Arsenic Phytoremediation Pilot Study Work Plan

FMC Corporation, Middleport, New York

Prepared for:

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1.0 INTRODUCTION

Geomatrix Consultants, Inc. has prepared this pilot study work plan (plan) on behalf of FMC Corporation (FMC) to evaluate the effectiveness and feasibility of phytoremediation to address soil with elevated arsenic levels in various FMC study areas in Middleport, New York. Figure 1 illustrates the location of the FMC Plant Site (Site or Facility). This pilot study will be performed under the under the terms and conditions of the 1991 Administrative Order of Consent, Docket No. II RCRA-90-3008(h)-0209, entered into by FMC, the New York State Department of Environmental Conservation (NYSDEC), and the United States Environmental Protection Agency (EPA).

This plan includes background information on arsenic in soils and plant species used for phytoremediation of arsenic in soil, a description of the goals of the study, and a detailed scope of work for the pilot study. Appendix A includes several reprints of professional papers that provide detailed information on arsenic in soil and vegetation. These papers are available to provide the reader with additional information on the complex nature of arsenic geochemistry in the environment and potential arsenic uptake by plants.

2.0 BACKGROUND

Phytoremediation of arsenic compounds in soils has been documented by a number of researchers throughout the United States. The chemistry of arsenic is very complex and is present in the environment in many forms; however, the main forms are arsenate and arsenite. Arsenic is also present as organo-arsenicals in soil. Arsenate is the primary form of arsenic in oxygenated environments, such as well drained upper soil layers. It is soluble in water and will adsorb to reactive clay particles and oxides of aluminum and iron. Arsenate that becomes adsorbed in soils is relatively immobile in a soil environment. Any arsenate that remains in soil solution (soil pore water) is available for uptake by plants. Under reducing conditions, arsenite is generally the predominant species formed. At near neutral pH (i.e., less than 9), arsenite is less mobile in the soil (and less available to plants) than arsenate.

Researchers at the Argonne National Laboratory have shown uptake and partitioning of arsenic in willows and poplars trees grown on contaminated soil and the same species grown in quartz sand irrigated with water containing sodium arsenite. Analysis of plant material after the study showed that arsenic accumulated in both the leaves and roots of the plants with considerably more arsenic sequestered in the roots (Hinchman et al., 1998). Other work on arsenic phytoremediation has focused on developing genetically engineered plants that can uptake plant available arsenate from the soil and then reduce it to (the less-mobile) arsenite in aboveground tissue. This is accomplished via inserting an arsenate reductase gene into the plant, which ultimately facilitates trapping arsenite in the aboveground biomass. The objective of this approach is to facilitate transport of arsenic within the plant and reducing the arsenate to arsenite once the chemical has moved to the above ground biomass in the plant (ENS, 2002).

Research on other arsenic accumulator plants has resulted in a widely marketed plant species for cleanup of soils contaminated with arsenic. The plant Brake Fern (*Pteris ensiformis*) is a perennial and is native to southern latitudes (Ma et al., 2001). The plant is marketed by EdenSpace Systems Corporation. The EdenSpace website contains detailed information on the Brake Fern and its application as an arsenic hyperaccumulator (http://www.edenspace.com/edenfern.html). The Brake Fern may lack the hardiness and frost tolerance to survive as a perennial plant in the northern latitudes; however, it may be an effective plant for arsenic soil remediation in the northeastern United States if it is replanted each year. In addition to the Brake Fern, other herbaceous plant species have been demonstrated to take up high levels of arsenic, but accumulation is largely within the roots. Some of these are well adapted to the Middleport, New York climate and persist over the winter. Because the plants will persist over the winter, the biomass in year 2 will be significantly greater than with an annual plant.

In discussions with researchers, other practical approaches to phytoremediation of arsenic have been identified. In particular, discussions with Dr. Gary Banuelos of the United States Department of Agriculture, Agricultural Research Service in Parlier, California, indicated that since arsenic uptake by plants is analogous to phosphorus uptake, then phosphorus accumulator plants might be potential species to evaluate for arsenic phytoremediation (personal communication, 2006). Many of these types of plants and forbs are fast growing (typically one growing season) and can be easily harvested and removed from the site. In addition to the Brake Fern, other herbaceous species that will be considered as having potential to be successful soil arsenic accumulators and candidates for a pilot study include: Sudan grass, Sunflower, and Canola. Because of the relatively slow growing nature of poplars and willow trees, as compared to the above herbaceous species, they have not been included in this initial pilot study but may be evaluated at a later time.

Soil amendments may also increase the availability of arsenic to plants. Certain ionic species exists in the soil with properties similar to that of arsenate, which is the most common form of arsenic in soil. These ionic species will compete with binding sites of arsenate in soil and thereby make the arsenate more bioavailable to the plant. Some of these may also limit toxicity of arsenic to plants by competing for binding sites within the plants. In addition, chelation of heavy metals with ethylenediaminetetraacetic acid or the like may also improve the ability of arsenic to be accumulated within the plant. The specific arsenic species that may accumulate within the plants is unknown at this time; however, research has shown that inorganic forms of arsenic predominate in plants grown on soils with elevated arsenic concentrations.

3.0 PILOT STUDY OBJECTIVE

The overall objective of this phytoremediation pilot study is to evaluate the effectiveness and feasibility of phytoremediation to reduce the arsenic levels in the soil in the study areas. Information and data (e.g., time required to reduce soil arsenic levels, reduction levels, and associated costs) obtained during these studies will be incorporated into the corrective measures study for the site. In order to evaluate the effectiveness and feasibility of phytoremediation, the pilot study will focus on the following study questions:

1. What plants can reduce soil arsenic levels in the study area?
    - Will the Brake Fern effectively grow in the cooler Middleport climate?
    - What other plant species can be used?

2. For the plants being evaluated, what, if any, soil amendments will help increase plant uptake of soil arsenic?

3. How much arsenic is removed from the soil by plants?
    - How will the harvested plant material be handled?
    - What are the disposal options for the harvested plants?

4. What area and depth can the plants reduce the soil arsenic levels?

5. What will be the requirements (i.e., watering, weeding, fertilizing, pest control, etc.) for maintaining the plants?

4.0 SCOPE OF WORK

The scope of work includes seven tasks. The effectiveness of the remediation will be evaluated based on the ability of the various plantings to accumulate arsenic from the soil as measured by the sampling task described below. The feasibility will be evaluated based on a qualitative assessment of the growth and hardiness of the various plant species and any agronomic factors that might limit the applicability of phytoremediation to the FMC study areas.

A second study intended to evaluate uptake of arsenic in a riparian environment is currently being considered and may be included as part of this pilot study. At this point we anticipate that this additional work would be to evaluate arsenic uptake by existing vegetation in an impacted riparian area and would not require additional plantings. Prior to implementing this work, a work plan addendum will be submitted to the agencies for review and approval.

4.1 TASK 1 – EVALUATING EXISTING SITE SOIL DATA

Based on a review of the existing soil sampling data for the study areas and on discussions with affected property owners and the agencies, the proposed pilot study sites ("Study Sites") that have been identified include the following:

- The primary pilot study site will be located within an agricultural field to the northeast of the FMC Middleport Plant site and adjacent to the southeastern portion of the Royalton-Hartland School property. (Shown on Figures 1 and 2).

- The protected root zone (PRZ) of an approximately 15-inch diameter breast height crimson maple tree on a residential property (Property AB4) north of the Erie Barge Canal. Soil containing elevated arsenic levels was removed from Property AB4, except from within the PRZ of the tree, as part of the 2007 Early Actions (completed in November 2007). In order to save the crimson maple tree, soil was not excavated within the PRZ, which is an area approximately 20 feet (critical root radius) around the trunk to prevent damage to the root zone.

- The unexcavated area (referred to as the "P10 Root Zone") of the Wooded Parcel within a 24-foot radius from the trunk of a 24-inch diameter box elder tree that is situated within the boundaries of residential P-Block Property P10. Soil containing elevated arsenic levels was removed from the Wooded Parcel, except from within the P10 Root Zone, as part of the 2007 Early Actions (completed in November 2007).

- Additional residential properties, as appropriate. A limited number of other properties/areas may be included in the pilot study on a case-by-case basis if requested by the property owner and determined to appropriate (based on discussions with the property owner, the soil sample data available for the property, and property characteristics) with concurrence of the NYSDEC and EPA.

Written access permission from the owners of the above Study Sites must be obtained prior to performing any field activities.

Existing soil data from the selected Study Sites will be evaluated for suitability for plant growth. Both physical and chemical characteristics will be evaluated. Physical characteristics that will be evaluated include soil texture, drainage characteristics, depth to water, and existing vegetative cover. These data will be determined from review of existing soil survey data obtained from previous environmental studies conducted by FMC and site reconnaissance, if necessary. Chemical characteristics to be evaluated include soil pH, soil oxidation/reduction status, and total and soluble arsenic concentrations in soil. In the event that certain data are not available, additional soil samples and field measurements may be necessary and will be collected during the pilot study soil sampling task (Task 3).

4.2 TASK 2 – LABORATORY STUDY

A pre-field laboratory study will be conducted by Cornell University to look at various combinations of plants, competitive ions, chelating agents, and root colonizing microorganisms to determine the most effective combinations for the demonstration study to be implemented in the spring of 2008. After completion of the laboratory study, a letter-report will be prepared to summarize the study results and recommendations for the field pilot study.

4.3 TASK 3 – SOIL SAMPLING AND EVALUATION FOR DESIGN

Soil samples will be collected at the Study Sites to evaluate the baseline concentrations of arsenic in soil. The Study Sites are anticipated to be isolated blocks that measure approximately 30 feet by 40 feet (Figure 3). Soil samples will be collected on a 10-foot by 10-foot grid. Samples will be collected at 0 to 6 inches, 6 to 12 inches, and 12 to 24 inches. Plots and grids located at a residential property or within a protected root zone area will be scaled to fit the area of concern. The samples will be collected at evenly spaced intervals over the area of the plot and will be collected from 0 to 6 inches, 6 to 12 inches, and 12 to 24 inches. Soil samples will be analyzed for total arsenic, soluble arsenic, and pH using EPA-approved methods. Additional analyses may also be performed if chemical data needed to evaluate the suitability of the respective soil for plant growth were not available in work performed during Task 1. In addition, soils will be collected from the primary pilot study site (agricultural filed) and submitted to Dr. Gary Harman at Cornell University for laboratory analysis and bench scale studies. Dr. Harman and his staff will evaluate appropriate soil amendments and possible chelating agents that will make the arsenic in the soil more bio-available to the plants. The results of this testing will be incorporated into the pilot study design.

4.4 TASK 4 – FIELD PILOT STUDY DESIGN

The pilot study will consist of one or more vegetation test plots located on the Study Sites. A conceptual layout of these plots is shown on Figure 3. The anticipated size of the test plots will be about 30 feet by 40 feet; however, the final size and configuration will be determined upon inspection of the Study Sites. The scale of the test plots at some of the Study Sites may need to be at a reduced because of the available space and/or any limitations from the property owners.

Four annual plants have been identified for inclusion in the field pilot study: Sudan grass, Sunflower, Canola, and Brake Fern. The Cornell Cooperative Extension Service reports Sudan grass and Sunflower can uptake phosphorus at rates of about 0.36 and 1.02 percent of dry matter produced. Specific yields for these crops are based on specific management practices and climatic conditions but can be as high as 3 tons per acre for Sudan grass and about 8 tons per acre for Sunflowers. Assuming, for example, that the plants remove arsenic at ¼ the removal rate reported for phosphorus, the amount of arsenic that could be potentially removed from the system would be about 1,500 pounds per acre for Sudan grass and about 4,000 pounds per acre for Sunflower (assuming arsenic is present in these quantities). Canola has a much lower phosphorus requirement and will uptake about 100 to 150 pounds of phosphorus per acre. It should be noted that information to directly compare the uptake rate of arsenic with phosphorus for these species is not available so the actual rate may be higher or lower than these estimates. The fourth plant that will be evaluated is the Brake Fern. These ferns are capable of accumulating high levels of arsenic. Edenspace Systems Corporation reports that their "edenfern" has the capability of removing arsenic concentrations at rates 200 times that of other plants grown in the same environment. Other researchers have reported arsenic concentrations in excess of 7,500 parts per million in aboveground portions of the Brake Fern. The actual amount of arsenic that can be removed by the Brake Fern will be dependent upon the aboveground biomass produced by each plant and the availability of arsenic in site soils for plant uptake.

In addition to the above species, Dr. Harman at Cornell University has indicated that he will include in the pilot study novel plants with specialized storage organs that will accumulate arsenic. These plants will be identified prior to spring planting and will be incorporated into the design of the pilot study. A portion of this pilot study will focus on using the combination of plants with subterranean storage organs that accumulate arsenic in roots together with appropriate addition of phosphate, bicarbonate or chelating compounds, and possibly root symbiotic microbes.

A report summarizing this work will be submitted to the Agencies in the spring of 2008.

4.5 TASK 5 – PILOT STUDY IMPLEMENTATION

After completion of the design and receipt of appropriate approvals from the regulatory agencies, the pilot study will be ready to implement. The agricultural field site will be graded for drainage (if needed) and disked (cultivated) prior to planting to prepare the ground. The fertility of the soil will be evaluated prior to planting by collecting samples, submitting the samples to a local agricultural laboratory, and supplying the soil with appropriate nutrients for optimum plant growth. Portions of the plots will have soil amendments added based on the results of bench scale testing performed at Cornell University during the winter of 2007/2008. Planting of the annual vegetation will be conducted using standard agricultural equipment. Sudan grass and Canola will be planted by either drilling or broadcasting seed depending on availability of equipment for planting. Sunflowers will be planted in rows (drilled or similar method of planting) with an anticipated spacing of about 2 feet. The Brake Fern will be transplanted from potted plants into individually dug holes with an anticipated spacing of 1 to 2 feet between each plant.

To facilitate germination of seeds, a temporary irrigation system will be installed on the plot to keep the soil surface moist until the seeds have germinated and are actively growing. The irrigation system will be available to supply water throughout the growing season. Drip irrigation will be installed to provide irrigation water to the ferns. Sprinklers will be installed to irrigate the other plantings. It is anticipated that a tank for storing irrigation water and a timer based control system will be installed to facilitate irrigation. A gasoline or diesel powered water pump will provide the necessary water pressure for the sprinkler portion of the irrigation system.

Planting will occur in the spring of 2008. The actual planting time selected will depend on several factors including the timing of regulatory approval, availability of plant materials, contractor availability, and weather conditions.

At this time we anticipate that the test plots will be surrounded by a fenced enclosure to eliminate the possible damage to the plantings from wildlife and vandals.

The planting procedures may be modified based on the Study Sites physical characteristics (e.g., presence of tree roots) and on discussions with the owners of the Study Sites.

4.6 TASK 6 – MONITORING AND REPORTING

Once the field study has been implemented, weekly monitoring will be conducted to evaluate the performance of the vegetation. It is anticipated that weekly monitoring will be conducted from the end of planting until the first killing frost. Monitoring will consist of making visual observation on the health and vigor of the plants including insect or other pest problems and documenting those observations on inspection forms. If irrigation is necessary, the irrigation system will be monitored during weekly inspections. After the first growing season (fall 2008) or each harvest (sudan grass), samples of the vegetation will be collected and submitted to a laboratory for analysis of arsenic to determine the amount of arsenic accumulating in the plant biomass. The duration of the study may be extended based on the findings after the first growing season. In addition, after the final harvest or at the end of the first growing season, soil samples will be collected for analysis, as described in Task 3.

Upon completion of the first year of monitoring and sampling, a report will be prepared that documents the design and installation of the demonstration study, the performance of the various plant species, and recommendations for future work or remediation applications.

4.7 TASK 7 – PLANT UPTAKE EVALUATION

As previously described, at the end of the first growing season or after each harvest (sudan grass), the plant material will be submitted to the laboratory to determine the concentration of arsenic in the plant. Since there is little information on arsenic uptake potential or the plants that are proposed for this pilot study, the results of the plant uptake evaluation will be used to determine appropriate handling precautions and proper transport/disposal needs, and the plants will be managed accordingly. Information provided by Edenspace Systems Corporation on the Brake Fern indicates that touching or handling the ferns is not hazardous to people or animals; however, because arsenic accumulation in the plant, ferns (or other plants) that have accumulated arsenic should not be ingested (http://www.edenspace.com/edenfern.html).

5.0 SCHEDULE

The arsenic phytoremediation study work plan will be implemented upon approval of the regulatory agencies. The following summarizes the anticipated schedule for the pilot studies:

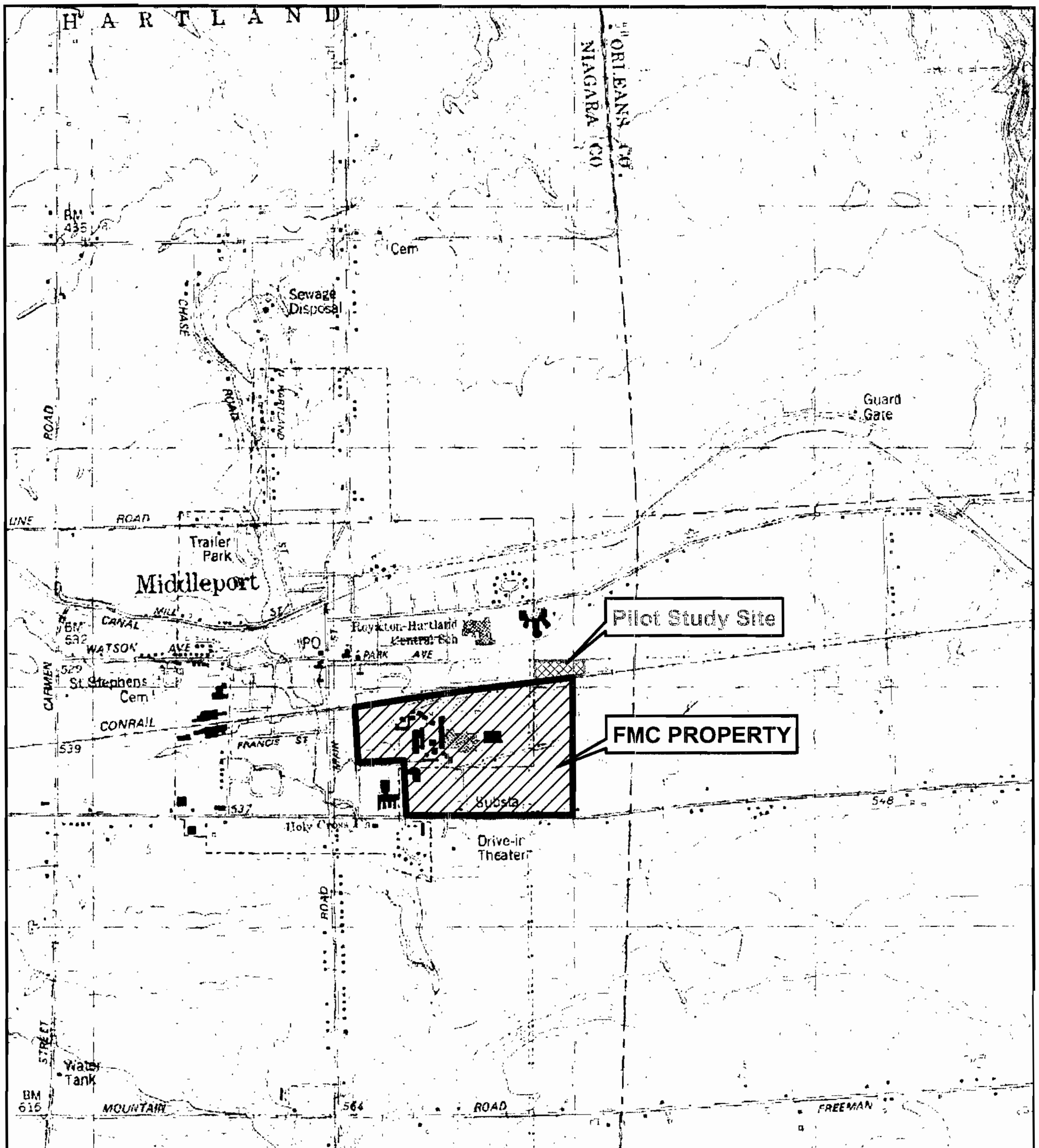
- Order Brake Ferns for spring 2008 planting – late November 2007
- Submit work plan for review and approval by Agencies – December 2007
- Collect bulk soil samples from the primary pilot study site (i.e, the agricultural field site) for Cornell University laboratory study – December 2007
- Plan and prepare for fieldwork – winter 2007/2008
- Respond to comments on work plan – winter 2008
- Submit summary report of Cornell University laboratory studies with modifications to pilot study design – spring 2008
- Collect soil samples, as needed, for pilot study evaluation – spring 2008 (as soon as site(s) is (are) accessible)
- Field layout/construction of pilot study – spring 2008 (approximately 1 week)
- Pre-irrigation (if necessary) and planting – spring 2008
- Monitoring – daily for the first week after planting; weekly though September 2008
- Periodic harvest of plant material – submit to laboratory, as appropriate
- Final harvest of plant material – submit to laboratory in September–October 2008
- Collect soil samples, as needed, for pilot study evaluation – after final harvest of plant material in September–October 2008
- Prepare report of findings – December 2008

6.0 REFERENCES

Environment News Service, 2002, Engineered Plants Soak Up Arsenic, October 7 (www.ens-newswire.com).

Hinchman, R.R., M.C. Negri, E.G. Gatliff, 1998, Phytoremediation Using Green Plants to Clean Up Contamination Soil, Groundwater, and Wastewater: Argonne National Lab website, pp. 13, Argonne, IL.

Ma, L.Q., K. M. Komar, C. Tu, W. Zhang, Y. Cai, E.D. Kennelley, 2001, A Fern That Hyperaccumulates Arsenic: Nature, Vol. 409, February (www.nature.com).



Basemap modified from U.S.G.S. 7.5 minute Medina, New York topographic quadrangle.

APPROXIMATE SCALE IN FEET
0 1,000 2,000

0 300 600
APPROXIMATE SCALE IN METERS

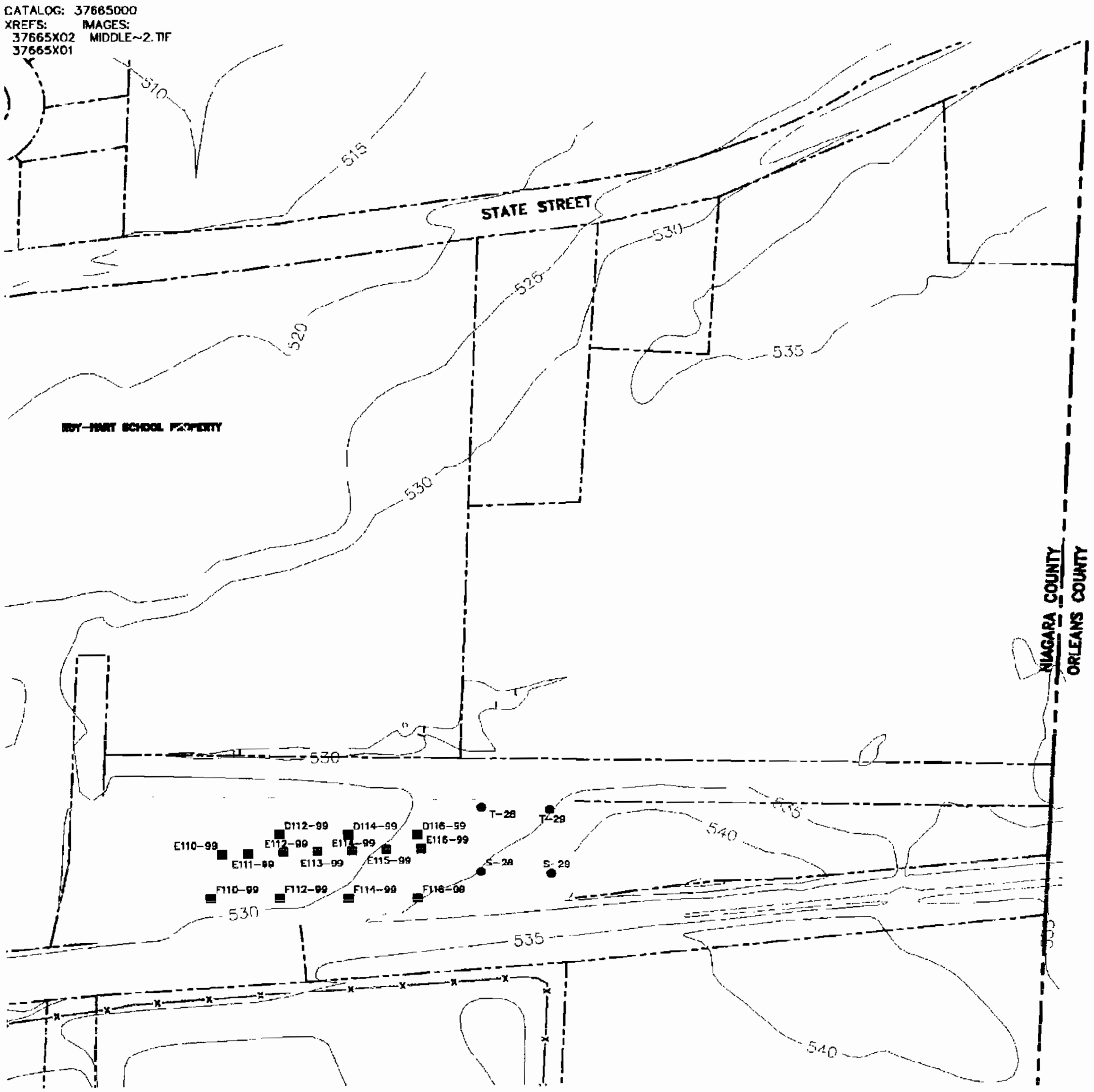
By: KLU	Date: 11/29/2007	Project No. 9936.000

SITE LOCATION MAP
FMC Corporation
Middleport, New York

Geomatrix

Figure 1

N:\9000s\009936\gis_SLM.mxd



LEGEND:

- APPROXIMATE BOUNDARY OF PILOT STUDY
- APPROXIMATE BOUNDARY OF PROPERTY
- APPROXIMATE PROPERTY BOUNDARY LINE
- EXISTING BUILDING
- 540 — EXISTING ELEVATION CONTOUR LINE (CONTOUR INTERVAL 1 FOOT)
- ■ RH26 — HISTORICAL SAMPLE LOCATION
- ● V-28 — 2004 SAMPLE LOCATION
- RAILROAD
- FMC PROPERTY FENCELINE

NOTES:

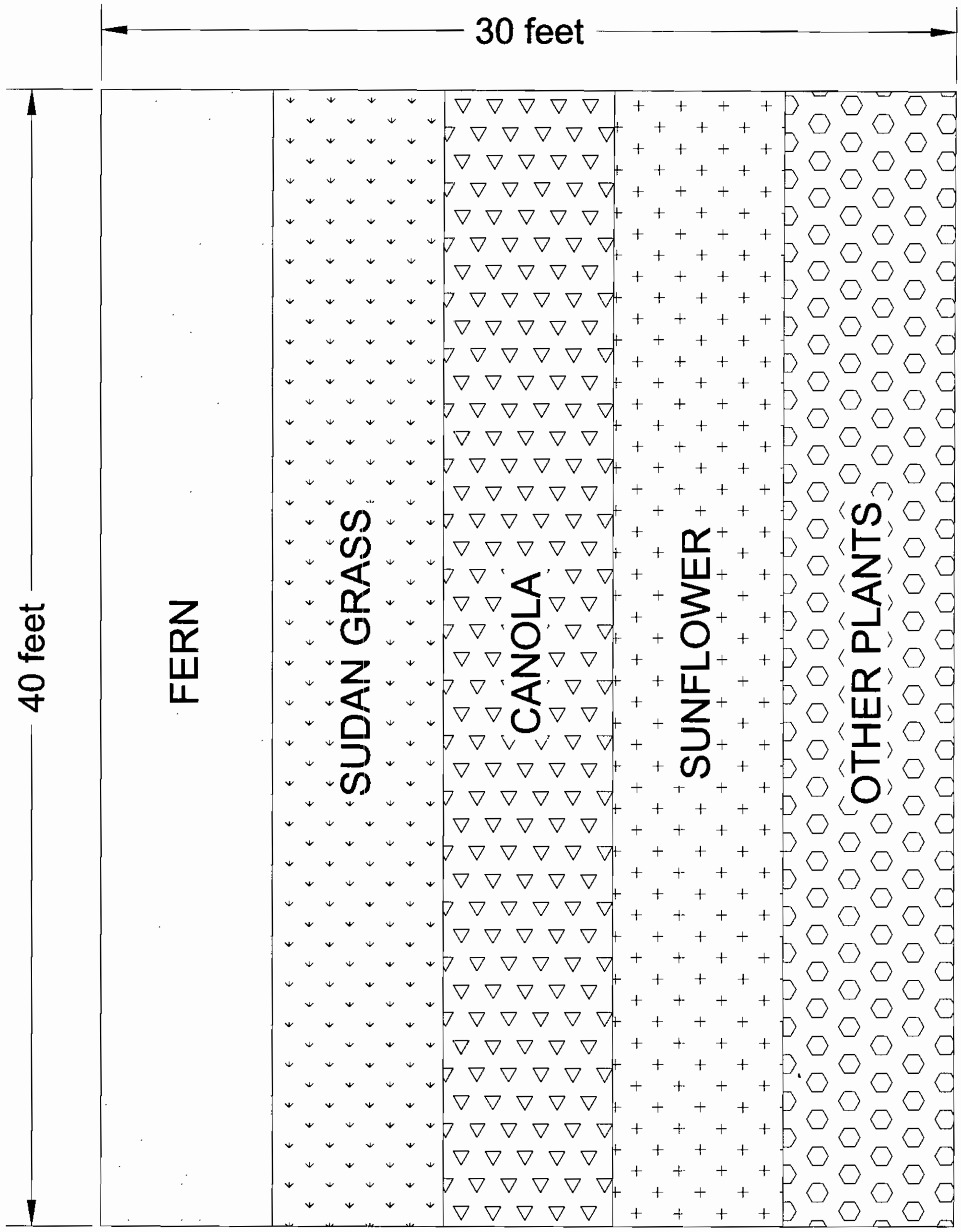
1. BASEMAP OBTAINED FROM A FIGURE BY CONESTOGA-ROVERS AND ASSOCIATES ENTITLED "HISTORIC ARSENIC SOIL/SEDIMENT DATA – NORTH RAILROAD PROPERTY" DATED OCTOBER 2003 AT A SCALE OF 1"=120'.
2. ALL LOCATIONS AND PROPERTY BOUNDARIES SHOWN ARE APPROXIMATE AND SUBJECT TO VERIFICATION.

0 240' 480'
GRAPHIC SCALE

PHYTOREMEDIATION
PILOT STUDY SITE
FMC Corporation
Middleport, New York

By: JBS	Date: 11/27/07	Project No.: 9936.000
Geomatrix		Figure 2

I:\9000s\9936.000\Pilot Study Site Figure.xls



FERN - 1' x 2' spacing
SUDAN GRASS - broadcast
CANOLA - broadcast
SUNFLOWER - 2' x 2' spacing

PHYTOREMEDIATION
PILOT STUDY LAYOUT
FMC Corporation
Middleport, New York

By: JBS	Date: 11/28/07	Project No. 9936.000
Geomatrix		Figure 3

Plot Date: 11/28/07 - 10:02am, Plotted by: jspink
Drawing Path: N:\9000s\009936\acad\, Drawing Name: phyto_layout.dwg

APPENDIX A

Relevant Papers on Arsenic in the Environment