and by the appropriate conversion factor. The daily loading will be used to determine compliance with any maximum daily loading limitations. When required by the document, report the maximum calculated daily loading for the month in the "MAXIMUM" column under "QUANTITY OR LOADING" on the DMRs.

Department means the Michigan Department of Environmental Quality.

Detection Level means the lowest concentration or amount of the target analyte that can be determined to be different from zero by a single measurement at a stated level of probability.

District Supervisor: The Plainwell District Supervisor of the Surface Water Quality Division is located at the Plainwell District Office-DEQ, Surface Water Quality Division, 1342 SR-89 W, Suite B, Plainwell, Michigan 49080-1915, telephone: 616-692-2120 (fax: 616-692-6969).

Division of Health Facility Services -- Health Facility Evaluation Section, Michigan Department of Consumer and Industry Services mailing address is P.O. Box 30195, Lansing, Michigan 48909.

Drinking Water and Radiological Protection Division -- Environmental Health, Michigan Department of Environmental Quality mailing address is P.O. Box 30630, Lansing, Michigan 48909-8130.

EC_{50} means a statistically or graphically estimated concentration that is expected to cause 1 or more specified effects in 50% of a group of organisms under specified conditions.

PART II

Section A. Definitions

Fecal coliform bacteria monthly is the geometric mean of the samples collected in a calendar month (or 30 consecutive days). The calculated monthly value will be used to determine compliance with the maximum monthly fecal coliform bacteria limitations. When required by the document, report the calculated monthly value in the "AVERAGE" column under "QUALITY OR CONCENTRATION" on the DMRs.

Fecal coliform bacteria 7-day is the geometric mean of the samples collected in any 7-day period. The calculated 7-day value will be used to determine compliance with the maximum 7-day fecal coliform bacteria limitations. When required by the document, report the maximum calculated 7-day concentration for the month in the "MAXIMUM" column under "QUALITY OR CONCENTRATION" on the DMRs.

Flow Proportioned sample is a composite sample with the sample volume proportional to the effluent flow.

Grab sample is a single sample taken at neither a set time nor flow.

IC_{25} means the toxicant concentration that would cause a 25% reduction in a nonquantal biological measurements for the test population.

Interference is a discharge which, alone or in conjunction with a discharge or discharges from other sources, both:
1) inhibits or disrupts the POTW, its treatment processes or operations, or its sludge processes, use or disposal; and
2) therefore, is a cause of a violation of any requirement of the POTW's NPDES document (including an increase in the magnitude or duration of a violation) or, of the prevention of sewage sludge use or disposal in compliance with the following statutory provisions and regulations or documents issued thereunder (or more stringent state or local regulations): Section 405 of the Clean Water Act, the Solid Waste Disposal Act (SWDA) (including Title II, more commonly referred to as the Resource Conservation and Recovery Act (RCRA), and including state regulations contained in any state sludge management plan prepared pursuant to Subtitle D of the SWDA), the Clean Air Act, the Toxic Substances Control Act, and the Marine Protection, Research and Sanctuaries Act. [This definition does not apply to sample matrix interference.]

LC_{50} means a statistically or graphically estimated concentration that is expected to be lethal to 50% of a group of organisms under specified conditions.

Maximum acceptable toxicant concentration (MATC) means the concentration obtained by calculating the geometric mean of the lower and upper chronic limits from a chronic test. A lower chronic limit is the highest tested concentration that did not cause the occurrence of a specific adverse effect. An upper chronic limit is the lowest tested concentration which did cause the occurrence of a specific adverse effect and above which all tested concentrations caused such an occurrence.

Monthly concentration is the sum of the daily concentrations determined during a reporting month (or 30 consecutive days) divided by the number of daily concentrations determined. The calculated monthly concentration will be used to determine compliance with any maximum monthly concentration limitations. When required by the document, report the calculated monthly concentration in the "AVERAGE" column under "QUALITY OR CONCENTRATION" on the DMRs.

For minimum percent removal requirements, the monthly influent concentration and the monthly effluent concentration shall be determined. The calculated monthly percent removal, which is equal to 100 times the quantity [1 minus the quantity (monthly effluent concentration divided by the monthly influent concentration)], shall be reported in the "MINIMUM" column under "QUALITY OR CONCENTRATION" on the DMRs.

Monthly loading is the sum of the daily loadings of a parameter divided by the number of daily loadings determined in the reporting month (or 30 consecutive days). The calculated monthly loading will be used to determine compliance with any maximum monthly loading limitations. When required by the document, report the calculated monthly loading in the "AVERAGE" column under "QUANTITY OR LOADING" on the DMRs.

National Pretreatment Standards are the regulations promulgated by or to be promulgated by the Federal Environmental Protection Agency pursuant to Section 307(b) and (c) of the Federal Act. The standards establish nationwide limits for specific industrial categories for discharge to a POTW.

PART II

Section A. Definitions

NOAEL means the highest tested dose or concentration of a substance that results in no observed adverse effect in exposed test organisms where higher doses or concentrations result in an adverse effect.

Noncontact Cooling Water is water used for cooling which does not come into direct contact with any raw material, intermediate product, by-product, waste product or finished product.

Nondomestic user is any discharger to a POTW that discharges wastes other than or in addition to water-carried wastes from toilet, kitchen, laundry, bathing or other facilities used for household purposes.

Pretreatment is reducing the amount of pollutants, eliminating pollutants, or altering the nature of pollutant properties to a less harmful state prior to discharge into a public sewer. The reduction or alteration can be by physical, chemical, or biological processes, process changes, or by other means. Dilution is not considered pretreatment unless expressly authorized by an applicable National Pretreatment Standard for a particular industrial category.

POTW is a publicly owned treatment works.

Quantification level means the measurement of the concentration of a contaminant obtained by using a specified laboratory procedure calculated at a specified concentration above the detection level. It is considered the lowest concentration at which a particular contaminant can be quantitatively measured using a specified laboratory procedure for monitoring of the contaminant.

Regional Administrator is the Region 5 Administrator, U.S. EPA, located at R-19J, 77 W. Jackson Blvd., Chicago, Illinois 60604.

7-day concentration is the sum of the daily concentrations determined during any 7 consecutive days in a reporting month divided by the number of daily concentrations determined. The calculated 7-day concentration will be used to determine compliance with any maximum 7-day concentration limitations. When required by the document, report the maximum calculated 7-day concentration for the month in the "MAXIMUM" column under "QUALITY OR CONCENTRATION" on the DMRs.

7-day loading is the sum of the daily loadings of a parameter divided by the number of daily loadings determined during any 7 consecutive days in a reporting month. The calculated 7-day loading will be used to determine compliance with any maximum 7-day loading limitations. When required by the document, report the maximum calculated 7-day loading for the month in the "MAXIMUM" column under "QUANTITY OR LOADING" on the DMRs.

Significant industrial user is a nondomestic user that: 1) is subject to Categorical Pretreatment Standards under 40 CFR 403.6 and 40 CFR Chapter I, Subchapter N; or 2) discharges an average of 25,000 gallons per day or more of process wastewater to a POTW (excluding sanitary, noncontact cooling and boiler blowdown wastewater); contributes a process wastestream which makes up five (5) percent or more of the average dry weather hydraulic or organic capacity of the POTW treatment plant; or is designated as such by the documenttee as defined in 40 CFR 403.12(a) on the basis that the industrial user has a reasonable potential for adversely affecting the POTW's treatment plant operation or violating any pretreatment standard or requirement (in accordance with 40 CFR 403.8(f)(6)).

Tier I value means a value for aquatic life, human health or wildlife calculated under R 323.1057 of the Water Quality Standards using a tier I toxicity data base.

Tier II value means a value for aquatic life, human health or wildlife calculated under R 323.1057 of the Water Quality Standards using a tier II toxicity data base.

Toxicity Reduction Evaluation (TRE) means a site-specific study conducted in a stepwise process designed to identify the causative agents of effluent toxicity, isolate the sources of toxicity, evaluate the effectiveness of toxicity control options, and then confirm the reduction in effluent toxicity.

Water Quality Standards means the Part 4 Water Quality Standards developed under Part 31 of Act No. 451 of the Public Acts of 1994, as amended, being Rules 323.1041 through 323.1117 of the Michigan Administrative Code.

PART II

Section A. Definitions

3-Portion Composite sample is a sample consisting of three equal volume grab samples collected at equal intervals over an 8-hour period.

24-Hour Composite sample is a flow proportioned composite sample consisting of hourly or more frequent portions that are taken over a 24-hour period.

PART II

Section B. Monitoring Procedures

1. Representative Samples

Samples and measurements taken as required herein shall be representative of the volume and nature of the monitored discharge.

2. Test Procedures

Test procedures for the analysis of pollutants shall conform to regulations promulgated pursuant to Section 304(h) of the Federal Act (40 CFR Part 136 - Guidelines Establishing Test Procedures for the Analysis of Pollutants). For parameters not specified in the document or covered by the regulations, test procedures shall be submitted for approval to the Plainwell District Supervisor of the Surface Water Quality Division.

The discharger shall periodically calibrate and perform maintenance procedures on all analytical instrumentation at intervals to ensure accuracy of measurements. The calibration and maintenance shall be performed as part of the discharger's laboratory Quality Control/Quality Assurance program.

3. Instrumentation

The discharger shall periodically calibrate and perform maintenance procedures on all monitoring instrumentation at intervals to ensure accuracy of measurements.

4. Recording Results

For each measurement or sample taken pursuant to the requirements of this document, the discharger shall record the following information: 1) the exact place, date, and time of measurement or sampling; 2) the person(s) who performed the measurement or sample collection; 3) the dates the analyses were performed; 4) the person(s) who performed the analyses; 5) the analytical techniques or methods used; 6) the date of and person responsible for equipment calibration; and 7) the results of all required analyses.

5. Records Retention

All records and information resulting from the monitoring activities required by this document including all records of analyses performed and calibration and maintenance of instrumentation and recordings from continuous monitoring instrumentation shall be retained for a minimum of three (3) years, or longer if requested by the Regional Administrator or the Michigan Department of Environmental Quality.

PART II

Section C. Reporting Requirements

1. Start-up Notification

If the discharger will not discharge during the first 60 days following the effective date of this document, the discharger shall notify the Plainwell District Supervisor of the Surface Water Quality Division within 14 days, and then 60 days prior to the commencement of the discharge.

2. Submittal Requirements for Self-Monitoring Data

Unless instructed on the effluent limits page to conduct "retained self-monitoring", the discharger shall submit self-monitoring data on the Environmental Protection Agency's Discharge Monitoring Report (DMR) forms (monthly summary information) and the Department's Daily Discharge Monitoring Report forms (daily information) to the PCS Unit, Surface Water Quality Division, Michigan Department of Environmental Quality, P.O. Box 30273, Lansing, Michigan, 48909-7773, for each calendar month of the authorized discharge period(s). The forms shall be postmarked no later than the 10th day of the month following each month of the authorized discharge period(s).

Alternative Daily Discharge Monitoring Report formats may be used if they provide equivalent reporting details and are approved by the Plainwell District Supervisor of the Surface Water Quality Division. For information on electronic submittal of this information, contact the Plainwell District Supervisor.

3. Retained Self-Monitoring Requirements

If instructed on the effluent limits page to conduct retained self-monitoring, the discharger shall maintain a year-to-date log of retained self-monitoring results and, upon request, provide such log for inspection to the staff of the Surface Water Quality Division, Michigan Department of Environmental Quality (in the case of mobile home parks, campgrounds, marinas and schools, to the staff of the Drinking Water and Radiological Protection Division -- Environmental Health, Michigan Department of Environmental Quality, or, in the case of hospitals, nursing homes and extended care facilities, to the staff of the Division of Health Facility Services -- Health Facility Evaluation Section, Michigan Department of Consumer and Industry Services). Retained self-monitoring results are public information and shall be promptly provided to the public upon request.

The discharger shall certify, in writing, to the Plainwell District Supervisor of the Surface Water Quality Division, on or before January 10th of each year, that: 1) all retained self-monitoring requirements have been complied with and a year-to-date log has been maintained; and 2) the application on which this document is based still accurately describes the discharge.

4. Additional Monitoring by Discharger

If the discharger monitors any pollutant at the location(s) designated herein more frequently than required by this document, using approved analytical methods as specified above, the results of such monitoring shall be included in the calculation and reporting of the values required in the Discharge Monitoring Report. Such increased frequency shall also be indicated.

Monitoring required pursuant to Part 41 of the Michigan Act or Rule 35 of the Mobile Home Park Commission Act (Act 96 of the Public Acts of 1987) for assurance of proper facility operation shall be submitted as required by the Department.

5. Compliance Dates Notification

Within 14 days of every compliance date specified in this document, the discharger shall submit a written notification to the Plainwell District Supervisor of the Surface Water Quality Division indicating whether or not the particular requirement was accomplished. If the requirement was not accomplished, the notification shall include an explanation of the failure to accomplish the requirement, actions taken or planned by the discharger to correct the situation, and an estimate of when the requirement will be accomplished. If a written report is required to be submitted by a specified date and the discharger accomplishes this, a separate written notification is not required.

PART II

Section C. Reporting Requirements

6. Noncompliance Notification

Compliance with all requirements set forth in the Federal Act, Parts 31 and 41 of the Michigan Act, and related regulations and rules is required. All instances of noncompliance shall be reported as follows:

a. 24-hour reporting - Any noncompliance which may endanger health or the environment (including maximum daily concentration discharge limitation exceedances) shall be reported, verbally, within 24 hours from the time the discharger becomes aware of the circumstances. A written submission shall also be provided within five (5) days.

b. other reporting - The discharger shall report, in writing, all other instances of noncompliance not described in a. above at the time monitoring reports are submitted; or, in the case of retained self-monitoring, within five (5) days from the time the discharger becomes aware of the noncompliance.

Written reporting shall include: 1) a description of the discharge and cause of noncompliance; and 2) the period of noncompliance, including exact dates and times; or, if not corrected, the anticipated time the noncompliance is expected to continue, and the steps taken to reduce, eliminate and prevent recurrence of the noncomplying discharge.

7. Spill Notification

The discharger shall immediately report any spill or loss of any product, by-product, intermediate product, oils, solvents, waste material, or any other polluting substance which occurs to the surface waters or groundwaters of the state by calling the Plainwell District Supervisor of the Surface Water Quality Division at 616-692-2120, , or if the notice is provided after regular working hours call the Department of Environmental Quality's 24-hour Emergency Response telephone number, 1-800-292-4706 (calls from out-of-state dial 1-517-373-7660); and within ten (10) days of the spill or loss, the discharger shall submit to the Plainwell District Supervisor of the Surface Water Quality Division a full written explanation as to the cause and discovery of the spill or loss, clean-up and recovery measures taken, preventative measures to be taken, and schedule of implementation.

8. Upset Noncompliance Notification

If a process "upset" (defined as an exceptional incident in which there is unintentional and temporary noncompliance with technology based permit effluent limitations because of factors beyond the reasonable control of the discharger) has occurred, the discharger who wishes to establish the affirmative defense of upset, shall notify the Plainwell District Supervisor of the Surface Water Quality Division by telephone within 24-hours of becoming aware of such conditions; and within five (5) days, provide in writing, the following information:

a. that an upset occurred and that the discharger can identify the specific cause(s) of the upset;

b. that the permitted wastewater treatment facility was, at the time, being properly operated; and

c. that the discharger has specified and taken action on all responsible steps to minimize or correct any adverse impact in the environment resulting from noncompliance with this document.

In any enforcement proceedings, the discharger, seeking to establish the occurrence of an upset, has the burden of proof.

PART II

Section C. Reporting Requirements

9. Bypass Prohibition and Notification

a. Bypass Prohibition - Bypass or diversion of treatment facilities for groundwater remediations is prohibited. For discharges other than groundwater remediations, bypass is prohibited unless:

1) bypass was unavoidable to prevent loss of life, personal injury, or severe property damage;

2) there were no feasible alternatives to the bypass, such as the use of auxiliary treatment facilities, retention of untreated wastes, or maintenance during normal periods of equipment downtime. This condition is not satisfied if adequate backup equipment should have been installed in the exercise of reasonable engineering judgment to prevent a bypass; and

3) the discharger submitted notices as required under 9.b. or 9.c. below.

b. Notice of Anticipated Bypass - If the discharger knows in advance of the need for a bypass, it shall submit prior notice to the Plainwell District Supervisor of the Surface Water Quality Division, if possible at least ten days before the date of the bypass, and provide information about the anticipated bypass as required by the Plainwell District Supervisor. The Plainwell District Supervisor may approve an anticipated bypass, after considering its adverse effects, if it will meet the three conditions listed in 9.a. above.

c. Notice of Unanticipated Bypass - The discharger shall submit notice to the Plainwell District Supervisor of the Surface Water Quality Division of an unanticipated bypass by telephone at 616-692-2120 (if the notice is provided after regular working hours, use the following number: 1-800-292-4706) as soon as possible, but no later than 24 hours from the time the discharger becomes aware of the circumstances.

d. Written Report of Bypass - A written submission shall be provided within five (5) working days of commencing any bypass to the Plainwell District Supervisor of the Surface Water Quality Division, and at additional times as directed by the Plainwell District Supervisor. The written submission shall contain a description of the bypass and its cause; the period of bypass, including exact dates and times, and if the bypass has not been corrected, the anticipated time it is expected to continue; steps taken or planned to reduce, eliminate, and prevent reoccurrence of the bypass; and other information as required by the Plainwell District Supervisor.

e. Bypass Not Exceeding Limitations - The discharger may allow any bypass to occur which does not cause effluent limitations to be exceeded, but only if it also is for essential maintenance to assure efficient operation. These bypasses are not subject to the provisions of 9.a., 9.b., 9.c., and 9.d., above. This provision does not relieve the discharger of any notification responsibilities under Part II.C.10. of this document.

f. Definitions

1) Bypass means the intentional diversion of waste streams from any portion of a treatment facility.

2) Severe property damage means substantial physical damage to property, damage to the treatment facilities which causes them to become inoperable, or substantial and permanent loss of natural resources which can reasonably be expected to occur in the absence of a bypass. Severe property damage does not mean economic loss caused by delays in production.

PART II

Section C. Reporting Requirements

10. Notification of Changes in Discharge

The discharger shall notify the Plainwell District Supervisor of the Surface Water Quality Division, in writing, within 10 days of knowing, or having reason to believe, that any activity or change has occurred or will occur which would result in the discharge of: 1) detectable levels of chemicals on the current Michigan Critical Materials Register, priority pollutants or hazardous substances set forth in 40 CFR 122.21, Appendix D, or the Pollutants of Initial Focus in the Great Lakes Water Quality Initiative specified in 40 CFR 132.6, Table 6, which were not acknowledged in the application or listed in the application at less than detectable levels; 2) detectable levels of any other chemical not listed in the application or listed at less than detection, for which the application specifically requested information; or 3) any chemical at levels greater than five times the average level reported in the complete application submitted on February 6, 1998. Any other monitoring results obtained as a requirement of this document shall be reported in accordance with the compliance schedules.

11. Changes in Facility Operations

Any anticipated action or activity, including but not limited to facility expansion, production increases, or process modification, which will result in new or increased loadings of pollutants to the receiving waters must be reported to the Plainwell District Supervisor of the Surface Water Quality Division by a) submission of an increased use request (application) and all information required under Rule 323.1098 (Antidegradation) of the Water Quality Standards or b) by notice if the following conditions are met: 1) the action or activity will not result in a change in the types of wastewater discharged or result in a greater quantity of wastewater than currently authorized by this document; 2) the action or activity will not result in violations of the effluent limitations specified in this document; 3) the action or activity is not prohibited by the requirements of Part II.C.12.; and 4) the action or activity will not require notification pursuant to Part II.C.10. Following such notice, the document may be modified according to applicable laws and rules to specify and limit any pollutant not previously limited.

12. Bioaccumulative Chemicals of Concern (BCC)

Consistent with the requirements of Rules 323.1098 and 323.1215 of the Michigan Administrative Code, the discharger is prohibited from undertaking any action that would result in a lowering of water quality from an increased loading of a BCC unless an increased use request and antidegradation demonstration have been submitted and approved by the Department.

13. Transfer of Ownership or Control

In the event of any change in control or ownership of facilities from which the authorized discharge emanates, the discharger shall notify the succeeding owner or controller of the existence of this document by letter, a copy of which shall be forwarded to the Plainwell District Supervisor of the Surface Water Quality Division 30 days prior to the actual transfer of ownership or control.

PART II

Section D. Management Responsibilities

1. Duty to Comply

All discharges authorized herein shall be consistent with the terms and conditions of this document. The discharge of any pollutant identified in this document more frequently than or at a level in excess of that authorized shall constitute a violation of the document.

It is the duty of the discharger to comply with all the terms and conditions of this document. Any noncompliance with the Effluent Limitations, Special Conditions, or terms of this document constitutes a violation of the Michigan Act and/or the Federal Act and constitutes grounds for enforcement action; for document termination, revocation and reissuance, or modification; or denial of an application for document renewal.

2. Operator Certification

The discharger shall have the waste treatment facilities under direct supervision of an operator certified at the appropriate level for the facility certification by the Michigan Department of Environmental Quality, as required by Sections 3110 and 4104 of the Michigan Act.

3. Facilities Operation

The discharger shall, at all times, properly operate and maintain all treatment or control facilities or systems installed or used by the discharger to achieve compliance with the terms and conditions of this document. Proper operation and maintenance includes adequate laboratory controls and appropriate quality assurance procedures.

4. Power Failures

In order to maintain compliance with the effluent limitations of this document and prevent unauthorized discharges, the discharger shall either:

a. provide an alternative power source sufficient to operate facilities utilized by the discharger to maintain compliance with the effluent limitations and conditions of this document; or

b. upon the reduction, loss, or failure of one or more of the primary sources of power to facilities utilized by the discharger to maintain compliance with the effluent limitations and conditions of this document, the discharger shall halt, reduce or otherwise control production and/or all discharge in order to maintain compliance with the effluent limitations and conditions of this document.

5. Adverse Impact

The discharger shall take all reasonable steps to minimize any adverse impact to the surface waters or groundwaters of the state resulting from noncompliance with any effluent limitation specified in this document including, but not limited to, such accelerated or additional monitoring as necessary to determine the nature and impact of the discharge in noncompliance.

6. Containment Facilities

The discharger shall provide facilities for containment of any accidental losses of concentrated solutions, acids, alkalies, salts, oils, or other polluting materials in accordance with the requirements of the Part 5 Rules (Rules 323.1151 through 323.1169 of the Michigan Administrative Code). For a POTW, these facilities shall be approved under Part 41 of the Michigan Act.

PART II

Section D. Management Responsibilities

7. Waste Treatment Residues

Residuals, i.e. solids, sludges, biosolids, filter backwash, scrubber water, ash, grit or other pollutants removed from or resulting from treatment or control of wastewaters, shall be disposed of in an environmentally compatible manner and according to applicable laws and rules. These laws may include, but are not limited to, the Michigan Act, Part 31 for protection of water resources, Part 55 for air pollution control, Part 111 for hazardous waste management, Part 115 for solid waste management, Part 121 for liquid industrial wastes, Part 301 for protection of inland lakes and streams, and Part 303 for wetlands protection. Such disposal shall not result in any unlawful pollution of the air, surface waters or groundwaters of the state.

8. Right of Entry

The discharger shall allow the Michigan Department of Environmental Quality, any agent appointed by the Department or the Regional Administrator, upon the presentation of credentials:

a. to enter upon the discharger's premises where an effluent source is located or in which any records are required to be kept under the terms and conditions of this document; and

b. at reasonable times to have access to and copy any records required to be kept under the terms and conditions of this document; to inspect process facilities, treatment works, monitoring methods and equipment regulated or required under this document; and to sample any discharge of pollutants.

9. Availability of Reports

Except for data determined to be confidential under Section 308 of the Federal Act and Rule 2128 (Rule 323.2128 of the Michigan Administrative Code), all reports prepared in accordance with the terms of this document shall be available for public inspection at the offices of the Department and the Regional Administrator. As required by the Federal Act, effluent data shall not be considered confidential. Knowingly making any false statement on any such report may result in the imposition of criminal penalties as provided for in Section 309 of the Federal Act and Sections 3112, 3115, 4106 and 4110 of the Michigan Act.

PART II

Section E. Activities Not Authorized by This Permit

1. Discharge to the Groundwaters

This document does not authorize any discharge to the groundwaters. Such discharge may be authorized by a groundwater discharge permit issued pursuant to the Michigan Act.

2. Facility Construction

This document does not authorize or approve the construction or modification of any physical structures or facilities. Approval for such construction for a POTW must be by permit issued under Part 41 of the Michigan Act. Approval for such construction for a mobile home park, campground or marina shall be from the Drinking Water and Radiological Protection Division -- Environmental Health, Michigan Department of Environmental Quality. Approval for such construction for a hospital, nursing home or extended care facility shall be from the Division of Health Facility Services -- Health Facility Evaluation Section, Michigan Department of Consumer and Industry Services upon request.

3. Civil and Criminal Liability

Except as provided in document conditions on "Bypass" (Part II.C.9.) pursuant to 40 CFR 122.41(m)), nothing in this document shall be construed to relieve the discharger from civil or criminal penalties for noncompliance, whether or not such noncompliance is due to factors beyond his control, such as accidents, equipment breakdowns, or labor disputes.

4. Oil and Hazardous Substance Liability

Nothing in this document shall be construed to preclude the institution of any legal action or relieve the discharger from any responsibilities, liabilities, or penalties to which the discharger may be subject under Section 311 of the Federal Act except as are exempted by federal regulations.

5. State Laws

Nothing in this document shall be construed to preclude the institution of any legal action or relieve the discharger from any responsibilities, liabilities, or penalties established pursuant to any applicable state law or regulation under authority preserved by Section 510 of the Federal Act.

6. Property Rights

The issuance of this document does not convey any property rights in either real or personal property, or any exclusive privileges, nor does it authorize violation of any federal, state or local laws or regulations, nor does it obviate the necessity of obtaining such permits or approvals from other units of government as may be required by law.

Appendix B

USEPA Method 9095A – Paint Filter Liquids Test

BBL®
BLASLAND, BOUCK & LEE, INC.
engineers, scientists, economists

METHOD 9095A USEPA PAINT FILTER LIQUIDS TEST

TIME CRITICAL REMOVAL ACTION WORK PLAN
ALLIED PAPER, INC./PORTAGE CREEK/KALAMAZOO RIVER SUPERFUND SITE
GEORGIA-PACIFIC CORPORATION
KALAMAZOO, MICHIGAN

I. Scope and Application

This method is used to determine the presence of free liquids in a representative sample of waste.

The method is used to determine compliance with 40 CFR 264.314 and 265.314.

II. Summary of Method

A predetermined amount of material is placed in a paint filter. If any portion of the material passes through and drops from the filter within the 5-min test period, the material is deemed to contain free liquids.

III. Interferences

- If filter media are observed to separate from the filter cone on exposure to alkaline materials. This development causes no problem if the sample is not disturbed.

- Temperature can affect the test results if the test is performed below the freezing point of any liquid in the sample. Tests must be performed above the freezing point and can, but are not required to, exceed room temperature of 25°C.

IV. Apparatus and Materials

- Conical paint filter: Mesh number 60 +/- 5% (fine meshed size). Available at local point stores such as Sherwin-Williams and Glidden.

- Glass funnel: If the paint filter, with the waste, cannot sustain its weight on the ring stand, then a fluted glass funnel or glass funnel with a mouth large enough to allow at least 1 in. of the filter mesh to protrude should be used to support the filter. The funnel should be fluted or

have a large open mouth in order to support the paint filter yet not interfere with the movement, to the graduated cylinder, of the liquid that passes through the filter mesh.

- Ring stand and ring, or tripod.

- Graduated cylinder or beaker: 100-mL.

V. Reagents

- None.

VI. Sample Collection, Preservation, and Handling

- All samples must be collected as described herein.

- A 100-mL or 100-g representative sample is required for the test. If it is not possible to obtain a sample of 100 mL or 100 g that is sufficiently representative of the waste, the analyst may use larger size samples in multiples of 100 mL or 100 g i.e., 200, 300, 400 mL or g. However, when larger samples are used, analysis shall divide the sample into 100-mL or 100-g portions and test each portion separately. If any portion contains free liquids, the entire sample is considered to have free liquids. If the sample is measured volumetrically, then it should lack major air spaces or voids.

VII. Procedure

- Place sample in the filter. A funnel may be used to provide support for the paint filter. If the sample is of such light bulk density that it overflow the filter, then the sides of the filter can be extended upward by taping filter paper to the inside of the filter and above the mesh. Settling the sample into the paint filter may be facilitated by lightly tapping the side of the filter as it is being filled.

- In order to assure uniformity and standardization of the test, material such as sorbent pads or pillows which do not conform to the shape of the paint filter, should be cut into small pieces and poured into the filter. Sample size reduction may be accomplished by cutting the sorbent

material with scissors, shears, knife, or other such device so as to preserve as much of the original integrity of the sorbent fabric as possible. Sorbents enclosed in a fabric should be mixed with the resultant fabric pieces. The particles to be tested should be reduced small than 1 cm (i.e., should be capable of passing through a 9.5 mm (0.375 inch) standard sieve). Grinding sorbent materials should be avoided as this may destroy the integrity of the sorbent and produce many "fine particles" which would normally not be present.

- For brittle materials larger than 1 cm that do not conform to the filter, light crushing to reduce oversize particles are acceptable if it is not practical to cut the material. Materials such as clay, silica gel, and some polymers may fall into this category.

- Allow sample to drain for 5 min into the graduated cylinder.

- If any portion of the test material collects in the graduated cylinder in the 5-min period, then the material is deemed to contain free liquids for purposes of 40 CFR 264.314 and 265.314.

VIII. Quality Control

- Duplicate samples should be analyzed on a routine basis.

IX. Method Performance

- No data provided.

X. References

- None provided.

Appendix C

USEPA Compendium Method TO-4A – PCB Ambient Air Monitoring

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EPA/625/R-96/010b

Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air

Second Edition

Compendium Method TO-4A

Determination of Pesticides and Polychlorinated Biphenyls in Ambient Air Using High Volume Polyurethane Foam (PUF) Sampling Followed by Gas Chromatographic/Multi-Detector Detection (GC/MD)

Center for Environmental Research Information
Office of Research and Development
U.S. Environmental Protection Agency
Cincinnati, OH 45268

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Method TO-4A
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Method TO-4 was originally published in April of 1984 as one of a series of peer reviewed methods in *"Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air,"* EPA 600/4-89-018. In an effort to keep these methods consistent with current technology, Method TO-4 has been revised and updated as Method TO-4A in this Compendium to incorporate new or improved sampling and analytical technologies. In addition, this method incorporates ASTM Method D 4861-94, *Standard Practice for Sampling and Analysis of Pesticides and Polychlorinated Biphenyls in Air.*

This Method is the result of the efforts of many individuals. Gratitude goes to each person involved in the preparation and review of this methodology.

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DISCLAIMER

This Compendium has been subjected to the Agency's peer and administrative review, and it has been approved for publication as an EPA document. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

METHOD TO-4A

Determination of Pesticides and Polychlorinated Biphenyls in Ambient Air Using High Volume Polyurethane Foam (PUF) Sampling Followed by Gas Chromatographic/Multi-Detector Detection (GC/MD)

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METHOD TO-4A

Determination of Pesticides and Polychlorinated Biphenyls in Ambient Air Using High Volume Polyurethane Foam (PUF) Sampling Followed by Gas Chromatographic/Multi-Detector Detection (GC/MD)

1. Scope

1.1 This document describes a method for sampling and analysis of a variety of common pesticides and for polychlorinated biphenyls (PCBs) in ambient air. The procedure is based on the adsorption of chemicals from ambient air on polyurethane foam (PUF) using a high volume sampler.

1.2 The high volume PUF sampling procedure is applicable to multicomponent atmospheres containing common pesticide concentrations from 0.001 to 50 $\mu g/m^3$ over 4- to 24-hour sampling periods. The limits of detection will depend on the nature of the analyte and the length of the sampling period.

1.3 Specific compounds for which the method has been employed are listed in Table 1. The analytical methodology described in Compendium Method TO-4A is currently employed by laboratories throughout the U.S. The sampling methodology has been formulated to meet the needs of common pesticide and PCB sampling in ambient air.

1.4 Compendium Method TO-4 was originally published in 1989 (1). Further updates of the sampling protocol were published as part of Compendium Method TO-13 (2). The method was further modified for indoor air application in 1990 (3). In an effort to keep the method consistent with current technology, Compendium Method TO-4 has incorporated the sampling and analytical procedures in ASTM Method D4861-94 (4) and is published here as Compendium Method TO-4A.

2. Summary of Method

2.1 A high-volume (~8 cfm) sampler is used to collect common pesticides and PCBs on a sorbent cartridge containing PUF. Airborne particles may also be collected, but the sampling efficiency is not known (5). The sampler is operated for 24-hours, after which the sorbent is returned to the laboratory for analysis.

2.2 Pesticides and PCBs are extracted from the sorbent cartridge with 10 percent diethyl ether in hexane and determined by gas chromatography coupled with an electron capture detector (ECD), nitrogen-phosphorus detector (NPD), flame photometric detector (FPD), Hall electrolytic conductivity detector (HECD), or a mass spectrometer (MS). For common pesticides, high performance liquid chromatography (HPLC) coupled with an ultraviolet (UV) detector or electrochemical detector may be preferable.

2.3 Interferences resulting from analytes having similar retention times during GC analysis are resolved by improving the resolution or separation, such as by changing the chromatographic column or operating parameters, or by fractionating the sample by column chromatography.

3. Significance

3.1 Pesticide usage and environmental distribution are common to rural and urban areas of the United States. The application of pesticides can cause adverse health effects to humans by contaminating soil, water, air, plants, and animal life. PCBs are less widely used, due to extensive restrictions placed on their manufacturer. However, human exposure to PCBs continues to be a problem because of their presence in various electrical products.

3.2 Many pesticides and PCBs exhibit bioaccumulative, chronic health effects; therefore, monitoring the presence of these compounds in ambient air is of great importance.

3.3 The relatively low levels of such compounds in the environment requires the use of high volume sampling techniques to acquire sufficient sample for analysis. However, the volatility of these compounds prevents efficient collection on filter media. Consequently, Compendium Method TO-4A utilizes both a filter and a PUF backup cartridge which provides for efficient collection of most common pesticides, PCBs, and many other organics within the same volatility range.

3.4 Moreover, modifications to this method has been successfully applied to measurement of common pesticides and PCBs in outdoor air (6), indoor air (3) and for personal respiratory exposure monitoring (3).

4. Applicable Documents

4.1 ASTM Standards

- D1356 *Definition of Terms Relating to Atmospheric Sampling and Analysis*
- D4861-94 *Standard Practice for Sampling and Analysis of Pesticides and Polychlorinated Biphenyls in Air*
- E260 *Recommended Practice for General Gas Chromatography Procedures*
- E355 *Practice for Gas Chromatography Terms and Relationships*
- D3686 *Practice for Sampling Atmospheres to Collect Organic Compound Vapors (Activated Charcoal Tube Adsorption Method*
- D3687 *Practice for Analysis of Organic Compound Vapors Collected by the Activated Charcoal Tube Adsorption*
- D4185 *Practice for Measurement of Metals in Workplace Atmosphere by Atomic Absorption Spectrophotometry*

4.2 EPA Documents

- *Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air: Method TO-10, Second Supplement,* U. S. Environmental Protection Agency, EPA 600/4-89-018, March 1989.
- *Manual of Analytical Methods for Determination of Pesticides in Humans and Environmental Standards*, U. S. Environmental Protection Agency, EPA 600/8-80-038, June 1980.
- *Compendium of Methods for the Determination of Air Pollutants in Indoor Air: Method IP-8,* U. S. Environmental Protection Agency, EPA 600/4-90-010, May 1990.

4.3 Other Documents

- Code of Federal Regulations, Title 40, Part 136, Method 604

5. Definitions

[Note: Definitions used in this document and in any user-prepared Standard operating procedures (SOPs) should be consistent with ASTM D1356, E260, and E355. All abbreviations and symbols are defined within this document at point of use.]

5.1 Sampling efficiency (SE)-ability of the sampling medium to trap analytes of interest. The percentage of the analyte of interest collected and retained by the sampling medium when it is introduced as a vapor in air or nitrogen into the air sampler and the sampler is operated under normal conditions for a period of time equal to or greater than that required for the intended use is indicated by %SE.

5.2 Retention efficiency (RE)-ability of sampling medium to retain a compound added (spiked) to it in liquid solution.

5.3 Retention time (RT)-time to elute a specific chemical from a chromatographic column, for a specific carrier gas flow rate, measured from the time the chemical is injected into the gas stream until it appears at the detector.

5.4 Relative retention time (RRT)-a rate of RTs for two chemicals for the same chromatographic column and carrier gas flow rate, where the denominator represents a reference chemical.

5.5 Method detection limit (MDL)-the minimum concentration of a substance that can be measured and reported with confidence and that the value is above zero.

5.6 Kuderna-Danish apparatus-the Kuderna-Danish (K-D) apparatus is a system for concentrating materials dissolved in volatile solvents.

5.7 MS-SIM-the GC is coupled to a mass spectrometer where the instrument is programmed to acquire data for only the target compounds and to disregard all others, thus operating in the select ion monitoring mode (SIM). This is performed using SIM coupled to retention time discriminators. The SIM analysis procedure provides quantitative results.

5.8 Sublimation-the direct passage of a substance from the solid state to the gaseous state and back into the solid form without any time appearing in the liquid state. Also applied to the conversion of solid to vapor without the later return to solid state, and to a conversion directly from the vapor phase to the solid state.

5.9 Surrogate standard-a chemically compound (not expected to occur in the environmental sample) which is added to each sample, blank and matrix spiked sample before extraction and analysis. The recovery of the surrogate standard is used to monitor unusual matrix effects, gross sample processing errors, etc. Surrogate recovery is evaluated for acceptance by determining whether the measured concentration falls within acceptable limits.

6. Interferences

6.1 Any gas or liquid chromatographic separation of complex mixtures of organic chemicals is subject to serious interference problems due to coelution of two or more compounds. The use of capillary or microbore columns with superior resolution or two or more columns of different polarity will frequently eliminate these problems. In addition, selectivity may be further enhanced by use of a MS operated in the selected ion monitoring (SIM) mode as the GC detector. In this mode, co-eluting compounds can often be determined.

6.2 The ECD responds to a wide variety of organic compounds. It is likely that such compounds will be encountered as interferences during GC/ECD analysis. The NPD, FPD, and HECD detectors are element specific, but are still subject to interferences. UV detectors for HPLC are nearly universal, and the electrochemical detector may also respond to a variety of chemicals. Mass spectrometric analyses will generally provide positive identification of specific compounds.

6.3 PCBs and certain common pesticides (e.g., chlordane) are complex mixtures of individual compounds which can cause difficulty in accurately quantifying a particular formulation in a multiple component mixture. PCBs may interfere with the determination of pesticides.

6.4 Contamination of glassware and sampling apparatus with traces of pesticides or PCBs can be a major source of error, particularly at lower analyte concentrations. Careful attention to cleaning and handling procedures is required during all steps of sampling and analysis to minimize this source of error.

6.5 The general approaches listed below should be followed to minimize interferences.

6.5.1 Polar compounds, including certain pesticides (e.g., organophosphorus and carbamate classes) can be removed by column chromatography on alumina. Alumina clean-up will permit analysis of most common pesticides and PCBs (7).

6.5.2 PCBs may be separated from other common pesticides by column chromatography on silicic acid (8,9).

6.5.3 Many pesticides can be fractionated into groups by column chromatography on Florisil (9).

7. Safety

7.1 The toxicity or carcinogencity of each reagent used in this method has not been precisely defined; however, each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be reduced to the lowest possible level by whatever means available. The laboratory is responsible for maintaining a current awareness file of Occupational Safety and Health Administration (OSHA) regulations regarding the safe handling of the chemicals specified in this method. A reference file of material data handling sheets should also be made available to all personnel involved in the chemical analysis. Additional references to laboratory safety are available and have been identified for the analyst (10-12).

7.2 PCBs have been classified as a known or suspected, human or mammalian carcinogen. Many of the other common pesticides have been classified as carcinogens. Care must be exercised when working with these substances. This method does not purport to address all safety problems associated with its use. It is the responsibility of whoever uses this method to consult and establish appropriate safety and health practices and

determine the applicability of regulatory limitations prior to use. The user should be thoroughly familiar with the chemical and physical properties of targeted substances.

7.3 Treat all target analytes as carcinogens. Neat compounds should be weighed in a glove box. Spent samples and unused standards are toxic waste and should be disposed according to regulations. Regularly check counter tops and equipment with "black light" for fluorescence as an indicator of contamination.

7.4 The collection efficiency for common pesticides and PCBs has been demonstrated to be greater than 95 percent for the sampling configuration described in the method (filter and backup adsorbent). Therefore, no field recovery evaluation will occur as part of this procedure.

8. Apparatus

[Note: This method was developed using the PS-1 semi-volatile sampler provided by General Metal Works, Village of Cleves, OH as a guideline. EPA has experience in use of this equipment during various field monitoring programs over the last several years. Other manufacturers' equipment should work as well. However, modifications to these procedures may be necessary if another commercially available sampler is selected.]

8.1 Sampling

8.1.1 High-volume sampler (see Figure 1). Capable of pulling ambient air through the filter/adsorbent cartridge at a flow rate of approximately 8 standard cubic feet per minute (scfm) (0.225 std m^3/min) to obtain a total sample volume of greater than 300 scm over a 24-hour period. Major manufacturers are:

- Tisch Environmental, Village of Cleves, OH
- Andersen Instruments Inc., 500 Technology Ct., Smyrna, GA
- Thermo Environmental Instruments, Inc., 8 West Forge Parkway, Franklin, MA

8.1.2 Sampling module (see Figure 2). Metal filter holder (Part 2) capable of holding a 102-mm circular particle filter supported by a 16-mesh stainless-steel screen and attaching to a metal cylinder (Part 1) capable of holding a 65-mm O.D. (60-mm I.D.) x 125-mm borosilicate glass sorbent cartridge containing PUF. The filter holder is equipped with inert sealing gaskets (e.g., polytetrafluorethylene) placed on either side of the filter. Likewise, inert, pliable gaskets (e.g., silicone rubber) are used to provide an air-tight seal at each end of the glass sorbent cartridge. The glass sorbent cartridge is indented 20 mm from the lower end to provide a support for a 16-mesh stainless-steel screen that holds the sorbent. The glass sorbent cartridge fits into Part 1, which is screwed onto Part 2 until the sorbent cartridge is sealed between the silicone gaskets. Major manufacturers are:

- Tisch Environmental, Village of Cleves, OH
- Andersen Instruments Inc., 500 Technology Ct., Smyrna, GA
- Thermo Environmental Instruments, Inc., 8 West Forge Parkway, Franklin, MA

A field portable unit has been developed by EPA (see Figure 3).

8.1.3 High-volume sampler calibrator. Capable of providing multipoint resistance for the high-volume sampler. Major manufacturers are:

- Tisch Environmental, Village of Cleves, OH
- Andersen Instruments Inc., 500 Technology Ct., Smyrna, GA
- Thermo Environmental Instruments, Inc., 8 West Forge Parkway, Franklin, MA

8.1.4 Ice chest. To hold samples at <4°C or below during shipment to the laboratory after collection.

8.1.5 Data sheets. For each sample for recording the location and sample time, duration of sample, starting time, and volume of air sampled.

8.2 Sample Clean-up and Concentration (see Figure 4).

8.2.1 Soxhlet apparatus extractor (see Figure 4a). Capable of extracting filter and adsorbent cartridges (2.3" x 5" length), 1,000 mL flask, and condenser, best source.

8.2.2 Pyrex glass tube furnace system. For activating silica gel at 180°C under purified nitrogen gas purge for an hour, with capability of raising temperature gradually, best source.

8.2.3 Glass vial. 40 mL, best source.

8.2.4 Erlenmeyer flask. 50 mL, best source.

[Note: Reuse of glassware should be minimized to avoid the risk of cross contamination. All glassware that is used, especially glassware that is reused, must be scrupulously cleaned as soon as possible after use. Rinse glassware with the last solvent used in it and then with high-purity acetone and hexane. Wash with hot water containing detergent. Rinse with copious amount of tap water and several portions of distilled water. Drain, dry, and heat in a muffle furnace at 400°C for 4 hours. Volumetric glassware must not be heated in a muffle furnace; rather, it should be rinsed with high-purity acetone and hexane. After the glassware is dry and cool, rinse it with hexane, and store it inverted or capped with solvent-rinsed aluminum foil in a clean environment.]

8.2.5 White cotton gloves. For handling cartridges and filters, best source.

8.2.6 Minivials. 2 mL, borosilicate glass, with conical reservoir and screw caps lined with Teflon®-faced silicone disks, and a vial holder, best source.

8.2.7 Teflon®-coated stainless steel spatulas and spoons. Best source.

8.2.8 Kuderna-Danish (K-D) apparatus (see Figure 4b). 500 mL evaporation flask (Kontes K-570001-500 or equivalent), 10 mL graduated concentrator tubes (Kontes K570050-1025 or equivalent) with ground-glass stoppers, and 3-ball macro Snyder Column (Kontes K-570010500, K-50300-0121, and K-569001-219, or equivalent), best source.

8.2.9 Adsorption column for column chromatography (see Figure 4c). 1-cm x 10-cm with stands.

8.2.10 Glove box. For working with extremely toxic standards and reagents with explosion-proof hood for venting fumes from solvents, reagents, etc.

8.2.11 Vacuum oven. Vacuum drying oven system capable of maintaining a vacuum at 240 torr (flushed with nitrogen) overnight.

8.2.12 Concentrator tubes and a nitrogen evaporation apparatus with variable flow rate. Best source.

8.2.13 Laboratory refrigerator. Best source.

8.2.14 Boiling chips. Solvent extracted, 10/40 mesh silicon carbide or equivalent, best source.

8.2.15 Water bath. Heated, with concentric ring cover, capable of ±5°C temperature control, best source.

8.2.16 Nitrogen evaporation apparatus. Best source.

8.2.17 Glass wool. High purity grade, best source.

8.3 Sample Analysis

8.3.1 Gas chromatograph (GC). The GC system should be equipped with appropriate detector(s) and either an isothermally controlled or temperature programmed heating oven. Improved detection limits may be obtained with a GC equipped with a cool on-column or splitless injector.

8.3.2 Gas chromatographic column. As an example, a 0.32-mm (I.D.) x 3-mm DB-5, DB-17, DB-608, DB-1701 are available. Other columns may also provide acceptable results.

8.3.3 HPLC column. As an example, a 4.6-mm x 25-cm Zorbax SIL or µBondpak C-18. Other columns may also provide acceptable results.

8.3.4 Microsyringes. 5 µL volume or other appropriate sizes.

8.3.5 Balance. Mettler balance or equivalent.

8.3.6 All required syringes, gases, and other pertinent supplies. To operate the GC/MS system.

8.3.7 Pipettes, micropipettes, syringes, burets, etc. To make calibration and spiking solutions, dilute samples if necessary, etc., including syringes for accurately measuring volumes such as 25 µL and 100 µL.

9. Equipment and Materials

9.1 Materials for Sample Collection (see Figure 5)

9.1.1 Quartz fiber filter. 102-millimeter bindless quartz microfiber filter, Whatman Inc., 6 Just Road, Fairfield, NJ 07004, Filter Type QMA-4.

9.1.2 Polyurethane foam (PUF) plugs (see Figure 5a). 3-inch thick sheet stock polyurethane type (density .022 g/cm^3). The PUF should be of the polyether type used for furniture upholstery, pillows, and mattresses. The PUF cylinders (plugs) should be slightly larger in diameter than the internal diameter of the cartridge. Sources of equipment are Tisch Environmental, Village of Cleves, OH; University Research Glassware, 116 S. Merritt Mill Road, Chapel Hill, NC; Thermo Environmental Instruments, Inc., 8 West Forge Parkway, Franklin, MA; Supelco, Supelco Park, Bellefonte, PA; and SKC Inc., 334 Valley View Road, Eighty Four, PA.

9.1.3 Teflon® end caps (see Figure 5a). For sample cartridge. Sources of equipment are Tisch Environmental, Village of Cleves, OH and University Research Glassware, Chapel Hill, NC.

9.1.4 Sample cartridge aluminum shipping containers (see Figure 5b). For sample cartridge shipping. Sources of equipment are Tisch Environmental, Village of Cleves, OH and University Research Glassware, Chapel Hill, NC.

9.1.5 Glass sample cartridge (see Figure 5a). For sample collection. Sources of equipment are Tisch Environmental, Village of Cleves, OH; Thermo Environmental Instruments, Inc., 8 West Forge Parkway, Franklin, MA; University Research Glassware, 116 S. Merritt Mill Road, Chapel Hill, NC; and Supelco, Supelco Park, Bellefonte, PA.

9.1.6 Aluminum foil. Best source.

9.1.7 Hexane, reagent grade. Best source.

9.2 Sample Extraction and Concentration

9.2.1 Methylene chloride. Chromatographic grade, glass-distilled, best source.

9.2.2 Sodium sulfate-anhydrous (ACS). Granular (purified by washing with methylene chloride followed by heating at 400°C for 4 hours in a shallow tray).

9.2.3 Boiling chips. Solvent extracted or heated in a muffle furnace at 450°C for 2 hours, approximately 10/40 mesh (silicon carbide or equivalent).

9.2.4 Nitrogen. High purity grade, best source.
9.2.5 Ether. Chromatographic grade, glass-distilled, best source.
9.2.6 Hexane. Chromatographic grade, glass-distilled, best source.
9.2.7 Dibromobiphenyl. Chromatographic grade, best source. Used for internal standard.
9.2.8 Decafluorobiphenyl. Chromatographic grade, best source. Used for internal standard.
9.2.9 Glass wool. Silanized, extracted with methylene chloride and hexane, and dried.
9.2.10 Diethyl ether. High purity, glass distilled.
9.2.11 Hexane. High purity, glass distilled.
9.2.12 Silica gel. High purity, type 60, 70-230 mesh.
9.2.13 Round bottom evaporative flask. 500 mL, T 24/40 joints, best source.
9.2.14 Capacity soxhlet extractors. 500 mL, with reflux condensers, best source.
9.2.15 Kuderna-Danish concentrator. 500 mL, with Snyder columns, best source.
9.2.16 Graduated concentrator tubes. 10 mL, with 19/22 stoppers, best source.
9.2.17 Graduated concentrator tubes. 1 mL, with 14/20 stoppers, best source.
9.2.18 TFE fluorocarbon tape. 1/2 in., best source.
9.2.19 Filter tubes. Size 40-mm (I.D.) x 80-mm.
9.2.20 Serum vials. 1 mL and 5 mL, fitted with caps lined with TFE fluorocarbon.
9.2.21 Pasteur pipetter. 9 in., best source.
9.2.22 Glass wool. Fired at 500°C, best source.
9.2.23 Alumina. Activity Grade IV, 100/200 mesh.
9.2.24 Glass chromatographic column. 2-mm I.D. x 15-cm long.
9.2.25 Vacuum oven. Connected to water aspirator, best source.
9.2.26 Die. Best source.
9.2.27 Ice chest. Best source.
9.2.28 Silicic Acid. Pesticide quality, best source.
9.2.29 Octachloronaphthalene (OCN). Research grade, best source.
9.2.30 Florisil. Pesticide quality, best source.

9.3 GC Sample Analysis

9.3.1 Gas cylinders of hydrogen, nitrogen, argon/methane, and helium. Ultra high purity, best source.
9.3.2 Combustion air. Ultra high purity, best source.
9.3.3 Zero air. Zero air may be obtained from a cylinder or zero-grade compressed air scrubbed with Drierite® or silica gel and 5A molecular sieve or activated charcoal, or by catalytic cleanup of ambient air. All zero air should be passed through a liquid argon cold trap for final cleanup.
9.3.4 Chromatographic-grade stainless steel tubing and stainless steel fitting. For interconnections, Alltech Applied Science, 2051 Waukegan Road, Deerfield, IL 60015, 312-948-8600, or equivalent.

[Note: All such materials in contact with the sample, analyte, or support gases prior to analysis should be stainless steel or other inert metal. Do not use plastic or Teflon® tubing or fittings.]

10. Preparation of PUF Sampling Cartridge

[Note: This method was developed using the PS-1 sample cartridge provider by General Metal Works, Village of Cleves, OH as a guideline. EPA has experience in use of this equipment during various field monitoring

programs over the last several years. Other manufacturers' equipment should work as well. However, modifications to these procedures may be necessary if another commercially available sampler is selected.]

10.1 Summary of Method

10.1.1 This part of Compendium Method TO-4A discusses pertinent information regarding the preparation and cleaning of the filter, adsorbent, and filter/adsorbent cartridge assembly. The separate batches of filters and adsorbents are extracted with the appropriate solvent.

10.1.2 At least one PUF cartridge assembly and one filter from each batch, or 10 percent of the batch, whichever is greater, should be tested and certified clean before the batch is considered for field use.

10.2 Preparation of Sampling Cartridge

10.2.1 Bake the Whatman QMA-4 quartz filters at 400°C for 5 hours before use.

10.2.2 Set aside the filters in a clean container for shipment to the field or prior to combining with the PUF glass cartridge assembly for certification prior to field deployment.

10.2.3 The PUF plugs are 6.0-cm diameter cylindrical plugs cut from 3-inch sheet stock and should fit, with slight compression, in the glass cartridge, supported by the wire screen (see Figure 2). During cutting, rotate the die at high speed (e.g., in a drill press) and continuously lubricate with deionized or distilled water. Pre-cleaned PUF plugs can be obtained from many of the commercial sources identified in Section 9.1.2.

10.2.4 For initial cleanup, place the PUF plugs in a Soxhlet apparatus and extract with acetone for 16 hours at approximately 4 cycles per hour. When cartridges are reused, use diethyl ether/hexane (10 percent volume/volume [v/v]) as the cleanup solvent.

[Note: A modified PUF cleanup procedure can be used to remove unknown interference components of the PUF blank. This method consists of rinsing 50 times with toluene, acetone, and diethyl ether/hexane (5 to 10 percent v/v), followed by Soxhlet extraction. The extracted PUF is placed in a vacuum oven connected to a water aspirator and dried at room temperature for approximately 2 to 4 hours (until no solvent odor is detected). Alternatively, they may be dried at room temperature in an air-tight container with circulating nitrogen (zero grade). Place the clean PUF plug into a labeled glass sampling cartridge using gloves and forceps. Wrap the cartridge with hexane-rinsed aluminum foil and placed in a jar fitted with TFE fluorocarbon-lined caps. The foil wrapping may also be marked for identification using a blunt probe. The extract from the Soxhlet extraction procedure from each batch may be analyzed to determine initial cleanliness prior to certification.]

10.2.5 Fit a nickel or stainless steel screen (mesh size 200/200) to the bottom of a hexane-rinsed glass sampling cartridge to retain the PUF adsorbents, as illustrated in Figure 2. Place the Soxhlet-extracted, vacuum-dried PUF (2.5-cm thick by 6.5-cm diameter) on top of the screen in the glass sampling cartridge using polyester gloves.

10.2.6 Wrap the sampling cartridge with hexane-rinsed aluminum foil, cap with the Teflon® end caps, place in a cleaned labeled aluminum shipping container, and seal with Teflon® tape. Analyze at least 1 PUF plug from each batch of PUF plugs using the procedure described in Section 10.3, before the batch is considered acceptable for field use. A blank level of <10 ng/plug and filter for single component compounds is considered to be acceptable. For multiple component mixtures (e.g., PCBs), the blank level should be <100 ng/plug and filter. Cartridges are considered clean for up to 30 days from date of certification when stored in their sealed containers.

10.3 Procedure for Certification of PUF Cartridge Assembly

10.3.1 Extract 1 filter and PUF adsorbent cartridge by Soxhlet extraction and concentrate using a Kuderna-Danish (K-D) evaporator for each lot of filters and cartridges sent to the field.

10.3.2 Assemble the Soxhlet apparatus. Charge the Soxhlet apparatus (see Figure 4a) with 300 mL of the extraction solvent [10 percent (v/v) diethyl ether/hexane] and reflux for 2 hours. Let the apparatus cool, disassemble it, and discard the used extraction solvent. Transfer the filter and PUF glass cartridge to the Soxhlet apparatus (the use of an extraction thimble is optional).

[Note: The filter and adsorbent assembly are extracted together in order to reach detection limits, to minimize cost and to prevent misinterpretation of the data. Separate analyses of the filter and PUF would not yield useful information about the physical state of most of the common pesticides and PCBs at the time of sampling due to evaporative losses of the analyte from the filter during sampling.]

10.3.3 Add between 300 and 350 mL of diethyl ether/hexane (10 percent v/v) to the Soxhlet apparatus. Reflux the sample for 18 hours at a rate of at least 3 cycles per hour. Allow to cool, then disassemble the apparatus.

10.3.4 Assemble a K-D concentrator (see Figure 4b) by attaching a 10-mL concentrator tube to a 500-mL evaporative flask.

10.3.5 Transfer the extract by pouring it through a drying column containing about 10 cm of anhydrous granular sodium sulfate (see Figure 4c) and collect the extract in the K-D concentrator. Rinse the Erlenmeyer flask and column with 20 to 30 mL of 10 percent diethyl ether/hexane to complete the quantitative transfer.

10.3.6 Add 1 or 2 clean boiling chips and attach a 3-ball Snyder column to the evaporative flask. Pre-wet the Snyder column by adding about 1 mL of the extraction solvent to the top of the column. Place the K-D apparatus on a hot water bath (50°C) so that the concentrator tube is partially immersed in the hot water, and the entire lower rounded surface of the flask is bathed with hot vapor. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in one hour. At the proper rate of distillation, the balls of the column will actively chatter but the chambers will not flood with condensed solvent. When the apparent volume of liquid reaches approximately 5 mL, remove the K-D apparatus from the water bath and allow it to drain and cool for at least 5 minutes. Remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with 5 mL of hexane. A 5-mL syringe is recommended for this operation.

[Note: The solvent may have to be exchanged to another solvent to meet the requirements of the analytical procedure selected for the target analytes.]

10.3.7 Concentrate the extract to 1 mL and analyze according to Section 13.

10.3.8 Acceptable levels of common pesticides must be less than 10 ng for each pair of filter and adsorbent assembly analyzed. For multiple component mixtures (e.g., PCBs), the blank level should be less than 100 ng for each pair of filter and adsorbent. Once certified clean, the cartridges can be shipped to the field without being chilled.

11. Assembly, Calibration and Collection Using High-Volume Sampling System

[Note: This method was developed using the PS-1 semi-volatile sampler provided by General Metal Works, Village of Cleves, OH as a guideline. EPA has experience in use of this equipment during various field monitoring programs over the last several years. Other manufacturers' equipment should work as well.

However, modifications to these procedures may be necessary if another commercially available sampler is selected.]

11.1 Description of Sampling Apparatus

The entire sampling system is diagrammed in Figure 1. This apparatus was developed to operate at a rate of 4 to 10 scfm (0.114 to 0.285 std m^3/min) and is used by EPA for high-volume sampling of ambient air. The method write-up presents the use of this device.

The sampling module (see Figure 2) consists of a filter and a glass sampling cartridge containing the PUF utilized to concentrate common pesticides and PCBs from the air. A field portable unit has been developed by EPA (see Figure 3).

11.2 Calibration of Sampling System

Each sampler should be calibrated (1) when new, (2) after major repairs or maintenance, (3) whenever any audit point deviates from the calibration curve by more than 7 percent, (4) before/after each sampling event, and (5) when a different sample collection media, other than that which the sampler was originally calibrated to, will be used for sampling.

11.2.1 Calibration of Orifice Transfer Standard. Calibrate the modified high volume air sampler in the field using a calibrated orifice flow rate transfer standard. Certify the orifice transfer standard in the laboratory against a positive displacement rootsmeter (see Figure 6). Once certified, the recertification is performed rather infrequently if the orifice is protected from damage. Recertify the orifice transfer standard performed once per year utilizing a set of five multiple resistance plates.

[Note: The set of five multihole resistance plates are used to change the flow through the orifice so that several points can be obtained for the orifice calibration curve. The following procedure outlines the steps to calibrate the orifice transfer standard in the laboratory.]

11.2.1.1 Record the room temperature (T_1 in °C) and barometric pressure (P_b in mm Hg) on the Orifice Calibration Data Sheet (see Figure 7). Calculate the room temperature in K (absolute temperature) and record on Orifice Calibration Data Sheet.

$$T_1 \text{ in K} = 273° + T_1 \text{ in °C}$$

11.2.1.2 Set up laboratory orifice calibration equipment as illustrated in Figure 6. Check the oil level of the rootsmeter prior to starting. There are 3 oil level indicators, 1 at the clear plastic end and 2 site glasses, 1 at each end of the measuring chamber.

11.2.1.3 Check for leaks by clamping both manometer lines, blocking the orifice with cellophane tape, turning on the high volume motor, and noting any change in the rootsmeter's reading. If the rootsmeter's reading changes, there is a leak in the system. Eliminate the leak before proceeding. If the rootsmeter's reading remains constant, turn off the hi-vol motor, remove the cellophane tape, and unclamp both manometer lines.

11.2.1.4 Install the 5-hole resistance plate between the orifice and the filter adapter.

11.2.1.5 Turn manometer tubing connectors 1 turn counter-clockwise. Make sure all connectors are open.

11.2.1.6 Adjust both manometer midpoints by sliding their movable scales until the zero point corresponds with the meniscus. Gently shake or tap to remove any air bubbles and/or liquid remaining on tubing connectors. (If additional liquid is required for the water manometer, remove tubing connector and add clean water.)

11.2.1.7 Turn on the high volume motor and let it run for 5 minutes to set the motor brushes. Turn the motor off. Insure manometers are set to zero. Turn the high volume motor on.

11.2.1.8 Record the time, in minutes, required to pass a known volume of air (approximately 200 to 300 ft^3 of air for each resistance plate) through the rootsmeter by using the rootsmeter's digital volume dial and a stopwatch.

11.2.1.9 Record both manometer readings-orifice water manometer (ΔH) and rootsmeter mercury manometer (ΔP) on Orifice Calibration Data Sheet (see Figure 7).

[Note: ΔH is the sum of the difference from zero (0) of the two column heights.]

11.2.1.10 Turn off the high volume motor.

11.2.1.11 Replace the 5-hole resistance plate with the 7-hole resistance plate.

11.2.1.12 Repeat Sections 11.2.1.3 through 11.2.1.11.

11.2.1.13 Repeat for each resistance plate. Note results on Orifice Calibration Data Sheet (see Figure 7). Only a minute is needed for warm-up of the motor. Be sure to tighten the orifice enough to eliminate any leaks. Also check the gaskets for cracks.

[Note: The placement of the orifice prior to the rootsmeter causes the pressure at the inlet of the rootsmeter to be reduced below atmospheric conditions, thus causing the measured volume to be incorrect. The volume measured by the rootsmeter must be corrected.]

11.2.1.14 Correct the measured volumes on the Orifice Calibration Data Sheet:

$$V_{std} = V_m \left(\frac{P_a - \Delta P}{P_{std}}\right)\left(\frac{T_{std}}{T_a}\right)$$

where:

V_{std} = standard volume, std m^3

V_m = actual volume measured by the rootsmeter, m^3

P_a = barometric pressure during calibration, mm Hg

ΔP = differential pressure at inlet to volume meter, mm Hg

P_{std} = 760 mm Hg

T_{std} = 273 + 25°C = 298 K

T_a = ambient temperature during calibration, K.

11.2.1.15 Record standard volume on Orifice Calibration Data Sheet.

11.2.1.16 The standard flow rate as measured by the rootsmeter can now be calculated using the following formula:

$$Q_{std} = \frac{V_{std}}{\theta}$$

where:

Q_{std} = standard volumetric flow rate, std m^3/min

θ = elapsed time, min

11.2.1.17 Record the standard flow rates to the nearest 0.01 std m^3/min.

11.2.1.18 Calculate and record $\sqrt{\Delta H\ (P_1/P_{std})(298/T_1)}$ value for each standard flow rate.

11.2.1.19 Plot each $\sqrt{\Delta H\ (P_1/P_{std})(298/T_1)}$ value (y-axis) versus its associated standard flow rate (x-axis) on arithmetic graph paper and draw a line of best fit between the individual plotted points.

[Note: This graph will be used in the field to determine standard flow rate.]

11.2.2 Calibration of the High Volume Sampling System Utilizing Calibrated Orifice Transfer Standard

For this calibration procedure, the following conditions are assumed in the field:

- The sampler is equipped with a valve to control sample flow rate.
- The sample flow rate is determined by measuring the orifice pressure differential, using a Magnehelic gauge.
- The sampler is designed to operate at a standardized volumetric flow rate of 8 ft^3/min (0.225 m^3/min), with an acceptable flow rate range within 10 percent of this value.
- The transfer standard for the flow rate calibration is an orifice device. The flow rate through the orifice is determined by the pressure drop caused by the orifice and is measured using a "U" tube water manometer or equivalent.
- The sampler and the orifice transfer standard are calibrated to standard volumetric flow rate units (scfm or scmm).
- An orifice transfer standard with calibration traceable to NIST is used.
- A "U" tube water manometer or equivalent, with a 0- to 16-inch range and a maximum scale division of 0.1 inch, will be used to measure the pressure in the orifice transfer standard.
- A Magnehelic gauge or equivalent, with a 9- to 100-inch range and a minimum scale division of 2 inches for measurements of the differential pressure across the sampler's orifice is used.
- A thermometer capable of measuring temperature over the range of 32° to 122°F (0° to 50°C) to ±2°F (±1°C) and referenced annually to a calibrated mercury thermometer is used.
- A portable aneroid barometer (or equivalent) capable of measuring ambient barometric pressure between 500 and 800 mm Hg (19.5 and 31.5 in. Hg) to the nearest mm Hg and referenced annually to a barometer of known accuracy is used.
- Miscellaneous handtools, calibration data sheets or station log book, and wide duct tape are available.

11.2.2.1 Set up the calibration system as illustrated in Figure 8. Monitor the airflow through the sampling system with a venturi/Magnehelic assembly, as illustrated in Figure 8. Audit the field sampling system once per quarter using a flow rate transfer standard, as described in the EPA *High Volume-Sampling Method, 40 CVR 50, Appendix B*. Perform a single-point calibration before and after each sample collection, using the procedures described in Section 11.2.3.

11.2.2.2 Prior to initial multi-point calibration, place an empty glass cartridge in the sampling head and activate the sampling motor. Fully open the flow control valve and adjust the voltage variator so that a sample flow rate corresponding to 110 percent of the desired flow rate (typically 0.20 to 0.28 m^3/min) is indicated on the Magnehelic gauge (based on the previously obtained multipoint calibration curve). Allow the motor to warm up for 10 minutes and then adjust the flow control valve to achieve the desire flow rate. Turn off the sampler. Record the ambient temperature and barometric pressure on the Field Calibration Data Sheet (see Figure 9).

11.2.2.3 Place the orifice transfer standard on the sampling head and attach a manometer to the tap on the transfer standard, as illustrated in Figure 8. Properly align the retaining rings with the filter holder and secure

by tightening the three screw clamps. Connect the orifice transfer standard by way of the pressure tap to a manometer using a length of tubing. Set the zero level of the manometer or Magnehelic. Attach the Magnehelic gauge to the sampler venturi quick release connections. Adjust the zero (if needed) using the zero adjust screw on face of the gauge.

11.2.2.4 To leak test, block the orifice with a rubber stopper, wide duct tape, or other suitable means. Seal the pressure port with a rubber cap or similar device. Turn on the sampler.

Caution: Avoid running the sampler for too long a time with the orifice blocked. This precaution will reduce the chance that the motor will be overheated due to the lack of cooling air. Such overheating can shorten the life of the motor.

11.2.2.5 Gently rock the orifice transfer standard and listen for a whistling sound that would indicate a leak in the system. A leak-free system will not produce an upscale response on the sampler's Magnehelic. Leaks are usually caused either by damaged or missing gaskets by cross-threading and/or not screwing sample cartridge together tightly. All leaks must be eliminated before proceeding with the calibration. When the sample is determined to be leak-free, turn off the sampler and unblock the orifice. Now remove the rubber stopper or plug from the calibrator orifice.

11.2.2.6 Turn the flow control valve to the fully open position and turn the sampler on. Adjust the flow control valve until a Magnehelic reading of approximately 70 in. is obtained. Allow the Magnehelic and manometer readings to stabilize and record these values on the orifice transfer Field Calibration Data Sheet (see Figure 9).

11.2.2.7 Record the manometer reading under Y1 and the Magnehelic reading under Y2 on the Field Calibration Data Sheet. For the first reading, the Magnehelic should still be at 70 inches as set above.

11.2.2.8 Set the Magnehelic to 60 inches by using the sampler's flow control valve. Record the manometer (Y1) and Magnehelic (Y2) readings on the Field Calibration Data Sheet (see Figure 9).

11.2.2.9 Repeat the above steps using Magnehelic settings of 50, 40, 30, 20, and 10 inches.

11.2.2.10 Turn the voltage variator to maximum power, open the flow control valve, and confirm that the Magnehelic reads at least 100 inches. Turn off the sampler and confirm that the Magnehelic reads zero.

11.2.2.11 Read and record the following parameters on the Field Calibration Data Sheet. Record the following on the calibration data sheet:

Data, job number, and operator's signature;

- Sampler serial number;
- Ambient barometric pressure; and
- Ambient temperature.

11.2.2.12 Remove the "dummy" cartridge and replace with a sample cartridge.

11.2.2.13 Obtain the Manufacturer High Volume Orifice Calibration Certificate.

11.2.2.14 If not performed by the manufacturer, calculate values for each calibrator orifice static pressure (Column 6, inches of water) on the manufacturer's calibration certificate using the following equation:

$$\sqrt{\Delta H(P_a/760)(298/[T_a + 273])}$$

where:

P_a = the barometric pressure (mm Hg) at time of manufacturer calibration, mm Hg
T_a = temperature at time of calibration, °C

11.2.2.15 Perform a linear regression analysis using the values in Column 7 of the manufacturer High Volume Orifice Calibration Certificate for flow rate (Q_{std}) as the "X" values and the calculated values as the Y

values. From this relationship, determine the correlation (CC1), intercept (B1), and slope (M1) for the Orifice Transfer Standard.

11.2.2.16 Record these values on the Field Calibration Data Sheet (see Figure 9).

11.2.2.17 Using the Field Calibration Data Sheet values (see Figure 9), calculate the Orifice Manometer Calculated Values (Y3) for each orifice manometer reading using the following equation:

Y3 Calculation

$$Y3 = [Y1(P_a/760)(298/\{T_a + 273\})]^{1/2}$$

11.2.2.18 Record the values obtained in Column Y3 on the Field Calibration Data Sheet (see Figure 9).

11.2.2.19 Calculate the Sampler Magnehelic Calculate Values (Y4) using the following equation:

Y4 Calculation

$$Y4 = [Y2(P_a/760)(298/\{T_a + 273\})]^{1/2}$$

11.2.2.20 Record the value obtained in Column Y4 on the Field Calibration Data Sheet (see Figure 9).

11.2.2.21 Calculate the Orifice Flow Rate (X1) in scm, using the following equation:

X1 Calculation

$$X1 = \frac{Y3 - B1}{M1}$$

11.2.2.22 Record the values obtained in Column X1, on the Field Calibration Data Sheet (see Figure 9).

11.2.2.23 Perform a linear regression of the values in Column X1 (as X) and the values in Column Y4 (as Y). Record the relationship for correlation (CC2), intercept (B2), and slope (M2) on the Field Calibration Data Sheet.

11.2.2.24 Using the following equation, calculate a set point (SP) for the manometer to represent a desired flow rate:

$$\text{Set point (SP)} = [(\text{Expected } P_a)/(\text{Expected } T_a)(T_{std}/P_{std})][M2\ (\text{Desired flow rate}) + B2]^2$$

where:

P_a = Expected atmospheric pressure (P_a), mm Hg
T_a = Expected atmospheric temperature (T_a), °C
M2 = Slope of developed relationship
B2 = Intercept of developed relationship
T_{std} = Temperature standard, 25°C
P_{std} = Pressure standard, 760 mm Hg

11.2.2.25 During monitoring, calculate a flow rate from the observed Magnehelic reading using the following equations:

$$Y5 = [\text{Average Magnehelic Reading } (\Delta H)\ (P_a/T_a)(T_{std}/P_{std})]^{1/2}$$

$$X2 = \frac{Y5 - B2}{M2}$$

where:

Y5 = Corrected Magnehelic reading
X2 = Instant calculated flow rate, scm

11.2.2.26 The relationship in calibration of a sampling system between Orifice Transfer Standard and flow rate through the sampler is illustrated in Figure 10.

11.2.3 Single-Point Audit of the High Volume Sampling System Utilizing Calibrated Orifice Transfer Standard

Single point calibration checks are required as follows:

- Prior to the start of each 24-hour test period.
- After each 24-hour test period. The post-test calibration check may serve as the pre-test calibration check for the next sampling period if the sampler is not moved.
- Prior to sampling after a sample is moved.

For samplers, perform a calibration check for the operational flow rate before each 24-hour sampling event and when required as outlined in the user quality assurance program. The purpose of this check is to track the sampler's calibration stability. Maintain a control chart presenting the percentage difference between a sampler's indicated and measured flow rates. This chart provides a quick reference of sampler flow-rate drift problems and is useful for tracking the performance of the sampler. Either the sampler log book or a data sheet will be used to document flowcheck information. This information includes, but is not limited to, sampler and orifice transfer standard serial number, ambient temperature, pressure conditions, and collected flow-check data.

In this subsection, the following is assumed:

- The flow rate through a sampler is indicated by the orifice differential pressure;
- Samplers are designed to operate at an actual flow rate of 8 scfm, with a maximum acceptable flow-rate fluctuation range of ±10 percent of this value;
- The transfer standard will be an orifice device equipped with a pressure tap. The pressure is measured using a manometer; and
- The orifice transfer standard's calibration relationship is in terms of standard volumetric flow rate (Q_{std}).

11.2.3.1 Perform a single point flow audit check before and after each sampling period utilizing the Calibrated Orifice Transfer Standard (see Section 11.2.1).

11.2.3.2 Prior to single point audit, place a "dummy" glass cartridge in the sampling head and activate the sampling motor. Fully open the flow control valve and adjust the voltage variator so that a sample flow rate corresponding to 110 percent of the desired flow rate (typically 0.19 to 0.28 m^3/min) is indicated on the Magnehelic gauge (based on the previously obtained multipoint calibration curve). Allow the motor to warm up for 10 minutes and then adjust the flow control valve to achieve the desired flow rate. Turn off the sampler. Record the ambient temperature and barometric pressure on the Field Test Data Sheet (see Figure 11).

11.2.3.3 Place the flow rate transfer standard on the sampling head.

11.2.3.4 Properly align the retaining rings with the filter holder and secure by tightening the 3 screw clamps. Connect the flow rate transfer standard to the manometer using a length of tubing.

11.2.3.5 Using tubing, attach 1 manometer connector to the pressure tap of the transfer standard. Leave the other connector open to the atmosphere.

11.2.3.6 Adjust the manometer midpoint by sliding the movable scale until the zero point corresponds with the water meniscus. Gently shake or tap to remove any air bubbles and/or liquid remaining on tubing connectors. (If additional liquid is required, remove tubing connector and add clean water.)

11.2.3.7 Turn on high-volume motor and let run for 5 minutes.

11.2.3.8 Record the pressure differential indicated, ΔH, in inches of water, on the Field Test Data Sheet. Be sure stable ΔH has been established.

11.2.3.9 Record the observed Magnahelic gauge reading, in inches of water, on the Field Test Data Sheet. Be sure stable ΔM has been established.

11.2.3.10 Using previous established Orifice Transfer Standard curve, calculate Q_{xs} (see Section 11.2.2.23).

11.2.3.11 This flow should be within ±10 percent of the sampler set point, normally, 8 ft^3. If not, perform a new multipoint calibration of the sampler.

11.2.3.12 Remove flow rate transfer standard and dummy adsorbent cartridge.

11.3 Sample Collection

11.3.1 General Requirements

11.3.1.1 The sampler should be located in an unobstructed area, at least 2 meters from any obstacle to air flow. The exhaust hose should be stretched out in the downwind direction to prevent recycling of air into the sample head.

11.3.1.2 All cleaning and sample module loading and unloading should be conducted in a controlled environment, to minimize any chance of potential contamination.

11.3.1.3 When new or when using the sampler at a different location, all sample contact areas need to be cleared. Use triple rinses of reagent grade hexane contained in Teflon® rinse bottles. Allow the solvent to evaporate before loading the PUF modules.

11.3.2 Preparing Cartridge for Sampling

11.3.2.1 Detach the lower chamber of the cleaned sample head. While wearing disposable, clean, lint-free nylon, or powder-free surgical gloves, remove a clean glass adsorbent module from its shipping container. Remove the Teflon® end caps. Replace the end caps in the sample container to be reused after the sample has been collected.

11.3.2.2 Insert the glass module into the lower chamber and tightly reattach the lower chambers to the module.

11.3.2.3 Using clean rinsed (with hexane) Teflon-tipped forceps, carefully place a clean conditioned fiber filter atop the filter holder and secure in place by clamping the filter holder ring over the filter. Place the aluminum protective cover on top of the cartridge head. Tighten the 3 screw clamps. Ensure that all module connections are tightly assembled. Place a small piece of aluminum foil on the ball-joint of the sample cartridge to protect from back-diffusion of semi-volatile into the cartridge during transporting to the site.

[Note: Failure to do so could result in air flow leaks at poorly sealed locations which could affect sample representativeness.]

11.3.2.4 Place in a carrying bag to take to the sampler.

11.3.3 Collection

11.3.3.1 After the sampling system has been assembled, perform a single point flow check as described in Sections 11.2.3.

11.3.3.2 With the empty sample module removed from the sampler, rinse all sample contact areas using reagent grade hexane in a Teflon® squeeze bottle. Allow the hexane to evaporate from the module before loading the samples.

11.3.3.3 With the sample cartridge removed from the sampler and the flow control valve fully open, turn the pump on and allow it to warm-up for approximately 5 minutes.

11.3.3.4 Attach a "dummy" sampling cartridge loaded with the exact same type of filter and PUF media to be used for sample collection.

11.3.3.5 Turn the sampler on and adjust the flow control valve to the desired flow as indicated by the Magnehelic gauge reading determined in Section 11.2.2.24. Once the flow is properly adjusted, take extreme care not to inadvertently alter its setting.

11.3.3.6 Turn the sampler off and remove the "dummy" module. The sampler is now ready for field use.

11.3.3.7 Check the zero reading of the sampler Magnehelic. Record the ambient temperature, barometric pressure, elapsed time meter setting, sampler serial number, filter number, and PUF cartridge number on the Field Test Data Sheet (see Figure 11). Attach the loaded sampler cartridge to the sampler.

11.3.3.8 Place the voltage variator and flow control valve at the settings used in Section 11.3.2, and the power switch. Activate the elapsed time meter and record the start time. Adjust the flow (Magnehelic setting), if necessary, using the flow control valve.

11.3.3.9 Record the Magnehelic reading every 6 hours during the sampling period. Use the calibration factors (see Section 11.2.2.24) to calculate the desired flow rate. Record the ambient temperature, barometric pressure, and Magnehelic reading at the beginning and during sampling period.

11.3.4 Sample Recovery

11.3.4.1 At the end of the desired sampling period, turn the power off. Carefully remove the sampling head containing the filter and adsorbent cartridge. Place the protective "plate" over the filter to protect cartridge during transport to clean recovery area. Also, place a piece of aluminum foil around the bottom of adsorbent sampler head.

11.3.4.2 Perform a final calculated sampler flow check using the calibration orifice, as described in Section 11.3.2. If calibration deviates by more than 10 percent from initial reading, mark the flow data for that sample as suspect and inspect and/or remove from service, record results on Field Test Data Sheet, Figure 11.

11.3.4.3 Transport adsorbent sampler head to a clean recovery area.

11.3.4.4 While wearing disposable lint free nylon or powder-free surgical gloves, remove the PUF cartridge from the lower module chamber and lay it on the retained aluminum foil in which the sample was originally wrapped.

11.3.4.5 Carefully remove the glass fiber filter from the upper chamber using clean Teflon®-tipped forceps.

11.3.4.6 Fold the filter in half twice (sample side inward) and place it in the glass cartridge atop the PUF.

11.3.4.7 Wrap the combined samples in the original hexane rinsed aluminum foil, attached Teflon® end caps and place them in their *original* aluminum sample container. Complete a sample label and affix it to the aluminum shipping container.

11.3.4.8 Chain-of-custody should be maintained for all samples. Store the containers under dry ice and protect from UV light to prevent possibly photo-decomposition of collected analytes. If the time span between sample collection and laboratory analysis is to exceed 24 hours, refrigerate sample at 4°C.

11.3.4.9 Return at least 1 field filter/PUF blank to the laboratory with each group of samples. Treat a field blank exactly as the sample except that no air is drawn through the filter/adsorbent cartridge assembly.

11.3.4.10 Ship and store field samples chilled (<4°) (blue ice is acceptable) until receipt at the analytical laboratory, after which they should be refrigerated at less than or equal to 4°C. Extraction must be performed within 7 days of sampling and analysis within 40 days of extraction.

12. Sample Extraction Procedure

[Note: Sample extraction should be performed under a properly ventilated hood.]

12.1 Sample Extraction

12.1.1 All samples should be extracted within 1 week after collection. All samples should be stored at <4°C until extracted.

12.1.2 All glassware should be washed with a suitable detergent; rinsed with deionized water, acetone, and hexane; rinsed again with deionized water; and fired in an oven (500°C).

12.1.3 Prepare a spiking solution for determination of extraction efficiency. The spiking solution should contain one or more surrogate compounds that have chemical structures and properties similar to those of the analytes of interest. Octachloronaphthalene (OCN) and dibutylchlorendate have been used as surrogates for determination of organochlorine pesticides by GC with an ECD. Tetrachloro-m-xylene and decachlorobiphenyl can also be used together to insure recovery of early and late eluting compounds. For organophosphate pesticides, tributylphosphate or triphenylphosphate may be employed as surrogates. The surrogate solution should be prepared so that addition of 100 μL into the PUF plug results in an extract containing the surrogate compound at the high end of the instrument's calibration range. As an example, the spiking solution for OCN is prepared by dissolving 10 mg of OCN in 10 mL of 10% acetone in n-hexane, followed by serial dilution n-hexane to achieve a final spiking solution of OCN is 1 μg/mL.

[Note: Use the recoveries of the surrogate compounds to monitor for unusual matrix effects and gross sample processing errors. Evaluate surrogate recovery for acceptance by determining whether the measured concentration falls within the acceptance limits of 60-120 percent.]

12.1.4 The extracting solution (10% diethyl ether/hexane) is prepared by mixing 1800 mL of freshly opened hexane and 200 mL of freshly opened diethyl ether (preserved with ethanol) to a flask.

12.1.5 All clean glassware, forceps, and other equipment to be used should be rinsed with 10% diethyl ether/ hexane and placed on rinsed (10% diethyl ether/hexane) aluminum foil until use. The condensing towers should also be rinsed with 10% diethyl ether/hexane. Then add 700 mL of 10% diethyl ether/hexane to the 1,000 mL round bottom flask and add up to three boiling granules.

12.1.6 Using precleaned (i.e., 10% diethyl ether/hexane Soxhlet extracted) cotton gloves, the filter/PUF cartridge is removed from the sealed container, the PUF removed from the glass cartridge, and the filter/PUF together are placed into the 300 mL Soxhlet extractor using prerinsed forceps.

12.1.7 Before extraction begins, add 100 µL of the OCN solution directly to the top of the PUF plug.

[Note: Incorporating a known concentration of the solution onto the sample provides a quality assurance check to determine recovery efficiency of the extraction and analytical processes.]

12.1.8 Connect the Soxhlet extractor to the 1,000 mL boiling flask and condenser. Wet the glass joints with 10% diethyl ether/hexane to ensure a tight seal between the fittings. If necessary, the PUF plug can be adjusted

using forceps to wedge it midway along the length of the siphon. The above procedure should be followed for all samples, with the inclusion of a blank control sample.

12.1.9 The water flow to the condenser towers of the Soxhlet extraction assembly should be checked and the heating unit turned on. As the samples boil, the Soxhlet extractors should be inspected to ensure that they are filling and siphoning properly (4 to 6 cycles/hour). Samples should cycle for a minimum of 16 hours.

12.1.10 At the end of the extracting process (minimum of 16 hours), the heating unit is turned off and the sample cooled to room temperature.

12.1.11 The extracts are then concentrated to 5 mL using a Kuderna-Danish (K-D) apparatus. The K-D is set up, assembled with concentrator tubes, and rinsed. The lower end of the filter tube is packed with glass wool and filled with sodium sulfate to a depth of 40 mm. The filter tube is then placed in the neck of the K-D. The Soxhlet extractors and boiling flasks are carefully removed from the condenser towers and the remaining solvent is drained into each boiling flask. Sample extract is carefully poured through the filter tube into the K-D. Each boiling flask is rinsed three times by swirling hexane along the sides. Once the sample has drained, the filter tube is rinsed down with hexane. Each Snyder column is attached to the K-D and rinsed to wet the joint for a tight seal. The complete K-D apparatus is placed on a steam bath and the sample is evaporated to approximately 5 mL.

[Note: Do not allow samples to evaporate to dryness.]

Remove sample from the steam bath, rinse the Snyder column with a minimum of hexane, and allow to cool. Adjust sample volume to 10 mL in a concentrator tube, close with a glass stopper, and seal with TFE fluorocarbon tape. Alternatively, the sample may be quantitatively transferred (with concentrator tube rinsing) to prescored vials and brought up to final volume. Concentrated extracts are stored at <4°C until analyzed. Analysis should occur no later than 40 days after sample extraction.

12.2 Sample Cleanup

12.2.1 If only polar compounds are sought, an alumina cleanup procedure is appropriate. Before cleanup, the sample extract is carefully reduced to 1 mL using a gentle stream of clean nitrogen.

12.2.2 A glass chromatographic column (2-mm I.D. x 15-cm long) is packed with alumina (7), activity grade IV, and rinsed with approximately 20 mL of n-hexane. The concentrated sample extract is placed on the column and eluted with 10 mL of n-hexane at a rate of 0.5 mL/minute. The eluate volume is adjusted to exactly 10 mL and analyzed as per Section 13.

12.2.3 If both PCBs and common pesticides are sought, alternate cleanup procedures (8,9) may be required (i.e., silicic acid).

12.2.4 Finally, class separation and improved specificity can be achieved by column clean-up and separation on Florisil (9).

13. Analytical Procedure

13.1 Analysis of Organochlorine Pesticides by Capillary Gas Chromatography with Electron Capture Detector (GC/ECD)

[Note: Organochlorine pesticides, PCBs and many nonchlorinated pesticides are responsive to electron capture detection (see Table 1). Most of these compounds can be analyzed at concentration of 1 to 50 ng/mL by GC/ECD. The following procedure is appropriate. Sampling and analytical methods that have been used to determine pesticides and PCBs collected from air using a modification of this methodology have been published (14-22).]

13.1.1 Select GC column (e.g., 0.3-mm by 30-m DB-5 column) and appropriate GC conditions to separate the target analytes. Typical operating parameters for this column with splitless injection are: Carrier gas-chromatography grade helium at a flow rate of 1 to 2 mL/min and a column head pressure of 7 to 9 psi (48 to 60 kPa); injector temperature of 250°C; detector temperature of 350°C; initial oven temperature of 50°C held for 2.0 min., ramped at 15°C/min to 150°C for 8 min, ramped at 10°C/min to 295°C then held for 5 min; purge time of 1.0 min. A typical injection volume is 2 to 3 μL.

13.1.2 Remove sample extract from refrigerator and allow to warm to room temperature.

13.1.3 Prepare standard solution from reference materials of known purity. Analytically pure standards of organochlorine pesticides and PCBs are available from several commercial sources.

13.1.4 Use the standard solutions of the various compounds of interest to determine relative retention times (RRTs) to an internal standard such as p,p'-DDE, aldrin or octachloronaphthalene. Use 1 to 3-μL injections or other appropriate volumes.

13.1.5 Determine detector linearity by injecting standard solutions of three different concentrations (amounts) that bracket the range of analyses. The calibration is considered linear if the relative standard deviation (RSD) of the three response factors for the three standards is 20 percent or less.

13.1.6 Calibrate the system with a minimum of three levels of calibration standards in the linear range. The low standard should be near the analytical method detection limit. The calibration is considered linear if the relative standard deviation (RSD) of the three response factors for the three standards is 20 percent or less. The initial calibration should be verified by the analysis of a standard from an independent source. Recovery of 85 to 115 percent is acceptable. The initial calibration curve should be verified at the begining of each day and after every ten samples by the analysis of the midpoint standard; an RPD of 15% or less is acceptable for continuing use of the initial calibration curve.

13.1.7 Inject 1 to 3 μL of sample extract. Record volume injected to the nearest 0.05 μL.

13.1.8 A typical ECD response for a mixture of single component pesticides using a capillary column is illustrated in Figure 12. If the response (peak height or area) exceeds the calibration range, dilute the extract and reanalyze.

13.1.9 Quantify PCB mixtures by comparison of the total heights or areas of GC peaks (minimum of five) with the corresponding peaks in the best-matching standard. Use Aroclor 1242 for early-eluting PCBs and either Aroclor 1254 or Aroclor 1260 as appropriate for late-eluting PCBs.

13.1.10 If both PCBs and organochlorine pesticides are present in the same sample, use column chromatographic separation on silicic acid (8,9) prior to GC analysis.

13.1.11 If polar compounds are present that interfere with GC/ECD analysis, use column chromatographic cleanup or alumina (7), activity grade IV, in accordance with Section 12.2.

13.1.12 For confirmation use a second GC column such as DB-608. All GC procedures except GC/MS require second column confirmation.

13.1.13 For improved resolution use a capillary column such as an 0.25-mm I.D. x 30-m DB-5 with 0.25 μm film thickness. The following conditions are appropriate.

- Helium carrier gas at 1 mL/min.
- Column temperature program, 90°C (4 min)/16°C/min to 154°C/4°C/min to 270°C.
- Detector, ^{63}Ni ECD at 350°C.
- Make up gas, nitrogen, or 5% methane/95% argon at 60 mL/min.
- Splitless injection, 2 μL maximum.
- Injector temperature, 220°C.

13.1.14 Class separation and improved specificity can be achieved by column chromatographic separation on Florisil (9).

13.1.15 A Hall electrolytic conductivity detector (HECD) operated in the reductive mode may be substituted for the ECD for improved specificity. Sensitivity, however, will be reduced by at least an order of magnitude.

13.2 Analysis of Organophosphorus Pesticides by Capillary Gas Chromatography with Flame Photometric or Nitrogen-Phosphorus Detectors (GC/FPD/NPD)

[Note: Organophosphorus pesticides are responsive to flame photometric and nitrogen-phosphorus (alkali flame ionization) detection. Most of these compounds can be analyzed at concentrations of 50 to 500 ng/mL using either of these detectors.]

13.2.1 Procedures given in Section 13.1.1 through 13.1.9 and Section 13.1.13 through 13.1.14 apply, except for the selection of surrogates.

13.2.2 Use tributylphosphate, triphenylphosphate, or other suitable compound(s) as surrogates to verify extraction efficiency and to determine RRTs.

13.3 Analysis of Carbamate and Urea Pesticides by Capillary Gas Chromatography with Nitrogen-Phosphorus Detector

13.3.1 Trazine, carbamate, and urea pesticides may be determined by capillary GC (DB-5, DB-17, or DB-1701 stationary phase) using nitrogen-phosphorus detection or MS-SIM with detection limits in the 0.05 to 0.2 μL/mL range. Procedures given in Section 13.1.1 through 13.1.9 and Section 13.1.13 through 13.1.14 apply, except for the selection of surrogates, detector, and make up gas.

13.3.2 Thermal degradation may be minimized by reducing the injector temperature to 200°C. HPLC may also be used, but detection limits will be higher (1 to 5 μg/mL).

13.3.3 N-methyl carbamates may be determined using reverse-phase high performance liquid chromatography (HPLC) (C-18) (Section 13.4) and post-column derivization with o-phthaldehyde and fluorescence detection (EPA Method 531). Detection limits of 0.01 to 0.1 μg/mL can be achieved.

13.4 Analysis of Carbamate, Urea, Pyrethroid, and Phenolic Pesticides by High Performance Liquid Chromatography (HPLC)

[Note: Many carbamate pesticides, urea pesticides, pyrethrins, phenols, and other polar pesticides may be analyzed by high HPLC with fixed or variable wavelength UV detection. Either reversed-phase or normal phase chromatography may be used. Detection limits are 0.2 to 10 μg/mL of extract.]

13.4.1 Select HPLC column (i.e., Zorbax-SIL, 46-mm I.D. x 25-cm, or μ-Bondapak C18, 3.9-mm x 30-cm, or equivalent).

13.4.2 Select solvent system (i.e., mixtures of methanol or acetonitrile with water or mixtures of heptane or hexane with isopropanol).

13.4.3 Follow analytical procedures given in Sections 13.1.2 through 13.1.9.

13.4.4 If interferences are present, adjust the HPLC solvent system composition or use column chromatographic clean-up with silica gel, alumina, or Florisil (9).

13.4.5 An electrochemical detector may be used to improve sensitivity for some ureas, carbonates, and phenolics. Much more care is required in using this detector, particularly in removing dissolved oxygen from the mobile phase and sample extracts.

13.4.6 Chlorophenol (di- through penta-) may be analyzed by GC/ECD or GC/MS after derivatization with pentafluorobenzylbromide (EPA Method 604).

13.4.7 Chlorinated phenoxyacetic acid herbicides and pentachlorophenol can be analyzed by GC/ECD or GC/MS after derivatization with diazomethane (EPA Method 515). DB-5 and DBJ-1701 columns (0.25-mm I.D. x 30-m) at 60 to 300°C/4°C per min have been found to perform well.

13.5 Analysis of Pesticides and PCBs by Gas Chromatography with Mass Spectrometry Detection (GC/MS)

[Note: A mass spectrometer operating in the selected ion monitoring mode is useful for confirmation and identification of pesticides.]

13.5.1 A mass spectrometer operating in select ion monitoring (SIM) mode can be used as a sensitive detector for multi-residue determination of a wide variety of pesticides. Mass spectrometers are now available that provide detection limits comparable to nitrogen-phosphorus and electron capture detectors.

13.5.2 Most of the pesticides shown in Table 1 have been successfully determined by GC/MS-SIM. Typical GC operating parameters are as described in Section 13.1.1.

13.5.3 The mass spectrometer is typically operated using positive ion electron impact ionization (70 eV). Other instrumental parameters are instrument specific.

13.5.4 p-Terphenyl-d_{14} is commonly used as a surrogate for GC/MS analysis.

13.5.5 Quantification is typically performed using an internal standard method. 1,4-Dichlorobenzene, naphthalene-d_8, acenaphthene-d_{10}, phenanthrene-d_{10}, chrysene-d_{12} and perylene-d_{12} are commonly used as internal standards. Procedures given in Section 13.1.1 through 13.1.9 and Section 13.1.13 through 13.1.14 apply, except for the selection of surrogates, detector, and make up gas.

13.5.6 See ASTM Practice D 3687 for injection technique, determination of relative retention times, and other procedures pertinent to GC and HPLC analyses.

13.6 Sample Concentration

13.6.1 If concentrations are too low to detect by the analytical procedure of choice, the extract may be concentrated to 1 mL or 0.5 mL by carefully controlled evaporation under an inert atmosphere. The following procedure is appropriate.

13.6.2 Place K-D concentrator tube in a water bath and analytical evaporator (nitrogen blow-down) apparatus. The water bath temperature should be from 25°C to 50°C.

13.6.3 Adjust nitrogen flow through hypodermic needle to provide a gentle stream.

13.6.4 Carefully lower hypodermic needle into the concentrator tube to a distance of about 1 cm above the liquid level.

13.6.5 Continue to adjust needle placement as liquid level decreases.

13.6.6 Reduce volume to slightly below desired level.

13.6.7 Adjust to final volume by carefully rinsing needle tip and concentrator tube well with solvent (usually n-hexane).

14. Calculations

14.1 Determination of Concentration

14.1.1 The concentration of the analyte in the extract solution can be taken from a standard curve where peak height or area is plotted linearly against concentration in nanograms per milliliter (ng/mL). If the detector response is known to be linear, a single point is used as a calculation constant.

14.1.2 From the standard curve, determine the nanograms of analyte standard equivalent to the peak height or area for a particular compound.

14.1.3 Ascertain whether the field blank is contaminated. Blank levels should not exceed 10 ng/sample for organochlorine pesticides or 100 ng/sample for PCBs and other pesticides. If the blank has been contaminated, the sampling series must be held suspect.

14.2 Equations

14.2.1 Quantity of the compound in the sample (A) is calculated using the following equation:

$$A = 1000 \left(\frac{A_s \times V_e}{V_i} \right)$$

where:

A = total amount of analyte in the sample, ng.

A_s = calculated amount of material injected onto the chromatograph based on calibration curve for injected standards, ng.

V_e = final volume of extract, mL.

V_i = volume of extract injected, μL.

1000 = factor for converting microliters to milliliters.

14.2.2 The extraction efficiency (EE) is determined from the recovery of surrogate spike as follows:

$$EE(\%) = \left[\frac{S}{S_a}\right][100]$$

where:

EE = extraction efficiency, %

S = amount of spike recovered, ng.

S_a = amount of spike added to plug, ng.

The extraction efficiency (surrogate recovery) must fall between 60-120% to be acceptable.

14.2.3 The total volume of air sampled under ambient conditions is determined using the following equation:

$$V_a = \frac{\sum_{i=1}^{n} (T_i \times F_i)}{1000\ L/m^3}$$

where:

V_a = total volume of air sampled, m^3.

T_i = length of sampling segment between flow checks, min.

F_i = average flow during sampling segment, L/min.

14.2.4 The air volume is corrected to EPA standard temperature (25°C) and standard pressure (760 mm Hg) as follows:

$$V_s = V_a \left(\frac{P_b - P_w}{760\ mm\ Hg}\right)\left(\frac{298K}{t_A}\right)$$

where:

V_s = volume of air at standard conditions (25°C and 760 mm Hg), std. m^3.

V_a = total volume of air sampled, m^3.

P_b = average ambient barometric pressure, mm Hg.

P_w = vapor pressure of water at calibration temperature, mm Hg.

t_A = average ambient temperature, °C + 273.

14.2.5 If the proper criteria for a sample have been met, concentration of the compound in a standard cubic meter of air sampled is calculated as follows:

$$C_a(ng/std.\ m^3) = \left[\frac{(A)}{(V_s)}\right]$$

If it is desired to convert the air concentration value to parts per trillion (ppt) in dry air at standard temperature and pressure (STP), the following conversion is used:

$$ppt = 0.844\ (C_a)$$

The air concentration can be converted to parts per trillion (v/v) in air at STP as follows:

$$pptv = \left[\frac{(24.45)\ (C_a)}{(MW)}\right]$$

where:

MW = molecular weight of the compound of interest, g/g-mole.

14.2.6 If quantification is performed using an internal standard, a relative response factor (RRF) is calculated by the equation:

$$RRF = \left[\frac{(I_s)(C_{is})}{(I_{is})(C_s)}\right]$$

where:

I_s = integrated area of the target analyte peak, counts.
I_{is} = integrated area of the internal standard peak, counts.
C_{is} = concentration of the internal standard, ng/μL.
C_s = concentration of the analyte, ng/µL.

14.2.7 The concentration of the analyte (C_a) in the sample is then calculated as follows:

$$C_a = \frac{(I_s)(C_{is})}{(RRF)(I_{is})}$$

where:

I_s = integrated area of the target analyte peak, counts.
RRF = relative response factor (see Section 14.2.7).

15. Performance Criteria and Quality Assurance

[Note: This section summarizes required quality assurance (QA) measures and provides guidance concerning performance criteria that should be achieved within each laboratory.]

15.1 Standard Operating Procedures (SOPs)

15.1.1 Users should generate SOPs describing the following activities accomplished in their laboratory: (1) assembly, calibration, and operation of the sampling system, with make and model of equipment used; (2) preparation, purification, storage, and handling of sampling cartridges, (3) assembly, calibration, and operation of the analytical system, with make and model of equipment used; and (4) all aspects of data recording and processing, including lists of computer hardware and software used.

15.1.2 SOPs should provide specific stepwise instructions and should be readily available to, and understood by, the laboratory personnel conducting the work.

15.2 Process, Field, and Solvent Blanks

15.2.1 One filter/PUF cartridge from each batch of approximately twenty should be analyzed, without shipment to the field, for the compounds of interest to serve as a process blank.

15.2.2 During each sampling episode, at least one filter/PUF cartridge should be shipped to the field and returned, without drawing air through the sampler, to serve as a field blank.

15.2.3 Before each sampling episode, one PUF plug from each batch of approximately twenty should be spiked with a known amount of the standard solution. The spiked plug will remain in a sealed container and will not be used during the sampling period. The spiked plug is extracted and analyzed with the other samples. This field spike acts as a quality assurance check to determine matrix spike recoveries and to indicate sample degradation.

15.2.4 During the analysis of each batch of samples, at least one solvent process blank (all steps conducted but no filter/PUF cartridge included) should be carried through the procedure and analyzed.

15.2.5 Levels for process, field and solvent blanks should not exceed 10 ng/sample for single components or 100 ng/sample for multiple component mixtures (i.e., for organochlorine pesticides and PCBs).

15.3 Method Precision and Bias

15.3.1 Precision and bias in this type of analytical procedure are dependent upon the precision and bias of the analytical procedure for each compound of concern, and the precision and bias of the sampling process.

15.3.2 Several different parameters involved in both the sampling and analysis steps of this method collectively determine the precision and bias with which each compound is detected. As the volume of air sampled is increased, the sensitivity of detection increases proportionately within limits set by: (a) the retention efficiency for each specific component trapped on the polyurethane foam plug, and (b) the background interference associated with the analysis of each specific component at a given site sampled. The sensitivity of detection of samples recovered by extraction depends on: (a) the inherent response of the particular GC detector used in the determinative step, and (b) the extent to which the sample is concentrated for analysis. It is the responsibility of the analyst(s) performing the sampling and analysis steps to adjust parameters so that the required detection limits can be obtained.

15.3.3 The reproducibility of this method for most compounds for which it has been evaluated has been determined to range from ±5 to ±30% (measured as the relative standard deviation) when replicate sampling cartridges are used (N>5). Sample recoveries for individual compounds generally fall within the range of 90 to 110%, but recoveries ranging from 65 to 125% are considered acceptable.

15.4 Method Safety

15.4.1 This procedure may involve hazardous materials, operations, and equipment. This method does not purport to address all of the safety problems associated with its use.

15.4.2 It is the users responsibility to consult and establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to the implementation of this procedure. This should be part of the users SOP manual.

16. References

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TABLE 1. COMPOUNDS FOR WHICH PROCEDURE HAS BEEN TESTED[1]

Compound	Recommended Analysis[2]	Compound	Recommended Analysis
Alachlor	GC/ECD	Folpet	GC/ECD
Aldrin	GC/ECD	Heptachlor	GC/ECD
Allethrin	HPLC/UV	Heptachlor epoxide	GC/ECD
Aroclor 1242	GC/ECD	Hexachlorobenzene	GC/ECD
Aroclor 1254	GC/ECD	Lindane (γ-BHC)	GC/ECD
Aroclor 1260	GC/ECD	Linuron	HPLC/UV
Atrazine	GC/NPD	Malathion	GC/NPD or FPD
Bendiocarb	HPLC/UV	Methyl parathion	GC/NPD or FPD
BHC (α- and β-Hexachlorocyclohexanes)	GC/ECD	Methoxychlor	GC/FCD
Captan	GC/ECD	Metolachlor	GC/ECD
Carbaryl	HPLC/UV	Mexacarbate	GC/FCD
Carbofuran	HPLC/UV	Mirex	GC/ECD
Chlordane, technical	GC/ECD	Monuron	HPLC/UV
Chlorothalonil	GC/ECD	Trans-nonachlor	GC/ECD
Chlorotoluron	HPLC/UV	Oxychlordane	GC/ECD
Chlorpyritos	GC/ECD	Pentachlorobenzene	GC/ECD
2,4-D esters and salts	GC/ECD	Pentachlophenol	GC/ECD
Dacthal	GC/ECD	Permethrin (cis and trans)	HPLC/UV
ρ,ρ-'DDT	GC/ECD	o-Phenylphenol	HPLC/UV
ρ,ρ-'DDE	GC/ECD	Phorate	GC/NPD or FPD
Diazinon	GC/NPD or FPD	Propazine	GC/NPD
Dicloran	GC/ECD	Propoxur (Baygon)	HPLC/UV
Dieldrin	GC/ECD	Pyrethrin	HPLC/UV
Dicofol	GC/ECD	Resmethrin	HPLC/UV
Dicrotophos	HPLC/UV	Ronnel	GC/ECD
Diuron	HPLC/UV	Simazine	HPLC/UV
Ethyl parathion	GC/NPD or FPD	Terbuthiuron	HPLC/UV
Fenvalerate	HPLC/UV	Trifluralin	GC/ECD
Fluometuron	HPLC/UV		

[1] The following recommendations are specific for that analyte for maximum sensitivity.
[2] GC = gas chromatography; ECD = electron capture detector, FPD = flame photometric detector; HPLC = high performance liquid chromatography; NPD = nitrogen-phosphorus detector; UV = ultraviolet absorption detector; GC/MS = gas chromatography/mass spectrometry may also be used.

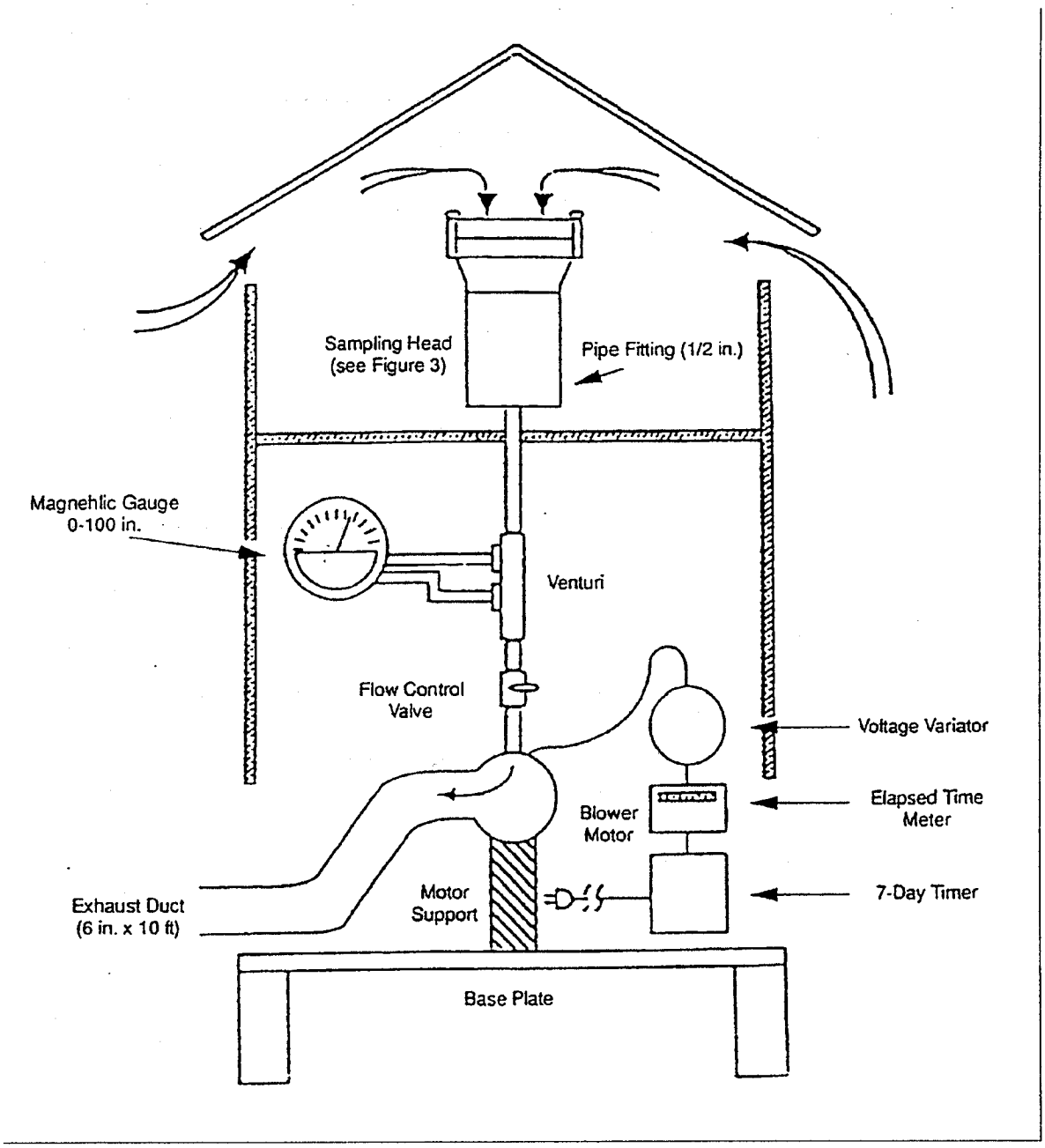

Figure 1. Typical high volume air sampler for monitoring common pesticides and PCBs.

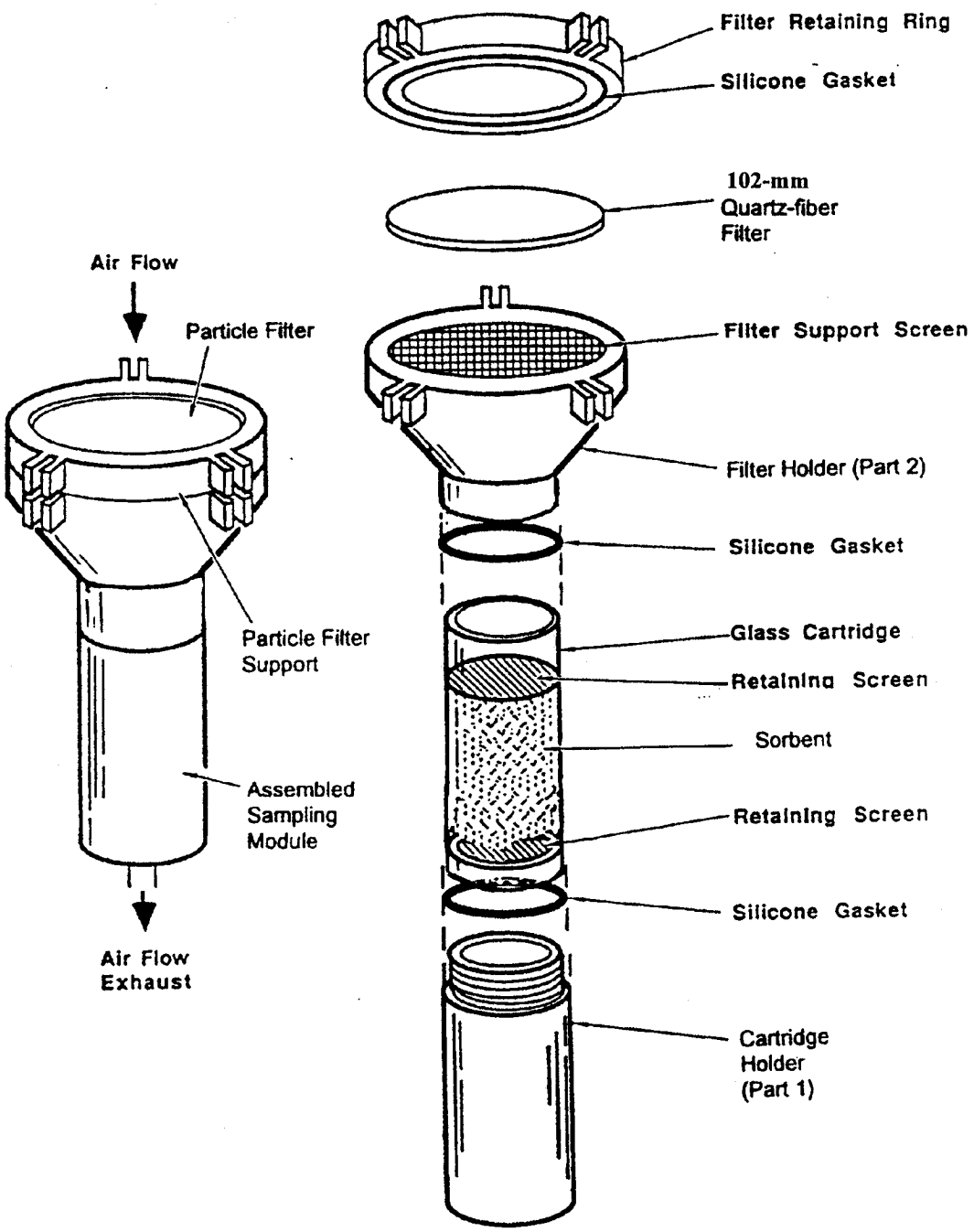

Figure 2. Typical absorbent cartridge assembly for sampling common pesticides and PCBs.

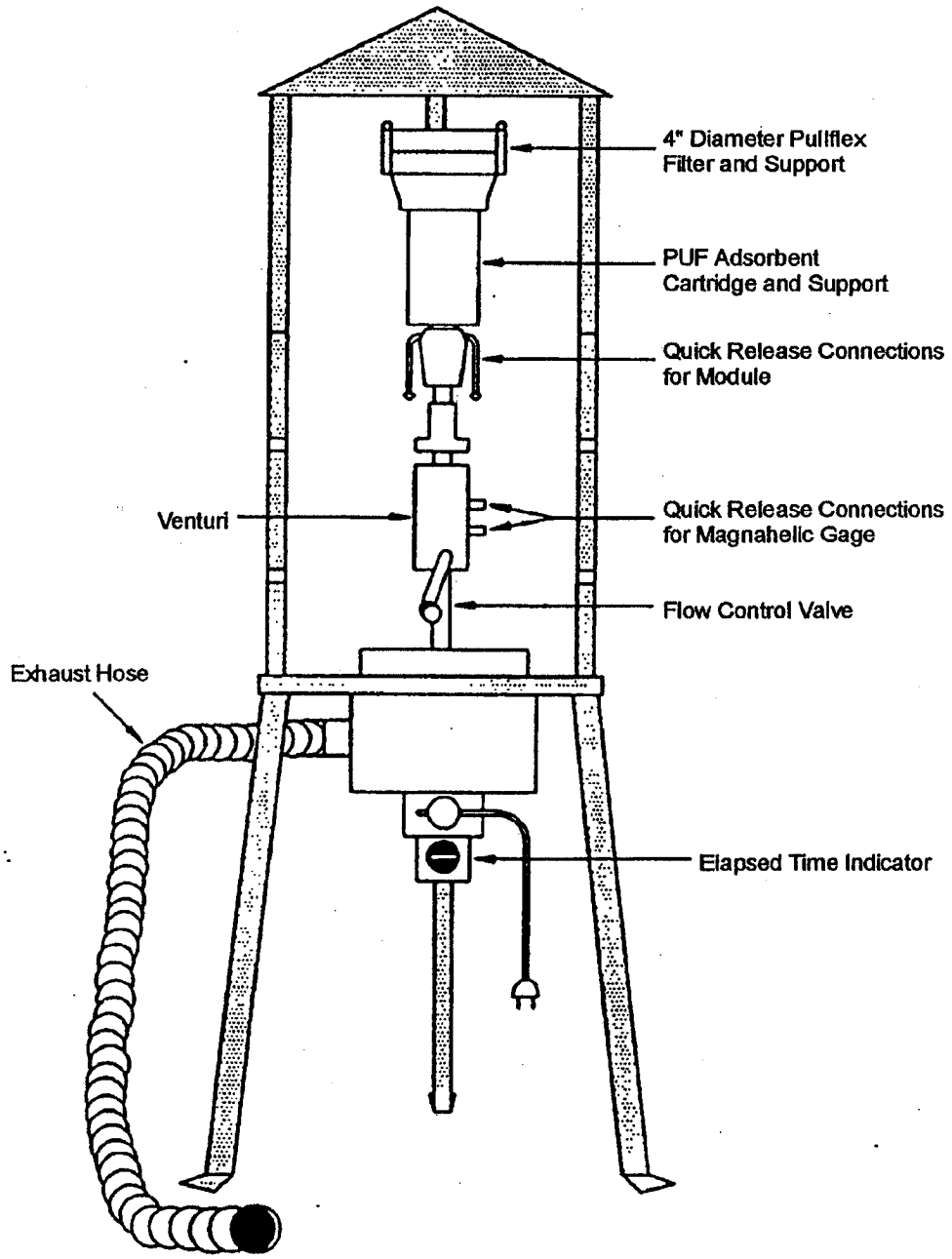

Figure 3. Portable high volume air sampler developed by EPA.

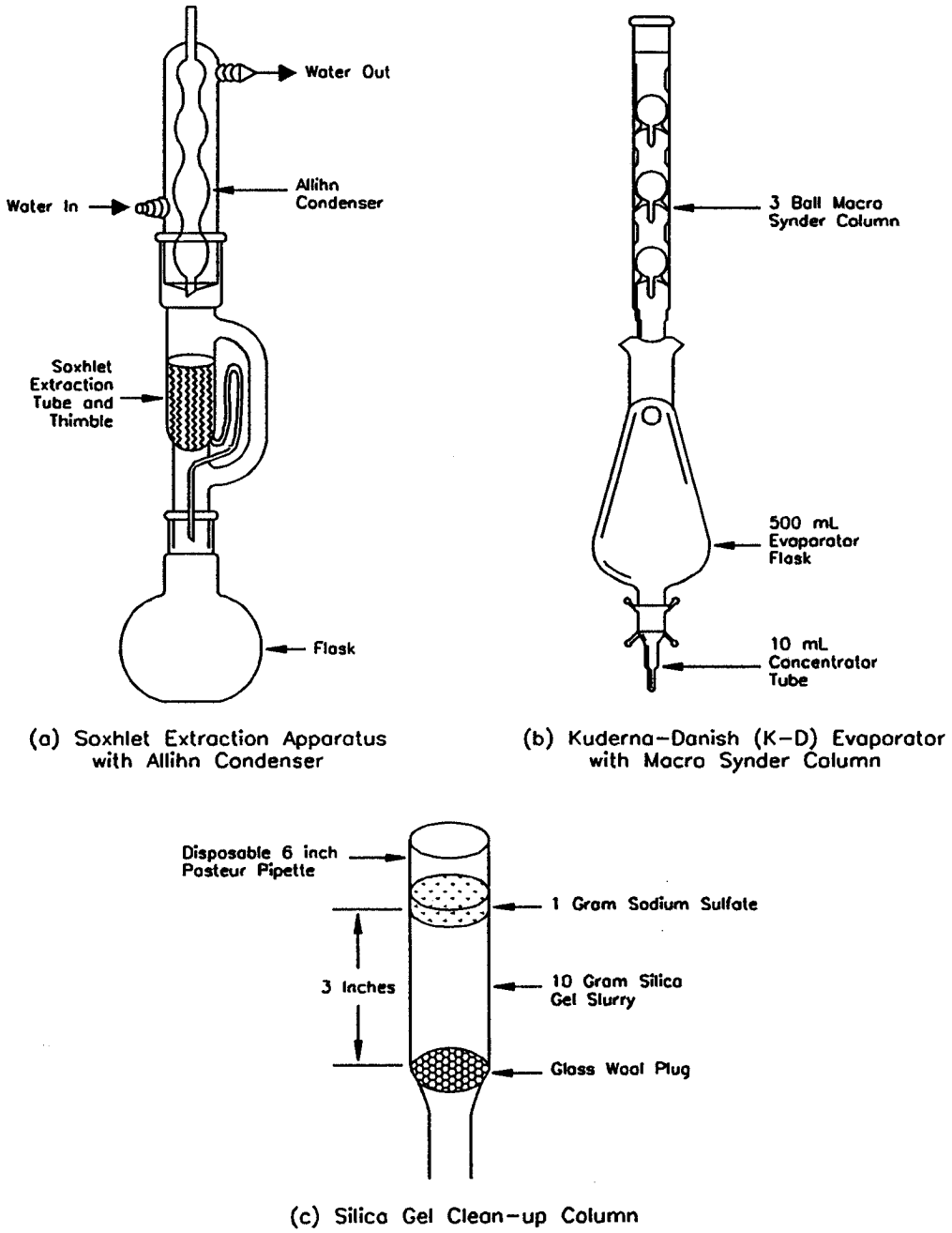

Figure 4. Apparatus used for sample clean-up and extraction.

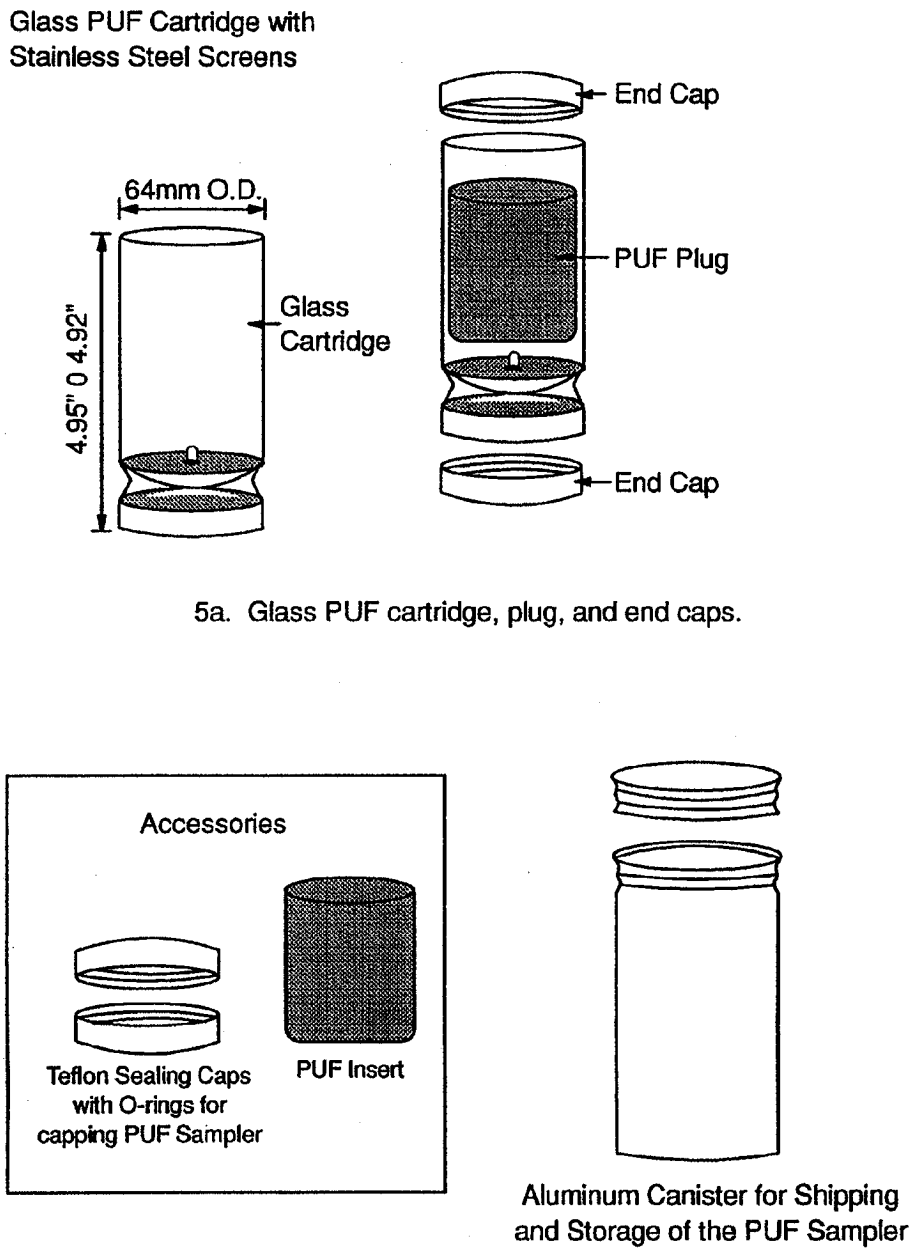

Figure 5. Glass PUF cartridge (5a) and shipping container (5b) for use with high-volume sampling systems.

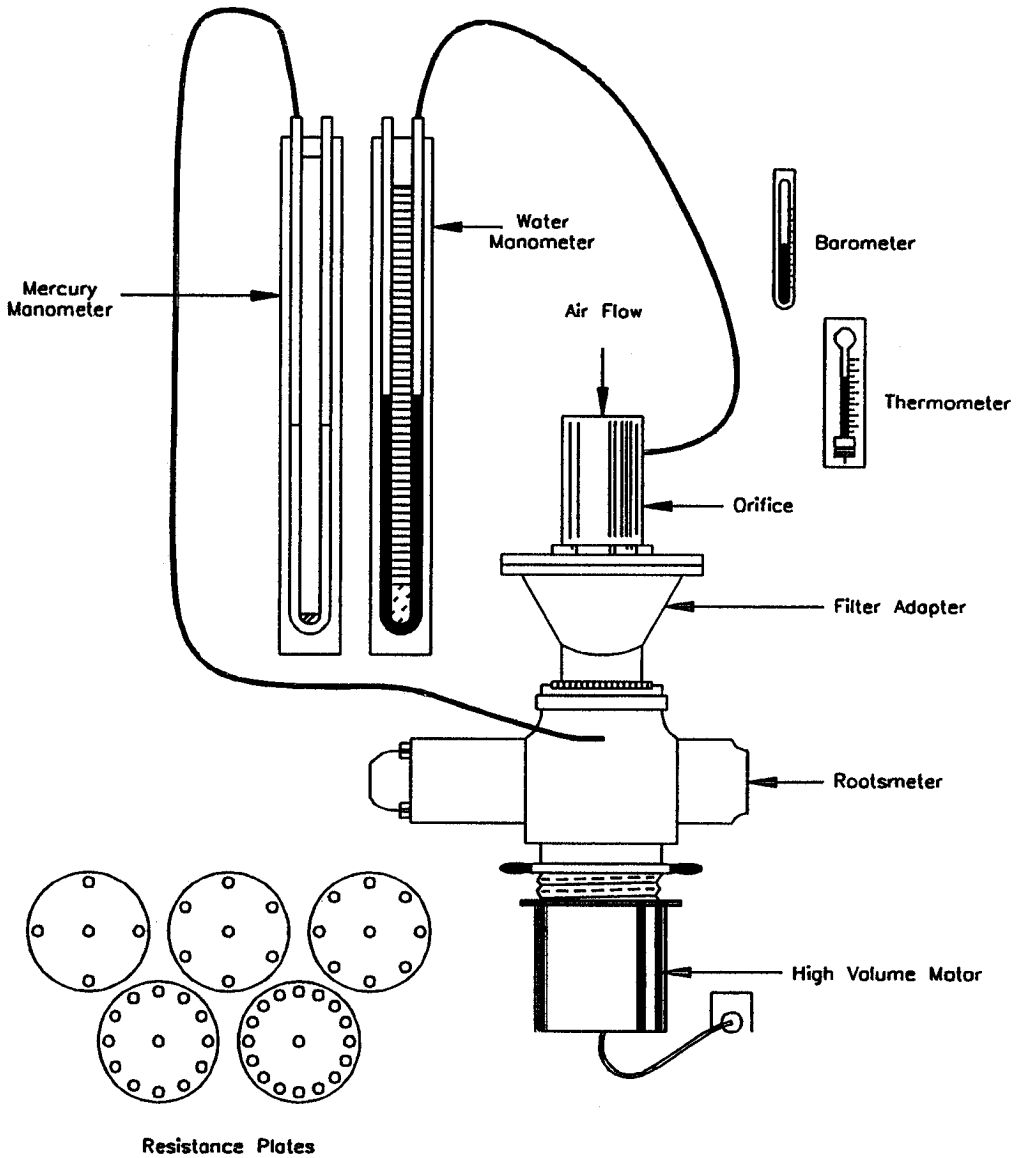

Figure 6. Positive displacement rootsmeter used to calibrate orifice transfer standard.

COMPENDIUM METHOD TO-4A
ORIFICE CALIBRATION DATA SHEET

T_1 _____ Name _____

P_1 _____ mmHg Date _____

Orifice No. _____

Rootsmeter No. _____

Resistance Plants (No. of holes)	Air Volume Measured by Rootsmeter V_m		Standard Volume, V_{std}, (std m^3)	Time for Air Volume to Pass Through Rootsmeter, θ (min)	Rootsmeter Pressure Differential, ΔP (mm Hg)	Pressure Drop Across Orifice, ΔH (in. H_2O)	x-Axis Standard Flowrate, Q_{std} (std m^3/min)	Y - axis $\sqrt{\Delta H(P_1/P_{std})(298/T_1)}$ value
	(R^3)	(m^3)						
5	200	5.66						
7	200	5.66						
10	300	8.50						
13	300	8.50						
18	300	8.50						

Factors: $(R^3)(0.02832\ \frac{m^3}{R^3}) = m^3$ and (in. Hg) $25.4\ (\frac{mm\ Hg}{in.\ Hg}) = mm\ Hg$

Calculation Equations:

1. $V_{std} = V_m\ (\frac{P_1 - \Delta P}{P_{std}})(\frac{T_{std}}{T_1})$

where:

$T_{std} = 296°K$
$P_{std} = 760.0$ mm Hg

2. $Q_{std} = \frac{V_{std}}{\theta}$

Figure 7. Orifice calibration data sheet.

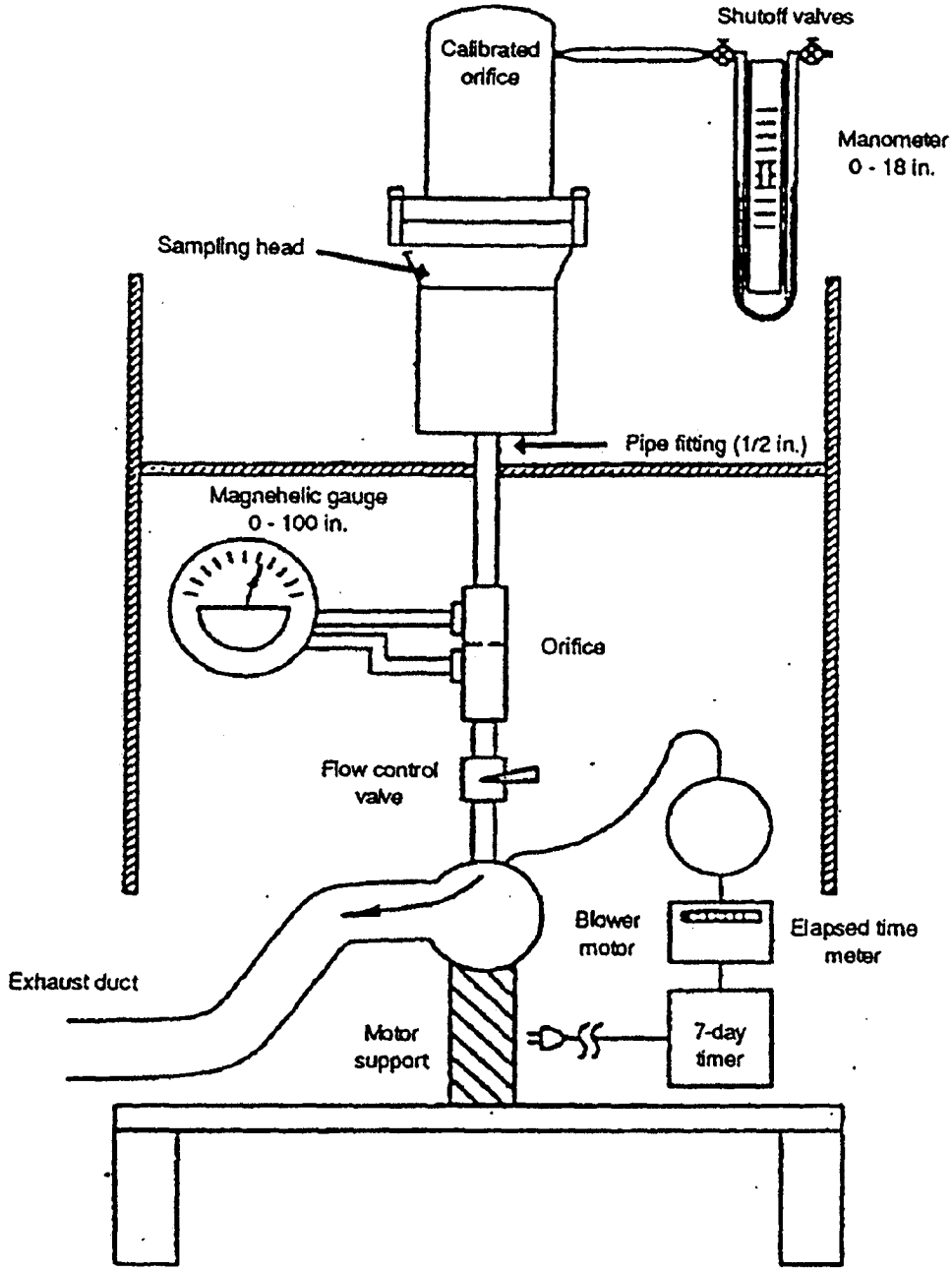

Figure 8. Field calibration configuration of the high-volume sampler for common pesticides and PCBs.

COMPENDIUM METHOD TO-4A
FIELD CALIBRATION DATA SHEET FOR SAMPLER CALIBRATION

Sampler ID:

Calibration Orifice ID:

Sampler Location:

Job No.:

High Volume Transfer Orifice Data:

Correlation Coefficient (CC1):
(CC2):

Slope (M1):
(M2):

Intercept (B1):
(B2):

Calibration Date: ____ Time:
Calibration Ambient Temperature: ____°F ____°C
Calibration Ambient Barometric Pressure: ____ "Hg ____ mm Hg
Calibration set point (SP): _____

CALIBRATOR'S SIGNATURE

SAMPLER CALIBRATION

Actual values from calibration		Calibrated values		
Orifice manometer, inches (Y1)	Monitor Magnehelic, inches (Y2)	Orifice manometer (Y3)	Monitor Magnehelic (Y4)	Calculated value orifice flow, scm (X1)
	70			
	60			
	50			
	40			
	30			
	20			
	10			

Definitions

Y1 = Calibration orifice reading, in. H_2O

Y2 = Monitor Magnehelic reading, in. H_2O

P_a = Barometric pressure actual, mm Hg

B1 = Manfacturer's Calibration orifice Intercept

M1 = Manufacturer's Calibration orifice manometer slope

Y3 = Calculated value for orifice manometer
= $[Y1(Pa/760)(298/\{Ta + 273\})]^{1/2}$

Y4 = Calculated value for Magnehelic
= $[Y2(Pa/760)(298/\{Ta + 273\})]^{1/2}$

X1 = Calculated value orifice flow, scm
= $\frac{Y3 - B1}{M1}$

P_{std} = Barometric pressure standard, 760 mm Hg

T_a = Temperature actual, °C

T_{std} = Temperature standard, 25°C

Figure 9. Orifice transfer standard field calibration data sheet.

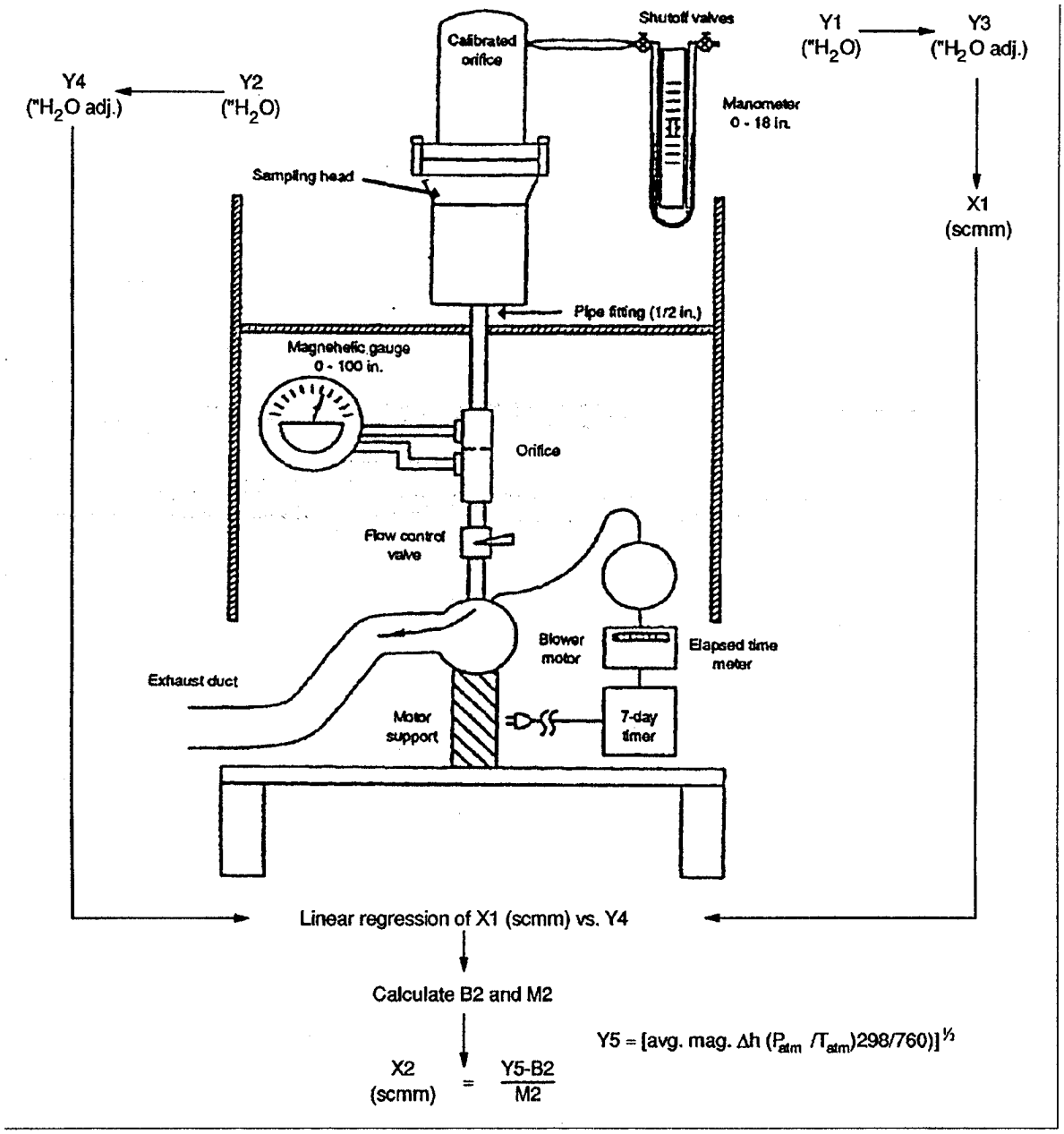

Figure 10. Relationship between orifice transfer standard and flow rate through sampler.

COMPENDIUM METHOD TO-4A
FIELD TEST DATA SHEET
GENERAL INFORMATION

Sampler I.D. No.: _____
Lab PUF Sample No.: _____
Sample location: _____
_____
_____

Operator: _____
Other: _____
_____
_____

PUF Cartridge Certification Date: _____
Date/Time PUF Cartridge Installed: _____
Elapsed Timer: _____
Start _____
Stop _____
Diff. _____
Sampling

M1 _____ **B1** _____
M2 _____ **B2** _____

	Start	Stop
Barometric pressure ("Hg)	_____	_____
Ambient Temperature (°F)	_____	_____
Rain	Yes _____	Yes _____
	No _____	No _____

Sampling time
Start _____
Stop _____
Diff. _____

Audit flow check within ±10 of set point
_____ **Yes**
_____ **No**

TIME	TEMP	BAROMETRIC PRESSURE	MAGNEHELIC READING	CALCULATED FLOW RATE (scmm)	READ BY
Avg.					

Comments

_____
_____
_____

Figure 11. Field test data sheet.

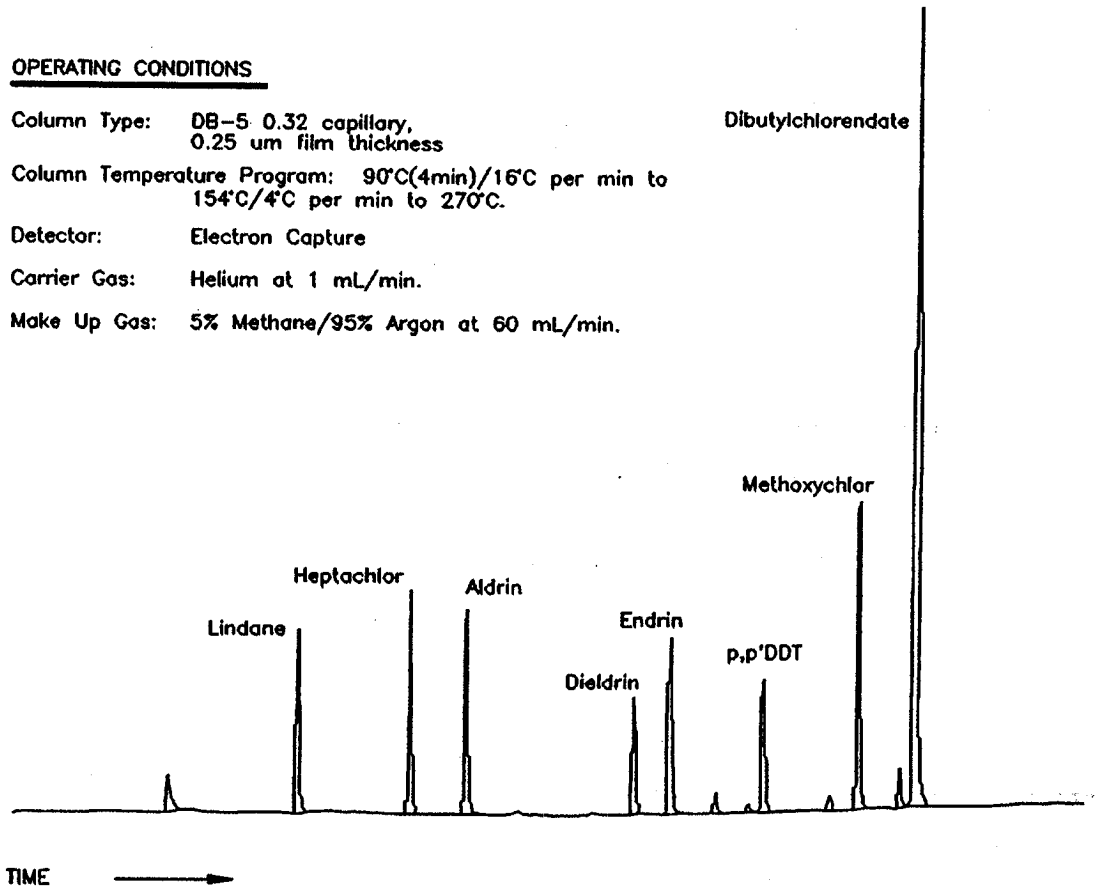

Figure 12. Chromatogram showing a mixture of single component pesticides determined by GC/ECD using a capillary column.

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Appendix D

Anticipated Verification Sampling Grids and Calculations

BBL®
BLASLAND, BOUCK & LEE, INC.
engineers, scientists, economists

CLIENT: Georgia-Pacific Corporation **PROJECT:** Georgia-Pacific Corporation Kalamazoo Mill and Former Hawthorne Mill Properties
TITLE: Sample Calculations **Prepared By:** D.O.K. **Date:** June 2005
SUBJECT: Verification Sampling Calculations – Refuse Area and Oxbow Area **Checked By:** D.J.H **Date:** June 2005

OBJECTIVE:

Determine the frequency of post-excavation verification samples required for the Refuse Area Removal Area and the Oxbow Area Removal Area of the Georgia-Pacific Corporation (Georgia-Pacific) Kalamazoo Mill Property (Kalamazoo Mill Property) and the former Hawthorne Mill Property (Hawthorne Mill Property), respectively.

REFERENCES:

1. MDEQ. 2002. *Sampling Strategies and Statistics Training Materials for Part 201 Cleanup Criteria* (MDEQ. April 14, 2004) Remediation and Redevelopment Division (MDEQ Guidance Document; Lansing, MI: 2002).

ASSUMPTIONS:

1. The removal areas were determined from the approximate Refuse Area Removal Area and Oxbow Area Removal Area limits on Figure 1 of the *Action Removal Area Work Plan* (Work Plan; BBL, 2005). The Refuse Area Removal Area equaled approximately 2 acres and the Oxbow Area Removal Area equaled approximately 4 acres.

2. The perimeter of the assumed excavation areas was determined from the approximate Refuse Area Removal Area and Oxbow Area Removal Area limits on Figure 1 of the Work Plan. The Refuse Area Removal Area perimeter equaled approximately 1,303 square feet (ft^2) and the Oxbow Area Removal Area perimeter equaled approximately 1,636 ft^2.

3. The Refuse Area and Oxbow Area excavation depths were assumed to be 9 feet (ft) and 2 ft, respectively, in accordance with the Work Plan.

4. The site factor (S.F.) for the Oxbow Area Removal Area was determined from the approximate Oxbow Area Removal Area limits on Figure 1 of the Work Plan.

CALCULATIONS:

Sampling Grid Interval Calculations

Consistent with the MDEQ Guidance Document the Refuse Area Removal Area is characterized as a medium site (i.e., an excavation area between 0.25 and 3.0 acres) and the Oxbow Area Removal Area is characterized as a large site (i.e., an excavation area greater than 3.0 acres), as such, the grid interval shall be calculated using the following equations:

Medium Site $$\frac{\sqrt{A/\pi}}{4} = G.I.$$

Large Site $$\sqrt{\frac{A * \pi}{SF}} = G.I.$$

where,

G.I. = Grid interval.
A = Area to be grid (ft ^{2} . The area equals the sum of the excavation base and sidewalls areas).
S.F. = Site factor, length of area to be grid (unit less).

Refuse Area Removal Area

Consistent with the MDEQ Guidance Document, the grid interval for a medium site is given by Equation 1. The excavation base area equaled 91,453 ft^2. The sidewall area was calculated by multiplying the length of the perimeter of the assumed excavation area by the depth of the excavation, and is given by the following:

$$A_{sidewall} = 1{,}303\,\text{ft} * 9\,\text{ft} = 11{,}726\,\text{ft}^2$$

The total area was calculated as the sum of the excavation base and sidewalls, as follows:

$$A_{Total} \cong 103{,}179\,\text{ft}^2 \cong 2.37\,\text{acres}$$

$$\text{G.I.} = \frac{\sqrt{103{,}179\,\text{ft}^2 / \pi}}{4} = 45\,\text{ft}$$

Assume a 45 ft gird interval, as such, the number of nodes was determined by:

$$91{,}453\,\text{ft}^2 / (45\,\text{ft} \times 45\,\text{ft}) = 45\,\text{nodes}$$

Consistent with the Guidance Document, the minimum number of samples was determined to be the greater of 9 samples or 25% of the number of nodes:

$$45\ \text{nodes} * 0.25 = 11.25$$

A minimum of 11 post-excavation samples will be taken within the Refuse Area.

Oxbow Area Removal Area

Consistent with the MDEQ Guidance Document, the grid interval for a large site is given by Equation 2. The excavation base area equaled 170,128 ft^2. The sidewall area was calculated by multiplying the length of the perimeter of the assumed excavation area by the assumed depth of the excavation, and is given by the following:

$$A_{sidewall} = 1{,}636\,\text{ft} * 2\,\text{ft} = 3{,}272\,\text{ft}^2$$

The total area was calculated as the sum of the excavation base and sidewalls, as follows:

$$A_{Total} \cong 173{,}400\ ft^2 \cong 3.98\ acres$$

$$G.I. = \sqrt{\frac{173{,}400\ ft * \pi}{635}} = 29.29\ ft$$

Assume a 30 ft gird interval, as such, the approximate number of nodes was determined by:

$$170{,}128\ ft^2 / (30\ ft * 30\ ft) = 189\ nodes$$

Consistent with the Guidance Document, the minimum number of samples was determined to be the greater of 9 samples or 25% of the number of nodes:

$$189\ nodes * 0.25 = 47.25 = 47$$

A minimum of 47 post-excavation samples will be taken within the Oxbow Area.

SUMMARY:

Based on the above calculations, a minimum number of 11 and 47 samples should have been taken from the Refuse Area and Oxbow Area excavations, respectively, for a total of 58 samples.

INDEPENDENT VERIFICATION SAMPLING CALCULATIONS – REFUSE AREA AND OXBOW AREA

REMOVAL ACTION WORK PLAN
ALLIED PAPER, INC./PORTAGE CREEK/KALAMAZOO RIVER SUPERFUND SITE
GEORGIA-PACIFIC CORPORATION
KALAMAZOO, MICHIGAN

Introduction

Verification sampling is to be preformed at the Refuse and Oxbow Areas as part of the paper-making residuals (residuals) removal activities. Verification sampling frequency requirements were determined based on the *Sampling Strategies and Statistics Training Materials for Part 201Cleanup Criteria* (MDEQ Guidance Document; MDEQ 2004). Independent sampling frequency and location requirements were developed for both the Refuse and Oxbow Areas as these are regarded as separate "sites" in relation to the MDEQ Guidance Document. A sampling strategy that facilitated the selection of unbiased sampling locations using girding was used, pursuant to the MDEQ Guidance Document.

Size of "Site"

As described in the MDEQ Guidance Document, the verification sampling frequency and locations are based on the planimetric area to be remediated, or, as designated in the MDEQ Guidance Document, the size of the "site". Determination of the "site" size includes calculating the combined area of the excavation sidewalls and base. This calculation, and a discussion of the "site" size based on the MDEQ Guidance Document, is presented below.

Determining the Appropriate Grid Interval

In accordance with MDEQ Guidance Document, the grid interval to be established for verification sample collection is determined based on "site" size (i.e., small, medium or large), and the corresponding total "site" area (sidewall plus base areas). The grid interval for a medium and large-size "site" is calculated using the following equations:

Medium Site $$\frac{\sqrt{A/p}}{4} = G.I.$$

Large Site $$\sqrt{\frac{A/p}{SF}} = G.I.$$

where:

G.I. = Grid Interval
A = "Site" Area; and
p = Pi (3.14).

Calculation of the grid interval for both the Refuse and Oxbow Areas are presented below.

Refuse Area

The total area of the Refuse Area excavation, including excavation sidewalls and base, is approximately 103,179 square feet (ft^2), thus utilizing the medium site size equation above, the grid interval equals 45 ft. Utilizing a 45-foot grid spacing to establish the verification sample collection locations results in 11 grid stations located within and along the sidewalls of the removal area.

Oxbow Area

The total area of the Oxbow Area excavation, including excavation sidewalls and base, is approximately 173,400 ft^2, thus utilizing the large site size equation above, the grid interval equals 30 ft. Utilizing a 30-foot grid spacing to establish the verification sample collection locations results in 189 grid stations located within and along the sidewalls of the removal area.

Estimating the Number of Samples to be collected on the Established Grid

As recommended in the MDEQ Guidance Document, a minimum of 9 samples or 25 percent of the total number of grid stations, whichever is larger, should be collected and analyzed as part of the verification sampling program. Applying this guidance information to the Refuse and Oxbow removal areas, and assuming grid intervals of 45 feet (ft), and 30 ft, respectively, the appropriate number of verification samples is determined as described below.

The sample collection requirements for the Refuse and Oxbow excavations are calculated based on the respective areas of the sidewall and base, and the sampling frequency criteria presented in the MDEQ Guidance Document. The table below presents calculations for the Refuse and Oxbow excavations. These calculations are based on the excavation areas presented above, under the *size of the "site"* section.

Removal Area	**Grid Station Area** (ft^2)	**Total Sidewall Area** (ft^2)	**Total Base Area** (ft^2)	**Number of Grid Stations**	**25% of Grid Stations**	**Minimum Number of Samples**
Refuse Area	2,025	11,726	91,453	45	11.25	11
Oxbow Area	900	3,272	170,128	189	47.25	47
					Total Samples	**58**

Based on the above calculations, a minimum number of 11, and 47 samples should be taken from each of the Refuse Area and Oxbow Area excavations, respectively, for a total of 58 samples.