



General Assistance Program (GAP) Pollution Inventory and Action Plan for Manistee Lake

Prepared for:

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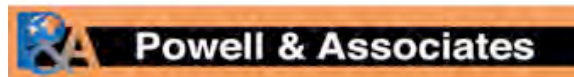


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Executive Summary

This report was developed as a deliverable to the Little River Band of Ottawa Indians under their USEPA General Assistance Program (GAP) grant (Grant #GA97546201-0). It provides a brief description of Manistee Lake within its watershed and a discussion of its background with respect to pollution. The history of Manistee Lake includes more than a century and a half of industrial usage. Contamination of the lake bottom sediments is extensive and profound. This has resulted in the near elimination of the natural populations of sediment-dwelling benthic organisms, creating a negative impact on the lake at all trophic levels. This report contains an inventory of potential pollution sources in the vicinity of Manistee Lake, discusses the lake contaminants and their significance, develops scores for the various industries based on these contaminants, and enumerates a list of issues centered around the pollution of the lake that need to be addressed. It then proceeds to develop an action plan consisting of numerous “action ideas” for addressing the lake issues. One of the most important of these action ideas is to further sample the lake to increase understanding of the severity of the problems, their sources, and the potential for remediation. A sampling plan is described that includes sampling lake waters, sediments and the shoreline. A somewhat novel geometrical approach to sampling the lake is proposed along with data analysis methods that should provide excellent comprehension of the results and any trends contained therein. Contaminant management approaches are then addressed with observations and suggestions.

Sixteen specific industries and two generic pollutant sources (coal storage piles and brine leakage) are listed and discussed in the potential pollution source inventory. Industrial contaminant information was obtained from several sources including the USEPA’s a) Toxic Release Inventory, b) Superfund/National Priorities List, c) Archived Superfund Sites, d) National Pollutant Discharge Elimination System, and e) the Michigan 201 list. A table summarizes important information about the contaminants at these facilities, the information sources, and the facility locations. Additional information about these facilities is provided in the form of text, tables, graphs, maps, photos and Internet URLs. To create industry rankings, the coal storage piles category was rolled into the specific industrial facilities that maintain and burn the coal and the facilities were ranked on the basis of their potential for generating the contaminants that had been found to be most significant during a stepwise regression analysis of contaminants versus toxicity to organisms. These significant contaminants were As, Cr, hexane extractables, PAH, Hg, and Se. Using a box and whiskers statistical plot three of the facilities plotted in a high group relative to the others, on the whisker. These were Packaging Corporation of America, Martin Marietta and Morton Salt. General Chemical was also high, plotting on the top hinge of the box. These are all facilities that store and/or burn coal in addition to their other processes.

A list of Manistee Lake issues that need to be addressed is presented in the graphical context of a mind map. These 15 issues are organized into five “Core Issues” categories, including 1) Current Contaminant Issues, 2) Reporting Issues, 3) Community Issues, 4) Mitigation Issues and 5) Future Contaminant Issues. Brainstorming was done to find possible solutions to these issues, resulting in at least 20 “Action Ideas” that were



incorporated into these same categories but as “ideas” rather than “issues,” creating an action plan.

Further sampling of Manistee Lake is a critical part of the action plan. Emphasis is placed on clear delineation of and agreement upon the sampling goals, with the agreement to be incorporated into formal data quality objectives and a quality assurance project plan. Ten objectives for the sampling of Manistee Lake are provided that would increase understanding of the contamination in and around the lake and of the transport, fate and risk of the contaminants. Plotted data, correlating the most significant contaminants versus toxicity versus sampling location, show peaks of both contamination and toxicity at sampling locations immediately in the vicinity of coal storage piles. The proposed locations for further sampling of Manistee Lake provide some focus in these areas and near the presumed infiltration zone of the PCA plume (from the PCA Superfund site lagoons) while providing broad coverage of the entire lake. Sampling within the lake is proposed for 27 new locations, including both sediments and the water above the sediments. Sampling locations were established in a manner that creates 12 linear transects (vectors) across the surface of the lake to allow multiple strategies for analyzing the resultant data. These strategies include evaluating the relationships between concentrations at sequential sampling points, exploratory data analysis, geochemical speciation modeling, an analogy to pseudo-1st order kinetics for concentration changes over time/distance, concentration integration within triangular grids, and the development of the geochemical portion of a conceptual model of Manistee Lake. Sampling of the vadose zone and groundwater along and around the shoreline is also recommended in the vicinities of the coal piles and in several other locations.

The phases to be sampled should include lake sediments, interstitial waters from the lake sediments, the overlying lake water column, and vadose zone and groundwater samples from the shoreline. These samples can be collected using VibraCore and Geoprobe direct push technologies. A list of analytes is proposed that corresponds with a previous study (Rediske et al., 2001), including the toxicity studies and organism counts, but adding tannins and lignins to the analyte list as well as emphasizing the need for analyzing geochemical indicator parameters such as pH, Eh, DO, sulfate, etc. These indicator parameters yield important information about the toxicity, bioavailability, transport and fate of the contaminants. The speciation of two of the important Manistee Lake contaminants, chromium and arsenic, is discussed and displayed to illustrate this point. A table of necessary geochemical indicator parameters is provided.

Currently there is no definitive evidence tying the various contaminants in Manistee Lake to specific sources, but prudent management of ongoing industrial practices could serve to reduce contaminant risk and potentially create a positive impact on the lake. Better management and maintenance of the existing coal storage piles is needed, including building dikes and using liners. Unused coal piles, such as the one at General Chemical, should be removed. Dredging of coal materials already in the lake should be considered but several issues are listed that should be addressed. Known contaminant plumes, such as the plume from the PCA lagoon Superfund site (as well as any discovered during sampling investigations) should be re-evaluated for assessing continuing contaminant



loading of the lake. Remediation solutions such as pump and treat or, preferably, permeable reactive barriers in the subsurface should be considered for plume mitigation. Work to locate and cap/plug all extant abandoned brine wells and piping should be continued and surface salt impoundments should be evaluated and eliminated when possible. Brine industries should be encouraged to maintain and update their equipment as well as maintain records of the disposition of brine that has been extracted from the subsurface.

Many of the inventoried industries around Manistee Lake release contaminants to the air. The coal-burning industries alone along Manistee Lake have had at least 4,315,719 lbs of air releases during the period 1987-2002. This is an average of 269,732 lbs per year. The value is actually probably higher because the Toxics Release Inventory reports seem to be missing data for periods of time and for certain constituents during the periods that are reported for some of the industries. Complete and accurate reporting to the TRI is an area that clearly needs improvement. Because of the current level of air pollution, air pollution impacts on the lake, and current coal contamination of the lake from storage piles it is recommended that no additional coal-burning industries be located in this area until further study and air quality monitoring can be done and reporting improvements implemented. Industries that are currently operating in the area should be encouraged to upgrade their processes, preferably to maximum achievable control technology levels.



Part 1: Watershed and Manistee Lake Information

Manistee Lake is in the Manistee watershed, USGS Cataloging Unit 04060103. Twelve counties are involved in this watershed include Antrim, Benzie, Crawford, Grand Traverse, Kalkaska, Lake, Manistee, Mason, Missaukee, Osceola, Otsego and Wexford. Figure 1 shows an overview of the watersheds of Michigan (Schaetzl, 2004), with the Manistee Watershed located in the northwest quadrant of the Lower Peninsula.



Figure 1 Michigan Watersheds (from Schaetzl, 2004)



The Manistee Watershed covers an area of more than 5000 km², 1930 mi² or 1, 240,000 acres (University of Michigan, 2002). From the Wexford County Plan Fact Book, Surface Water (Wexford County, MI, 2004):

“The Manistee River watershed can be further divided into 60 smaller drainage areas. Among them, some of the major ones include: Pine River, (including Poplar Creek and North Branch Pine River/Fairchild/Spalding Creeks), Slagle Creek, Fletcher Creek, Wheeler Creek (Lake Gitchegumee), Anderson Creek, Silver Creek, Manton Creek, and Fife Lake Outlet. Also there is a large number of named and unnamed feeder creeks to the Big Manistee River in the north central part of Wexford County representing artesian flows from groundwater moving north from the glacial hills toward the river.”

Manistee Lake (Figure 2a) is a drowned river mouth that is fed by the Manistee River from the northeast and the Little Manistee River from the southeast. A channel connects the northwest portion of Manistee Lake to Lake Michigan. Lake flow is generally from the southeast to the northwest (from the Little Manistee up the length of the lake) with crossflow across the northern portion of the lake from the Manistee River west to the Lake Michigan channel. Table 1 provides real-time flow information from three gauging stations along the Manistee River on 07/31/2004 to illustrate the volume of water moving through the northern portion of Lake Manistee from this source. Gauging information was not available for the Little Manistee River in the south. Manistee Lake has an area of about 930 acres², a maximum depth of about 50 feet and is at latitude 44.23310° and longitude -86.29970°. Figure 2b uses a combined topographic map and aerial photo to provide a closer view of the lake in relationship to surrounding communities.

Table 1 USGS Location 04124000 Manistee River Near Sherman MI, Daily Mean Flow Statistics for 7/31/2004 Based on 83 Years of Record in ft³/sec

USGS Location	Current Flow	Minimum	Mean	Maximum	80%*	50%*	20%*
04124000 Sherman, MI	821	695	899	1730	799	890	985
04124200 Mesick, MI	1020	867	948	1130	886	913	1052
04125550 Wellston, MI	1430	1190	1350	1550	1220	1350	1508

*Percent exceedance means that 80, 50, or 20 percent of all daily mean flows for 7/31 have been greater than the value shown.

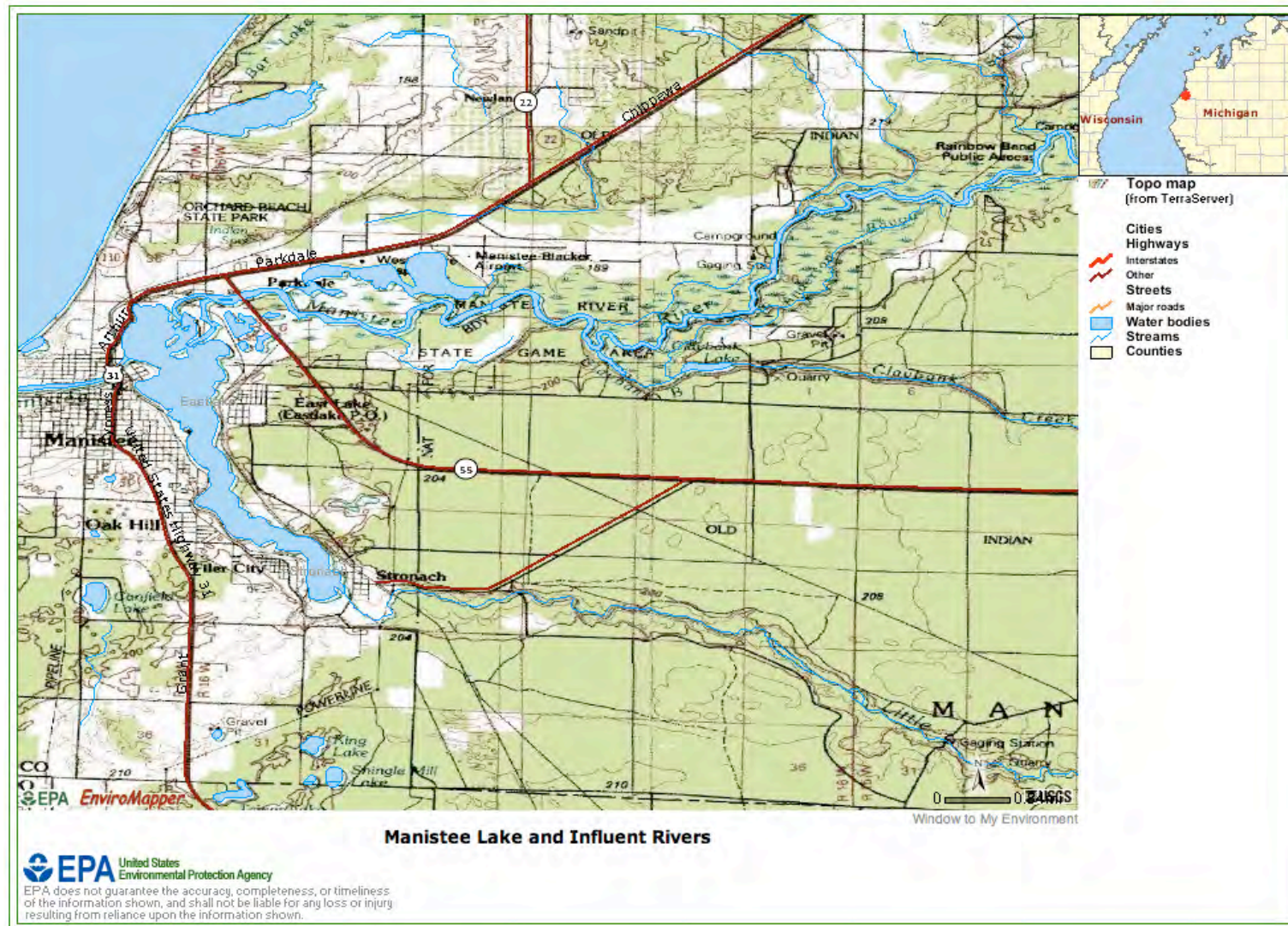


Figure 2a Manistee Lake and Environs

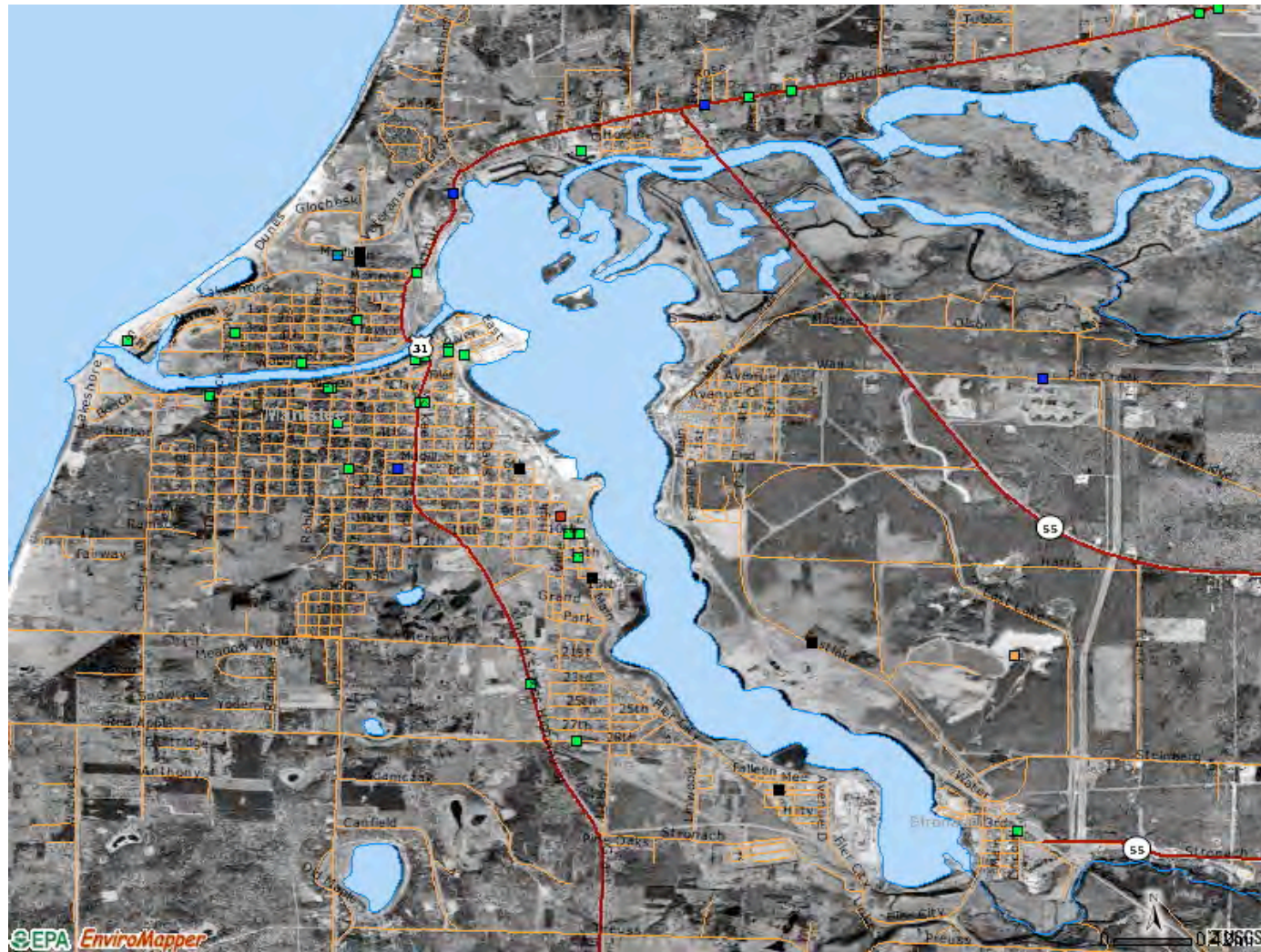


Figure 2b Manistee Lake and Surrounding Communities



Part 2: Historical Manistee Lake Pollution Sources

The rivers feeding Manistee Lake are largely uncontaminated relative to the lake, which itself has a long industrial history dating from the mid-1800s. The earliest industries in the area for which there are any records appear to be the timber/lumber, fishing, fur trade/tanning industries, with the American Fur Company Post established in downtown Manistee in the 1820s (<http://www.manisteedowntown.com/>). During this time downtown Manistee was also an extremely busy fishing port on Lake Michigan. The year 1841 saw the first permanent settlement of Manistee County; the first timber mill within the Manistee city limits was established and by 1852 the chief industry was the manufacture of lumber. More than 25 sawmills operated around Manistee in the 1850s, producing more than 300,000,000 board feet of lumber per year. During 1854 Sam Potter developed a deepwater harbor entrance (by ditch excavation, damming of the old channel, and building piers into Lake Michigan). This quickly resulted in Manistee becoming a busy port. In 1879 Charles Reitz and Bros. drilled the first salt well in Manistee. In 1881 a 25-foot thick rock salt stratum was found at 2000-foot depth and the production of salt began. By 1885 forty sawmills existed in the Manistee area.

An abbreviated list of businesses on South River Street in 1882 illustrates the types that might have contributed to pollution in Manistee Lake during this era. Among these were:

- William B. Crippen's foundry and machine shop
- Foundry and machine shop of Wheeler & Johnson
- Union Boiler Works of Andrew Jack
- Paint shop of Sayles & Gregory
- Joiner shop of Green & Long
- Manistee Lime Works, Wing & Buckley.
- Paint shop of Thorp Bros.
- Joiner shop, J. W. Tenant & Co.
- Planing mill, Gee & Preston
- Manistee Steam Boiler Works, Kirsch & Son.

At this time Manistee was the third largest oil-producing area of Michigan and remained a major salt producer. Ships were needed to transport the lumber from Manistee and Manistee became a ship building port. Shipping in the area and on the Great Lakes included timber, coal, limestone, iron ore, cement, salt, grain, sand and other products.

In 1917 the Filer Fiber Company, a pulp mill owned by P.P. Schnorback, began operations on the site of the old Filer and Sons mill and was soon expanded to include the making of paper using the Kraft process. The Continental Can Company acquired the plant, followed by The American Box Company (ABC) in 1947 that merged with Packaging Corporation of America (PCA) in 1959 (Childs, 1970). Wastes were dumped into Manistee Lake until 1951, when ABC laid a pipeline to lagoons north of Stronach to hold and infiltrate the clarifier sludge and condensate from the black-liquor recovery process. These lagoons received from 15 to 60 million gallons/month of discharge. In December 1982 the PCA lagoon site was placed on the National Priorities List (NPL,



Superfund) and a Record of Decision (EPA/ROD/R05-93/236 1993) was issued in 1993. The PCA plant continues to operate using additional waste-stream processes with discharge currently to Lake Michigan.

In 1927 the first chemical brine well was drilled and the Rademaker Chemical Company was formed (Childs, 1970). Magnesium and bromine were extracted from the brine and sold, with the remainder of the salt materials disposed as waste materials, a process that other companies have continued. The salt and chemical brine industry has had a significant impact on Manistee Lake due to the processes and equipment used for brine extraction, storage, system backflushing, and a variety of other operations at these facilities (Childs, 1970). In addition numerous salt and chemical wells were abandoned during the history of these operations, often without plugging, and the location and fate of many of these may be unknown. Because of these problems, Manistee Lake is heavily contaminated with dissolved salts, primarily NaCl but also others.

Coal has long been used to fuel the industrial processes around Manistee Lake, with the eventual addition of a coal fired electrical generation power plant. Several coal storage piles have been and continue to be located along the lake.

Part 3: Recent Manistee Lake Primary Potential Pollution Sources

Potential Pollution Source Summary

Table 2 provides a brief summary of industrial facilities in the area of Manistee Lake with the potential to have an impact on the pollutant loading of its waters and sediments. The table was compiled from several sources, including the USEPA's a) Toxic Release Inventory, b) Superfund/National Priorities List, c) Archived Superfund Sites, d) National Pollutant Discharge Elimination System, and e) the Michigan 201 list. These industries are then each specifically addressed in their own subsection of this report. Several of these facilities store and burn coal onsite. This issue is addressed separately.

Table 2 Potential Recent Pollution Sources for Manistee Lake

Facility Name	Facility Address	Federal Status/ Permits	Potential Contaminants of Concern (COC) and Chemical Releases	Source Longitude	Source Latitude
Axchem Inc.	317 Washington St. Manistee, MI 49660	TRI Reports, RCRA	Acrylamide, formaldehyde, diethylamine, HCl, H ₃ PO ₄ , H ₂ SO ₄ , NaOH	-86.323421	44.256987
Fablite Inc.	330 Washington St. Manistee, MI 49660	TRI Reports, RCRA	Toluene	-86.323408	44.257191



Facility Name	Facility Address	Federal Status/ Permits	Potential Contaminants of Concern (COC) and Chemical Releases	Source Longitude	Source Latitude
General Chemical (aka, Diamond Crystal Salt Co.Ambar, Akzo, American Salt)	1501 Main St. Manistee, MI 49660	TRI Reports, SF Archived (as Diamond Crystal Salt), NPDES Permit, MI 201, RCRA	Br ₂ , Cl ₂ , Cl ⁻ , Cu, Li, Zn, Oil & Grease, H ₃ PO ₄ , NaOH	-86.305619	44.232268
Harland's Sanitary Landfill	Franklin Rd Sec 29 Stronach, MI 49660	SF Archived, MI 201, RCRA	1,1,1 trichloroethane; benzene, chloroethane	-86.264684	44.191338
Manistee Area School Bus Garage	610 Parkdale US 31 Manistee, MI 49660	SF Archived, RCRA	Gasoline, benzene, other petroleum hydrocarbons	-86.290392	44.269594
Manistee Forge (PCA property)	509 Falleen Rd. Filer City, MI 49634	SF Archived, MI 201 RCRA	Fuel oil		
Manistee Plating Company	261 Sixth Ave. Manistee, MI 49660	SF Archived, MI 201, RCRA	Cu; Pb, CN ⁻ , sludges	-86.327863	44.248816
Manistee Waste Water Treatment Plant (MWWTP)	15 Ninth St. Manistee, MI 49660	NPDES	Water: Fecal coliform, Cu, Hg, N, P. Sludge/Bottom Deposits: As, Se, Cu, Cd, Mo, Zn, Pb, Ni, Hg, Cr	-86.308059	44.23698
Martin Marietta Magnesia Specialties, Inc. (also Martin Marietta Chemical Corp. Plating Site)	1800 East Lake Road Manistee, MI 49660	TRI Reports, SF Archived, NPDES Permit, MI 201, RCRA	Cl ₂ , Cl ⁻ , Li, Sr, HCl, Cr	-86.288861	44.227355
Martin Marietta Linke Rd.	Linke Rd. at Fox Farm Rd. Stronach, MI 49660	SF Archived	Cl ⁻ , Oil		
Morton Salt and Magnesia	180 Sixth St. Manistee, MI 49660	TRI Reports, NPDES Permit, RCRA	Cl ⁻ , Li, Oil & Grease, HCl, Pb, Thermal	-86.31123	44.240701
Morton Thiokol Plant Site	180 Sixth St. Manistee, MI 49660	SF Archived, MI 201	Cl ⁻	Same as Morton Salt	Same as Morton Salt



Facility Name	Facility Address	Federal Status/Permits	Potential Contaminants of Concern (COC) and Chemical Releases	Source Longitude	Source Latitude
Packaging Corporation of America*	2246 Udell St. Filer City, MI	SF ROD Issued (lagoons), TRI Reports, NPDES Permit, RCRA	NH ₃ , Sb, As, Ba, Cd, Cl ⁻ , Cr, Cu, Pb, Mn, Hg, H ₂ SO ₄ , Ni, Na, NO ₃ ⁻ , SO ₄ ²⁻ , V, Zn, trichloroethene, benzoic acid, bis(2-ethylhexyl) phthalate, 2-methylphenol, phenol, anthracene, benzo(a)anthracene, benzo(a)pyrene, chrysene, 2-methylnaphthalene, naphthalene, phenanthrene, acetaldehyde, dioxin, methanol,	-86.273331	44.226389
Rengo Oil Co. Manistee	217 Filer St. & 240 Arthur St. Manistee, MI 49660	SF Archived, MI 201	1,2,4 trimethylbenzene, benzene, ethylbenzene, toluene, xylenes		
Sweetwater Crafts	100 S. Glocheski Dr. Manistee, MI 49660	TRI Reports	Styrene	-86.325062	44.256933
T.E.S. Filer City	700 Mee St. Filer City, MI 49634	TRI Reports	Ba, Cr, Cu, dioxin, HCl, HF, Pb, Mn, Hg, H ₂ SO ₄ , Zn	-86.291389	44.216111

SF = Superfund

ROD = Record of Decision

SF Archived = The Archive designation means that assessment at a site has been completed and EPA has determined no steps will be taken to designate the site as a priority by listing it on the National Priorities List (NPL). No further remedial action is planned for these sites under the Superfund Program.

TRI Reports = Submitted Toxics Release Inventory Reports for at least some years.

MI 201 = Michigan's Part 201 (Environmental Remediation) of the Natural Resources and Environmental Protection Act (1994 PA 451, as amended) applies.

NPDES Permit = National Pollutant Discharge Elimination System Permit (allows discharges to water).

RCRA = Resource Conservation and Recovery Act. Site is indicated "RCRA" if it is listed by the RCRA query for Manistee County Michigan using the USEPA RCRAInfo database.

*PCA latitude and longitude are for the lagoon site rather than the facility.

Axchem Inc.

Table 2 lists several potential COCs for Axchem Inc., an industrial water and wastewater treatment company (<http://www.axchemsolutions.com/>). These COCs are the chemicals listed in the Toxic Release Inventory (TRI, USEPA) for years from 1987 through 2002 (http://oaspub.epa.gov/enviro/tris_web.dcn_details?tris_id=49660XCHMN317WA). The TRI Class Code for this facility is "POTENTIAL UNCONTROLLED EMISSIONS < 100 TONS/YR". Figure 3 shows the location of Axchem, Inc. in relation to Manistee Lake.



AXCHEM INCORPORATED
317 WASHINGTON STREET
MANISTEE MI 49660
Latitude: 44.256987 Longitude: -86.323421

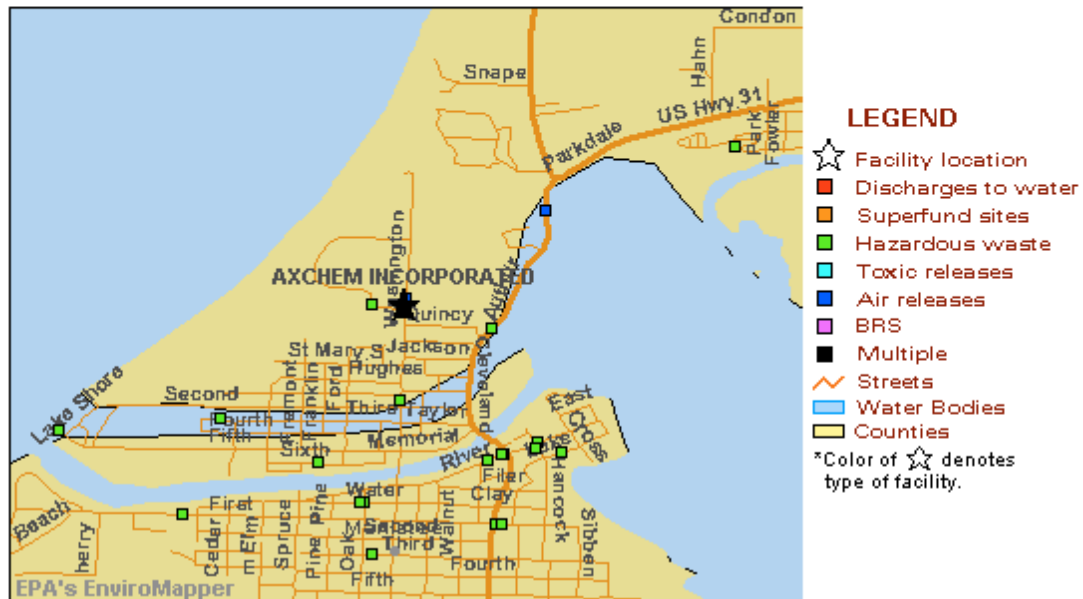
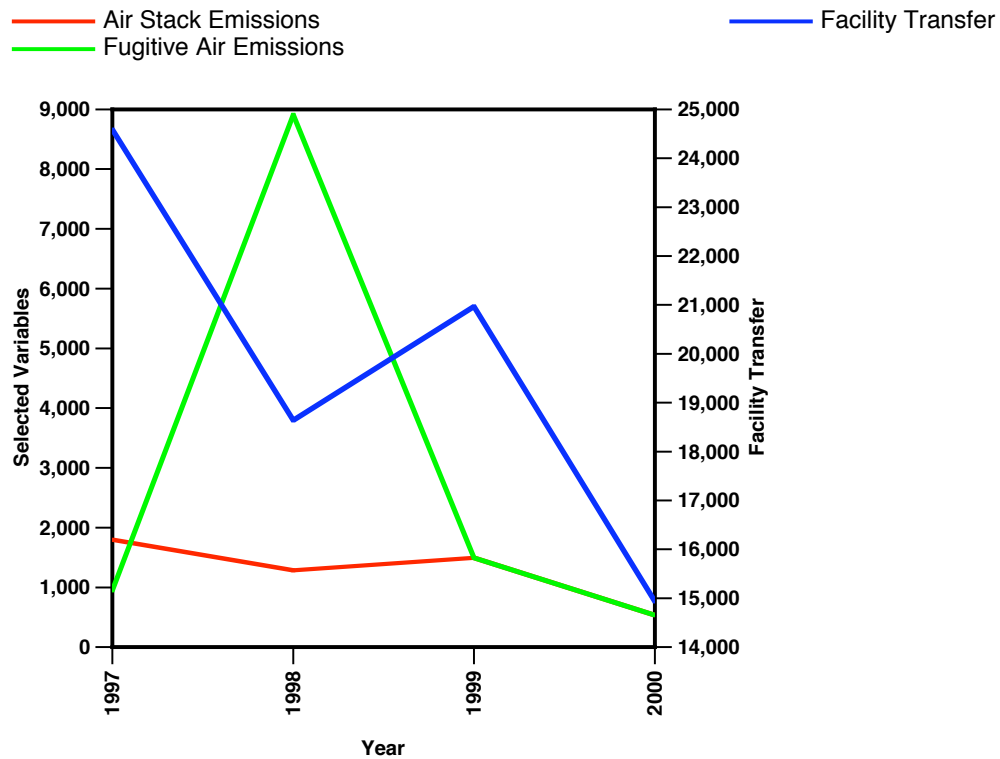


Figure 3 Location of Axchem Incorporated.

Fablite Inc.

Fablite, Inc. is an office furniture manufacturer that has had some air releases of toluene (Table 2). Figure 4 illustrates those releases over a four-year period. A decreasing trend in emissions/transfer of toluene seems to be occurring and the facility projected the years 2001 and 2002 to have 100 lbs or less of toluene to be transferred for recycling. Data is currently not available from USEPA for those years. Figure 5 indicates the location of Fablite Inc.



All values in lbs.

Figure 4 Toluene Air Emissions and Transfers for Fablite Inc.



FABLITE INCORPORATED
330 WASHINGTON ST.
MANISTEE MI 49660
Latitude: 44.257191 Longitude: -86.323408



Figure 5 Location of Fablite Inc.

General Chemical (Diamond Crystal, Ambar, Akzo, American Salt)

General Chemical at Manistee Michigan has had a number of previous names, including Diamond Crystal Salt Co., Ambar, Akzo, and American Salt. Tondur Corporation recently proposed this location for a coal-fired electric power generating utility, the Northern Lights Power Project (NLPP), but Tondur was unable to get approval for a Special Use Permit from the City of Manistee.

In 1999, Ambar Inc. opened a 14-Mkg (30-million-pound) elemental bromine (Br_2) facility at this site and also produced brominated salts. This was the first new elemental bromine plant constructed since the mid-1970's when two plants began producing elemental bromine. Ambar was supplied by pipeline with bromine-containing brines following magnesium hydroxide production at Martin Marietta Magnesia Specialties Inc. The plant opened, operated, and closed in 1999 (USGS, 1999).

The General Chemical Manistee plant is currently a calcium chloride production facility. It is one of two General Chemical calcium chloride facilities

(http://www.samicorp.com/AboutSAMIPages/ProjectPages/PH_GeneralChem.html) and



has a capacity of about 360,000 short tons of CaCl_2 per year. The General Chemical operation was reportedly permanently discontinued in December 2002 (http://www.findarticles.com/p/articles/mi_m0FVP/is_8_263/ai_98184428) but industrial activity, including drilling during early 2004, has been observed at the site (personal observation).

The industry at this location is listed on the TRI, is an archived Superfund site (as Diamond Crystal; qualified as No Further Remedial Action Planned and archived in March, 1987), has a National Pollutant Discharge Elimination System Permit (NPDES, allowing discharges to water) and Michigan's Part 201 (Environmental Remediation) of the Natural Resources and Environmental Protection Act (1994 PA 451, as amended) applies to the site (MI 201). Table 2 lists several potential contaminants of concern for impacts on Manistee Lake. In addition, General Chemical operated two coal-fired boilers at this location and large piles of coal are present along the shoreline that have contaminated the lake through water erosion and blowing coal dust. Other than 10 lbs of air emissions in 1998 (5 lbs Cl_2 and 5 lbs Br_2) the TRI has no information for General Chemical. Figure 6 shows the location of the site.

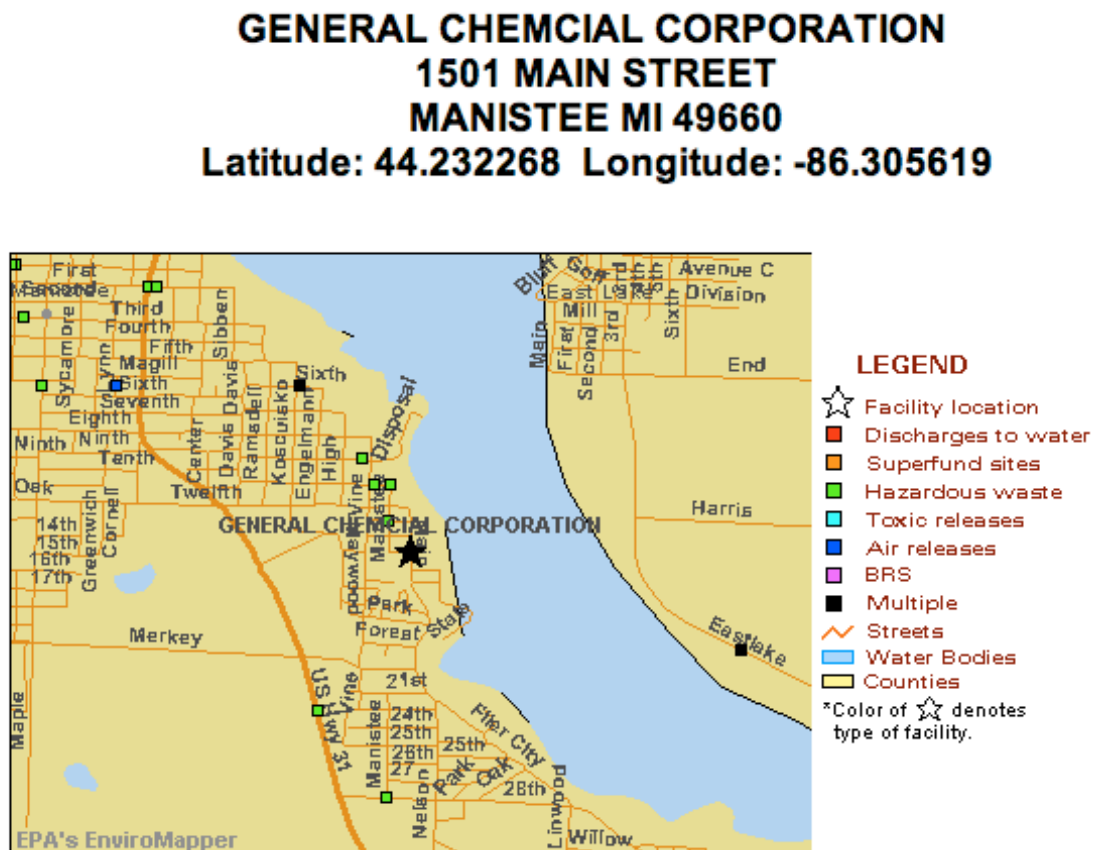


Figure 6 Location of General Chemical Corporation (Note: name misspelled on USEPA map)



Harland's Sanitary Landfill

This site is currently operated by Shoreline Waste Services. Table 2 shows that 1,1,1 trichloroethane; benzene, and chloroethane have been contaminants of concern at this site, it is an archived Superfund site and MI 201 rules apply, but little other information was found for the Harland Landfill. Figure 7 shows the location of the site.

HARLANDS SANITARY LANDFILL INCORPORATED
3890 CAMP RD
MANISTEE MI 49660
Latitude: 44.191338 Longitude: -86.264684

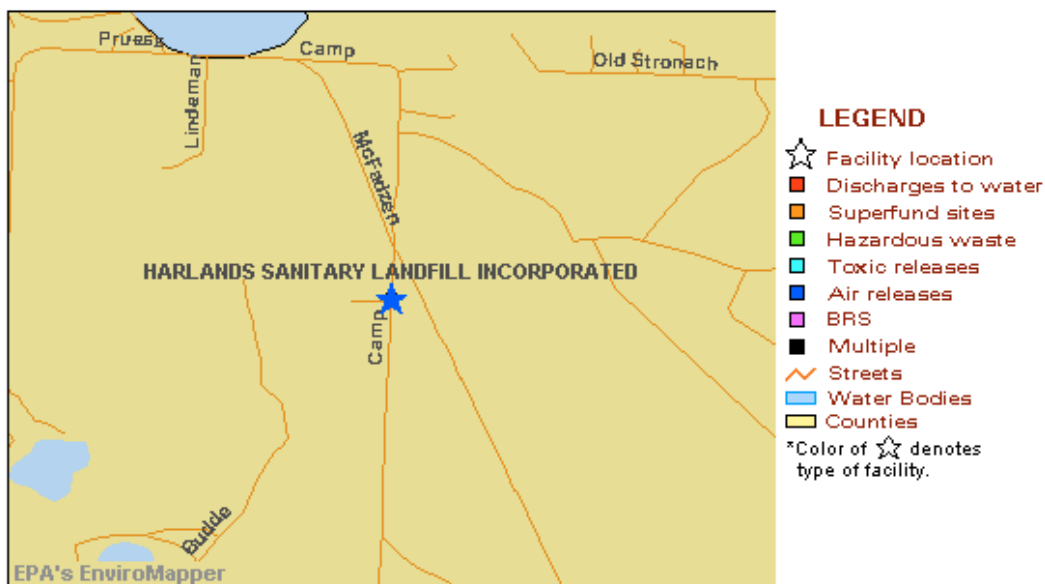


Figure 7 Location of Harland's Sanitary Landfill

Manistee Area School Bus Garage

Gasoline, benzene, other petroleum hydrocarbons were contaminants associated with the Manistee Area School Bus Garage and Table 2 shows that this location is also an archived Superfund site. The site is associated with the Michigan Department of Transportation and is located north of the Manistee River and northeast of Manistee Lake, as shown in Figure 8.



MI DEPT/TRANSPORTATION
610 E PARKDALE AVE
MANISTEE MI 49660
Latitude: 44.269594 Longitude: -86.290392

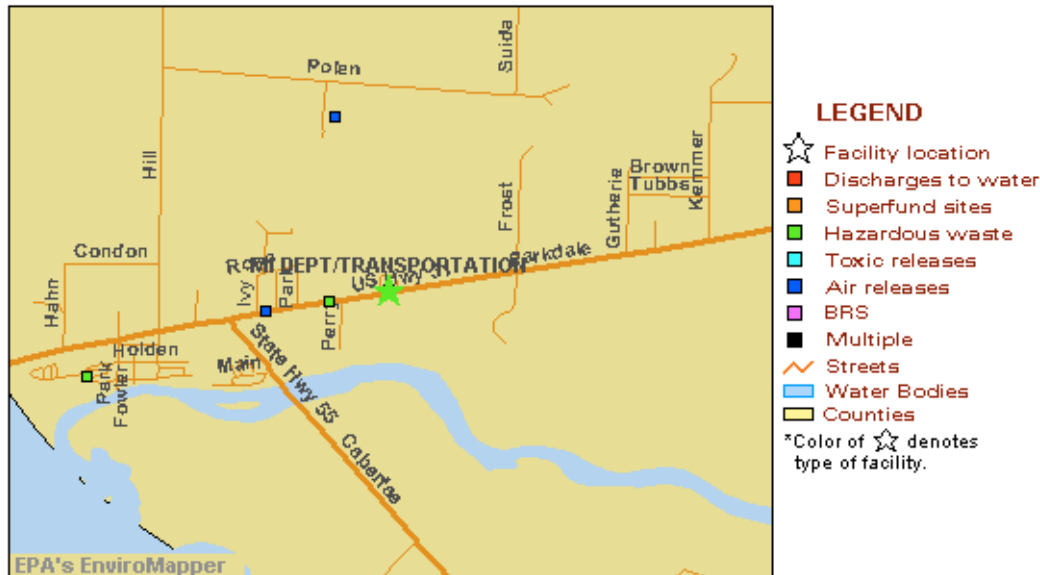


Figure 8 Location of the Manistee Area School Bus Garage

Manistee Drop Forge (PCA Property)

This site is also known as the Manistee Corp. Corge Forge Corp (SIA) (from USEPA Superfund Information Systems, Archived Sites). No useful information was found for this site online after extensive searching, other than its contaminant of concern being fuel oil, its status as MI 201 and that it is an archived Superfund site, archived on 3/26/85.

Manistee Plating Company

Manistee Plating Company used a plating process for brass and steel that incorporated copper, nickel, cyanide, and chromium and operated from 1945 to 1955. Primary concerns at this site included cyanide, heavy metals, and other liquids and soil contamination existed. Remedial actions were begun on 07/16/1993 and were completed on 11/24/1993 (original information from USEPA per <http://www.rivermedia.com/consulting/er/hazsubs/sitelib/56ae.htm>). Contaminated soil was excavated under a Superfund Emergency Response and a monitoring system was installed, at a cost of about \$450,000.00. (<http://www.epa.gov/superfund/sites/siteinfo.htm>).

Manistee Plating is currently an archived Superfund Site, a RCRA site and is subject to MI 201. Figure 9 shows the location of Manistee Plating Company.



MANISTEE PLATING CO
261 6TH AVE
MANISTEE MI 49660
Latitude: 44.248816 Longitude: -86.327863

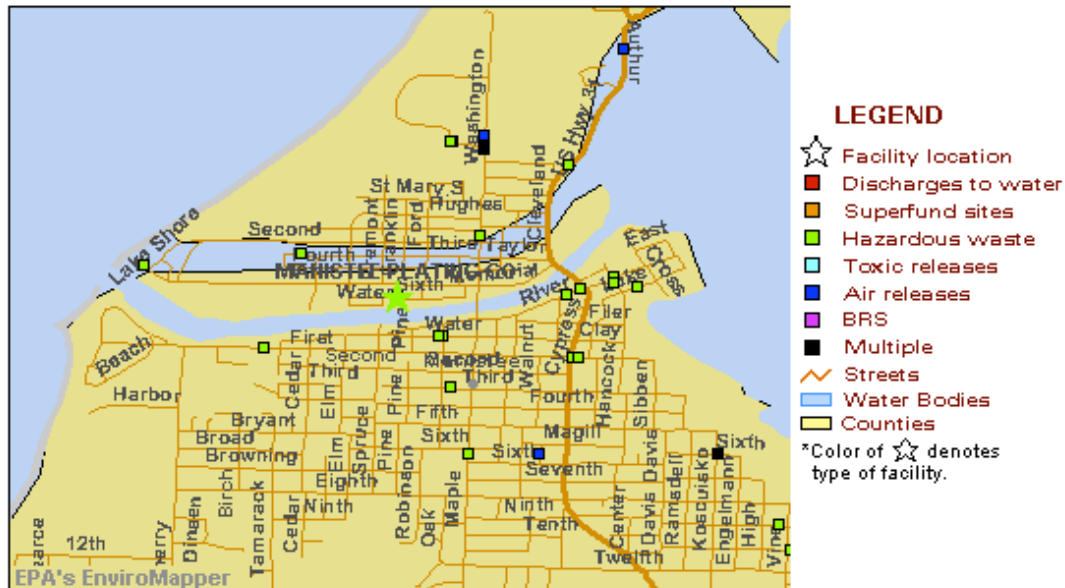


Figure 9 Location of the Manistee Plating Company

Manistee Waste Water Treatment Plant

The Manistee Waste Water Treatment Plant (MWWTP) operates the sewerage system and outfalls for Manistee. Nineteen outfall pipes are listed in the NPDES for the MWWTP, with only one outfall listed as “active” and 18 listed as “inactive.”

MWWTP currently treats approximately 350 million gallons of wastewater per year via a secondary treatment system that uses UV disinfection rather than chlorination and follows various protocols for additional environmental protection, including a Mercury Minimization Program, an Industrial Pretreatment Program, and a Program for Effective Residuals Management. More than 1,200,000 gallons/year of biosolids are generated and the Effective Residuals Management program promotes their beneficial reuse (City of Manistee, <http://www.ci.manistee.mi.us/CityWasteWater.html>). In March 2004 voters rejected a proposed expansion of the MWWTP, which would have increased capacity from approximately 1 million gallons/day to 2 million gallons/day. Increased capacity would probably be needed to support further industrial growth around Manistee Lake. Figure 10 depicts the location of the MWWTP.



MANISTEE WWTP
15 NINTH ST
MANISTEE MI 49660
Latitude: 44.23698 Longitude: -86.308059

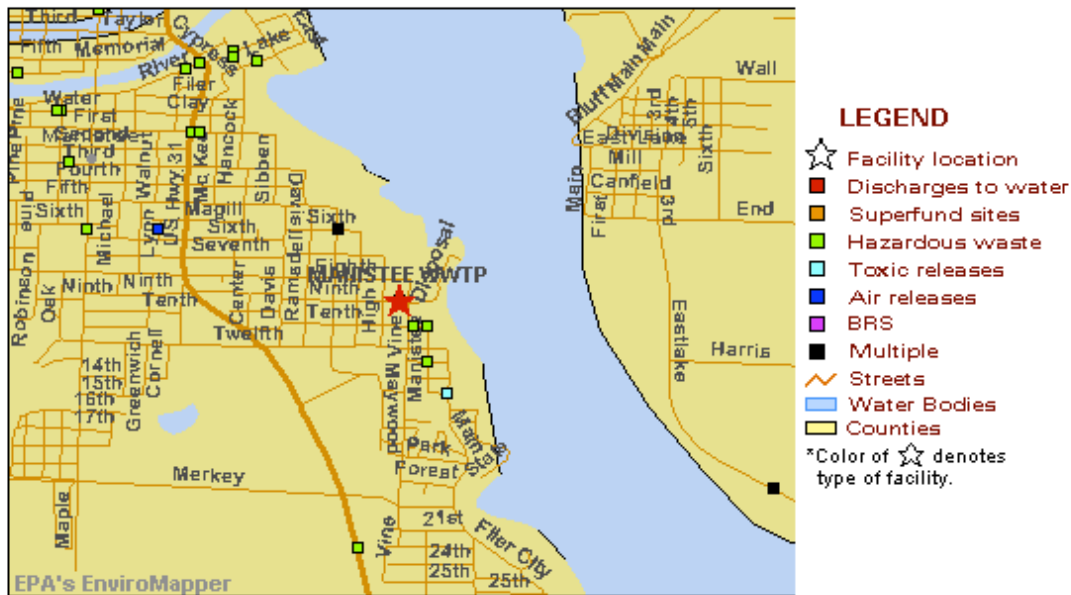


Figure 10 Location of the Manistee Waste Water Treatment Plant

Martin Marietta Magnesia Specialties, Inc./Martin Marietta Chemical Corp. Plating Site

Martin Marietta once operated Martin Marietta Chemical Corporation (MMCC) at the site of the current Martin Marietta Magnesia Specialties, Inc (MMMS), shown in Figure 11. The MMCC included a plating operation. Information on this plating operation is difficult to locate but would be desirable for understanding potential impacts to the lake.

The current operation at the site involves the processing of chemical brine to obtain magnesium chloride ($MgCl_2$). The $MgCl_2$ is converted to magnesium oxide (MgO) and sold for a wide variety of manufacturing, agricultural, water treatment and industrial processes. Bromine resulting from this process was previously piped to Ambar Chemical (currently General Chemical) for the production of elemental bromine and brominated salts.



MARTIN MARIETTA MAGNESIA SPECIALITES INCORPORATED
1800 EAST LAKE ROAD
MANISTEE MI 49660
Latitude: 44.227355 Longitude: -86.288861

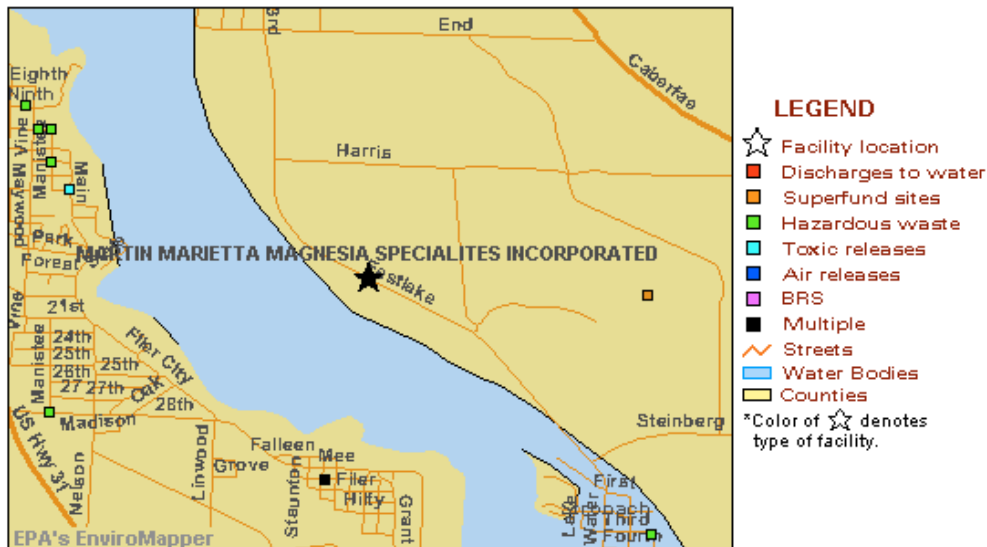


Figure 11 Location of Martin Marietta Magnesia Specialties

The Toxics Release Inventory data (Figure 12) from USEPA for the Martin Marietta facility show measurable quantities of chemical materials released to the air, no releases to water, and significant amounts transferred to off-site disposal or disposal by on-site injection during the period from 1987 through 1995. There is no information available in the TRI after 1995.

On-site underground injection was by far the most used method for disposing of waste materials from the Martin Marietta processes. Underground injection encompassed a range from 97.1% of the waste in 1990 to 99.97% in 1988. Therefore, based on Martin Marietta measurements/estimates, from 1987 to 1995 only about 0.03 to 3% of the waste stream was released to the air or moved to off-site disposal. No public records appear to be available for 1996 through 2004. Among the materials released to the air via point source or “stack” emissions were one lb of chromium in 1987 and two lbs of chromium in 1988. Although the author is uncertain of the dates of the Martin Marietta plating operations, it is possible that these releases were related to that operation. If so, it is somewhat surprising that no releases or spills of chromium to water or land surfaces are reported during that time because this has been a common problem with chrome plating sites around the nation. The remaining air emissions during the period 1987 to 1995 were reported to be hydrochloric acid, with 684 lbs of these being stack emissions and 96 lbs of “fugitive” emissions, for a total of 780 lbs of HCl released to the atmosphere.

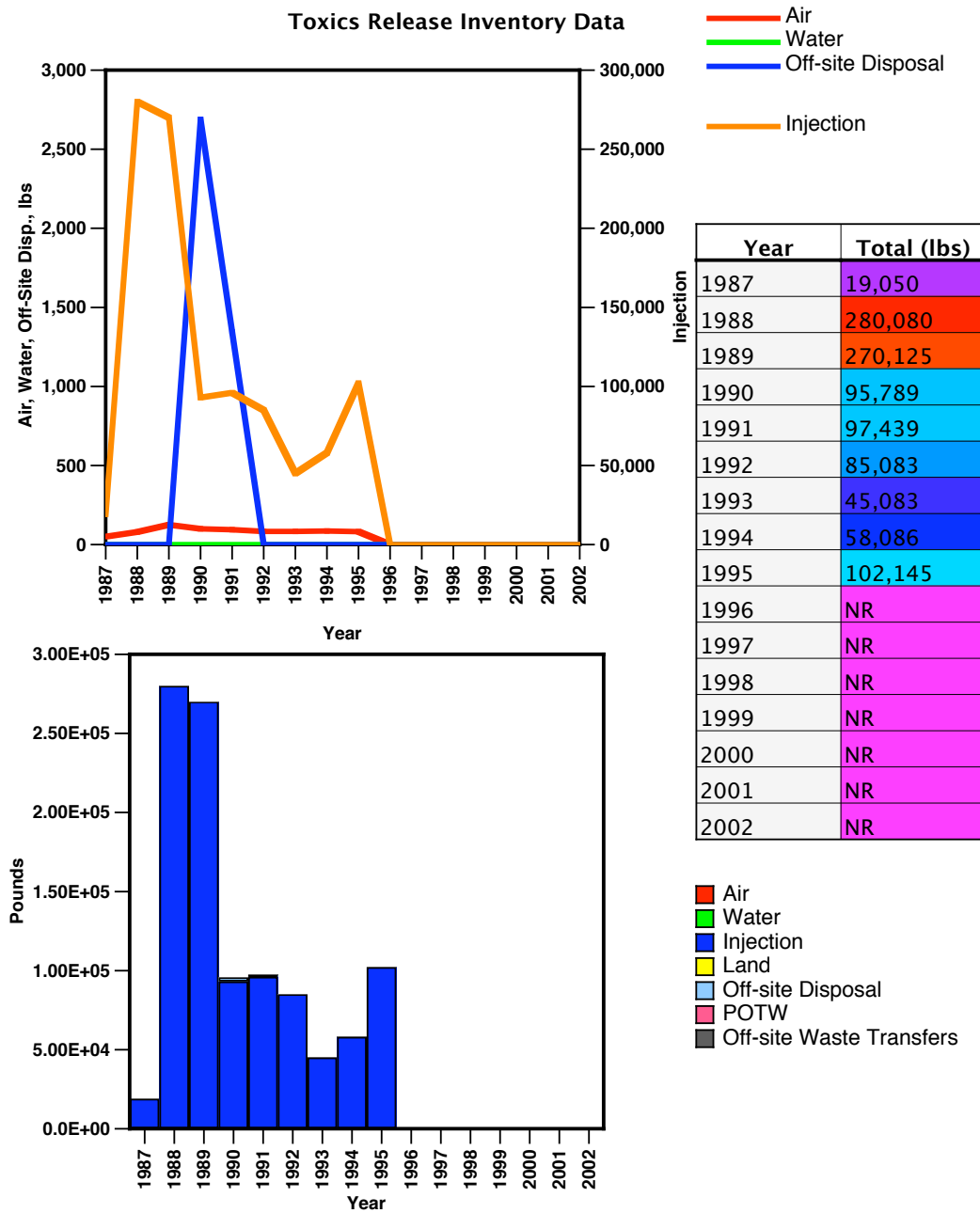


Figure 12 Toxic Release Inventory Data for Martin Marietta Magnesia Specialties

The current NPDES permit for MMMS lists three outfalls/pipes. Table 3 provides the monitored parameters for each of the outfall pipes.



Table 3 Measured Pipe Outfall Parameters per NPDES Permit for Martin Marietta Magnesia Specialties

Pipe Number	Measured Parameters
001	Temperature, pH, Flow, Chlorine (total residual), Chlorination Duration, Visual Outfall Observation.
002	Temperature, pH, Flow, Chlorine (total residual), Chlorination Duration, Visual Outfall Observation.
003	pH, Total Suspended Solids, Cl ⁻ , Sr, Li, Flow, Chlorine (total residual), Toxicity, Total Dissolved Solids, Chlorination Duration, Outfall Observation.

For the period 30 June 2001 through 29 February 2004, with monthly monitoring, discharge violations occasionally occurred due to high pH values and suspended solids content.

The Martin Marietta site is subject to the MI201 legislation.

Martin Marietta Linke Rd.

No information is available for this site other than being archived Superfund and that the contaminants were chloride and oil (Table 2). This site is possibly associated with a feeder wellhead that pumped the chemical brine to the Martin Marietta facility.

Morton Salt and Magnesia

In 1999 Rohm and Haas Company purchased Morton International, Inc. and now owns Morton Salt and Magnesia, which manufactures granulated and compressed salt products from brine at the Manistee location (Figure 13). In 1994 Morton had the capacity to produce 10,000 metric tons (as MgO) of magnesium carbonate, magnesium hydroxide, and caustic-calcined magnesia (USGS, 1994) and this capacity remained the same in 1999 (USGS, 1999b).

The Toxic Release Inventory data (Figure 14) shows a major increase in air emissions that corresponds with the time period subsequent to the purchase by Rohm and Haas. The author has no knowledge of whether there were production increases, whether new management changed the processes thereby increasing emissions, whether TRI reports simply became more accurate (there are no reports for the period 1995 through 2000) or if there is no causal relationship between the two events.



MORTON INTERNATIONAL INCORPORATED
180 SIXTH STREET
MANISTEE MI 49660
Latitude: 44.240701 Longitude: -86.31123

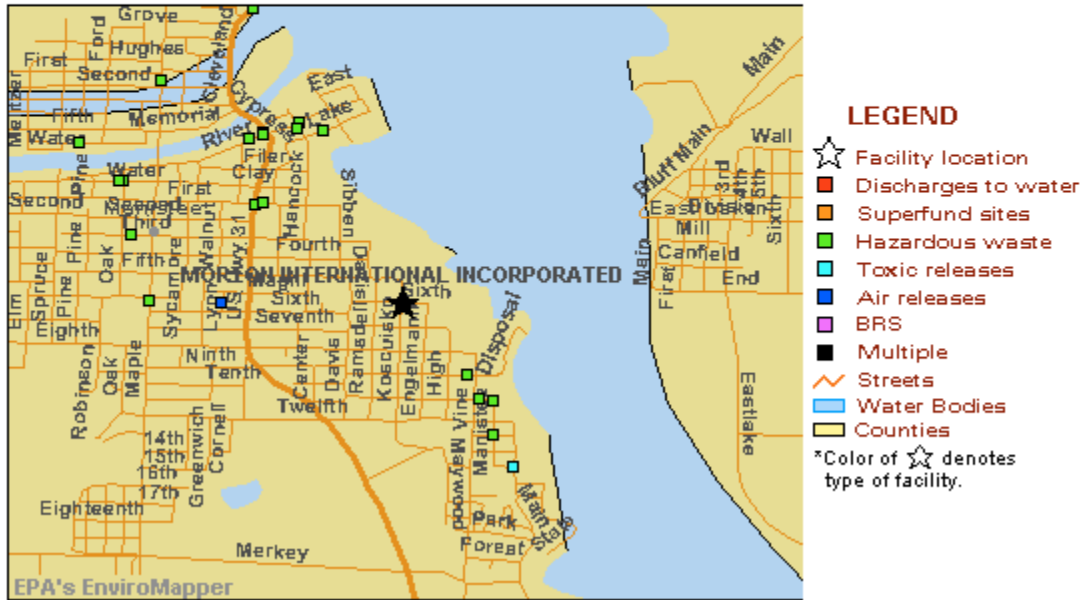


Figure 13 Location of Morton Salt and Magnesia

Table 4 provides additional detail about the emissions from Morton Salt and Magnesia that occurred in 2001 and 2002 and shows that large quantities (from a health-based perspective) of Pb were released during both years. These lead emissions have caused Scorecard.org (<http://www.scorecard.org>) to give the Morton Salt facility their highest possible non-cancer risk score of 90 to 100% and a cancer risk score of 70 to 80% for the year 2001, even though in total environmental releases they score the facility from 10 to 20%. Figure 15, from scorecard.org, illustrates their scoring of this facility.

Table 4 Reported TRI Emissions from Morton Salt and Magnesia for 2001 and 2002

Year	Pb, lbs (Stack Emission)	Pb, lbs (On-site landfill)	HCl, lbs (Stack Emission)
2001	492.7	94	Not Reported
2002	540.8	60.1	49236
Two Year Total	1033.5	154.1	49236

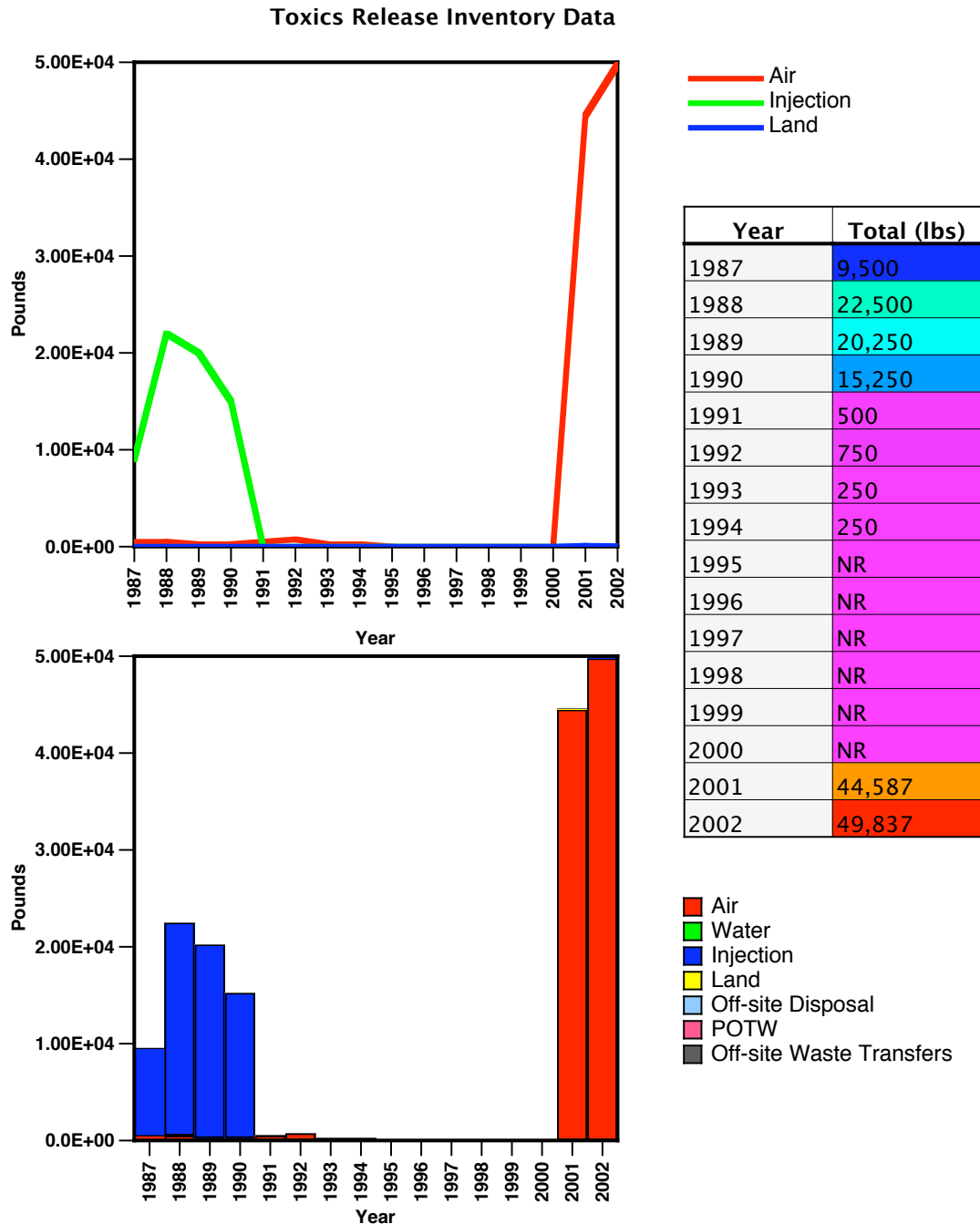
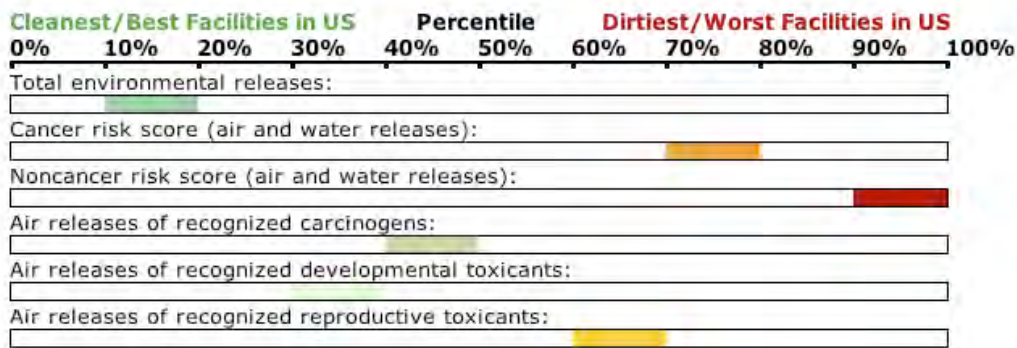


Figure 14 Toxic Release Inventory Data for Morton Salt and Magnesia

**2001 Rankings: Major Chemical Releases or Waste Generation at This Facility*****Figure 15 Scorecard.org 2001 Rankings for Morton Salt and Magnesia**

The NPDES permit for Morton Salt lists 6 pipe outfalls, 4 active and 2 inactive. Table 5 lists the monitored parameters for each of these active pipes. For the period Feb 2001 through April 2004 the only noted numeric violation was for total dissolved solids in Dec 2003.

Table 5 Measured Pipe Outfall Parameters per NPDES Permit for Morton Salt and Magnesia

Pipe Number	Measured Parameters
003A	Temperature, Thermal Discharge, Dissolved Oxygen, pH, Total Suspended Solids, Chloride, Lithium, Oil and Grease, Flow, Total Dissolved Solids, Visual Outfall Observation.
003B	Temperature, Thermal Discharge, Total Suspended Solids, Chloride, Flow, Total Dissolved Solids.
005	Temperature, Thermal Discharge, Dissolved Oxygen, pH, Total Suspended Solids, Chloride, Lithium, Oil and Grease, Flow, Total Dissolved Solids, Visual Outfall Observation.
006	Temperature, Thermal Discharge, Flow, Visual Outfall Observation.

Morton Thiokol Plant Site

Morton Thiokol was the former owner/name of the Morton Salt and Magnesia plant that is now owned by Rohm and Haas.

Packaging Corporation of America

The Packaging Corporation of America produces corrugated packaging (cardboard products) as their only line of business. PCA owns about 70 corrugated product plants, four mills, and three sawmills (<http://www.hoovers.com/>). It employs approximately



7900 people and had sales of \$1,735,000,000 in 2003. The Filer City location (Figure 16, approximate center of picture) on Manistee Lake is one of four PCA ISO 9002 certified paper mills that combined produce more than “2.2 million tons of linerboard and medium...” The Filer City mill produces about 280,000 tons of “semi-chemical” corrugating medium annually, using about 100,000 tons of old corrugated containers per year during production (<http://www.packagingcorp.com/>).



Figure 16 Aerial Photograph of PCA Industrial Facility, Filer City MI

PCA and its predecessor (American Box Board Company) operated a Kraft paper mill neutral sulfite semi-chemical process at the site. The Encyclopaedia Britannica Online (<http://www.britannica.com/ebc/article?eu=394732>) gives a good brief description of the Kraft process, as follows:

*Chemical method for producing wood pulp using caustic soda and sodium sulfide as the liquor in which the pulpwood is cooked to loosen the fibres. The process (from German **kraft**, “strong”) produces particularly strong and durable paper; another advantage is its capability of digesting pine chips; resins dissolve in the alkaline liquor and are recovered as tall oil, a valuable by-product. Recovery of sodium compounds is important in the economy of the process. In modern kraft mills, operations are completely contained; waste streams are recycled and reused, eliminating water pollution.*



The Encyclopaedia refers to “modern kraft mills” in which “operations are completely contained” and water pollution is eliminated. This was not and still is not fully the case at the PCA facility, which continues to discharge highly colored waters via a pipeline into Lake Michigan. The Kraft process used at PCA resulted in the generation of large quantities of waste liquid referred to as “black liquor” or spent cooking liquor. This material consists largely of dissolved lignin degradation products along with degradation products of hemicellulosic and cellulosic hexose and pentose sugars (<http://calvin.biotech.wisc.edu/jeffries/bioprocessing/pulping.html>). These liquors can also contain high levels of inorganic salts and trace metals.

a) PCA Lagoon Site and Historical Operations

As shown in Table 2, there are numerous concerns and potential concerns with contamination from the PCA operation. PCA is the only industry on Manistee Lake to have achieved full Superfund status with a remedial investigation (RI) and the issuance of a Record of Decision (ROD) for one of its locations (USEPA, 1993). This was not, however for the industrial location itself (Figure 16) but for spent Kraft liquor discharge lagoons on the opposite shore of Lake Manistee (Figures 17, 18 and 19).

Filer City, Michigan, United States 31 Mar 1999



Image courtesy of the U.S. Geological Survey

Figure 17 Aerial Photograph of the PCA Discharge Lagoons (USGS, 1999)

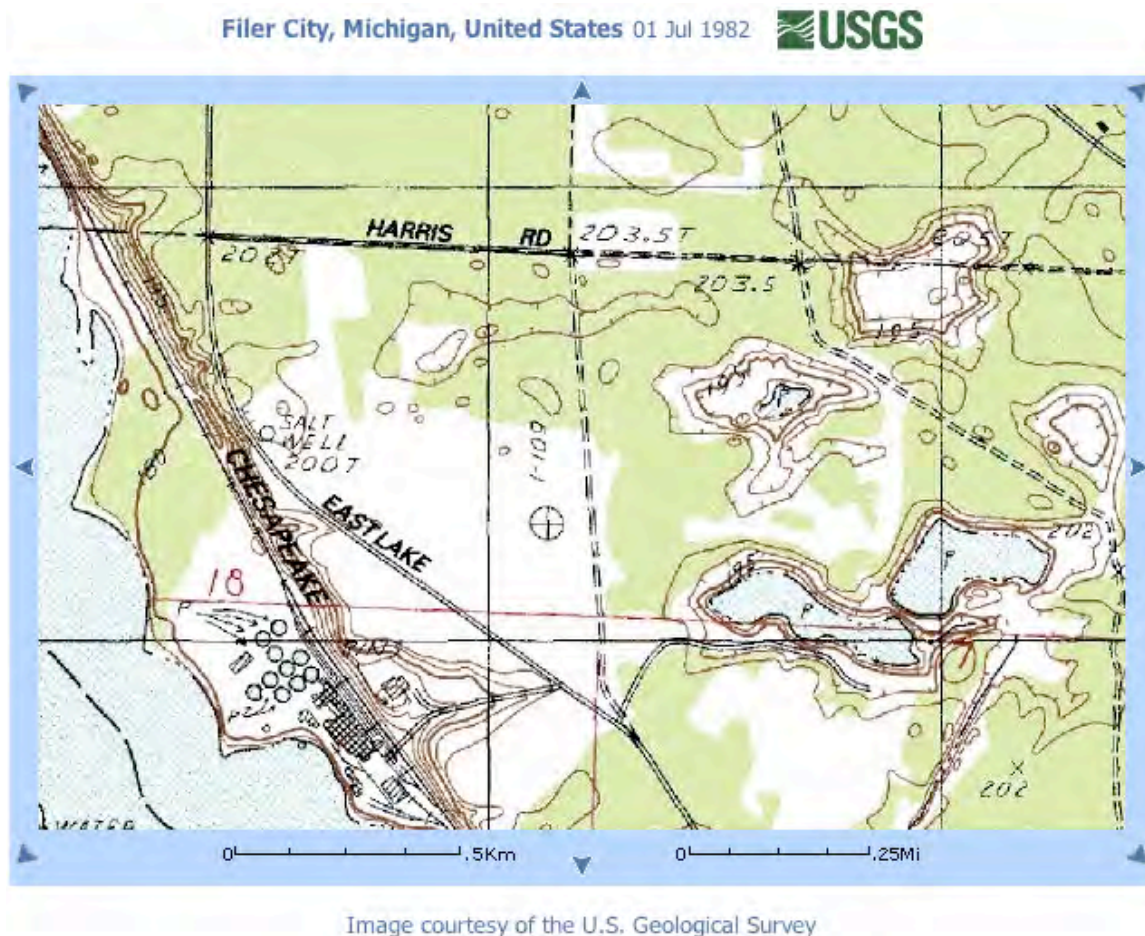


Figure 18 Topographic Map of the PCA Discharge Lagoons (USGS 1982)

The PCA lagoon site consists of approximately 700 acres on the east side of Manistee Lake. The site consists of eight unlined seepage lagoons, numbered 1 through 8. Lagoon 1 was the receiving lagoon with sequential overflow into each of the others upon filling (except Lagoon 8 which was an alternate receptor from Lagoon 3 overflow). Between 1951 and 1974 these lagoons received a total of 7.2 billion gallons of wastewater from the Kraft process (ATSDR, 1995). The Agency for Toxic Substances and Disease Registry report about the site (ATSDR, 1995) provides some of the history surrounding these lagoons and, to some extent, their impact on the environment:

Lagooning of the pulp mill effluents was phased out in the early 1970s. Between 1970 and 1976, the standing water in lagoons #3, #4, #5, #6, #7, and #8 was pumped out and sprayed onto four level areas near them (Areas A, B, C, and D in Figure 2 [Note: This is Figure 19 of this document]), where it seeped into the ground. Lagoon #1 had no standing water and lagoon #2 was full of cellulose sludge. The lagoons and seepage areas occupy a total of 105 acres. In 1972, PCA began operating a secondary wastewater treatment plant. All lagooning of effluents ended in 1974 [NOTE: Clean water was pumped into the lagoons during 1974-75 to keep the pipeline from freezing (USEPA, 1993)]. Effluents from the PCA plant are



currently treated in the plant's wastewater treatment plant, then discharged to Lake Michigan under a National Pollutant Discharge Elimination System (NPDES) permit.

One former lagoon (#3) has been used by PCA as a solid waste landfill under a license from Michigan Department of Natural Resources (MDNR). The company disposed of bark, construction debris, and recycling wastes (e.g. tape and plastics from recycled boxes that cannot be reprocessed) in the landfill. In late 1992, PCA stopped using the landfill in former lagoon #3. The company is dredging cellulose sludge from lagoon 2, mixing the sludge with fly ash, and using the mixture to fill and regrade the former landfill in lagoon #3. Approximately one-third of lagoon #3 was filled in mid-August 1993.

The bottoms of lagoons #2 and #3 are impermeable to water, sealed by cellulose fiber sludge from the wastes pumped into them. Lagoon #2 contained 30 feet of sludge before the current removal began (1)¹. Lagoon #2 contains standing water, mainly rainwater mixed with remnants of the "black liquor" that was pumped into it. Lagoon #3 was pumped dry when the lagoon system was abandoned, but it sometimes contains pools of rain water or leachate from the landfill in its west end. This water is pumped to the PCA plant water treatment system through the same pipe that had carried the "black liquor" from the plant to the lagoons. The other lagoons are typically dry, though they occasionally contain some accumulated rain water, and are heavily overgrown with trees, shrubs, and ground cover. One of these other lagoons was only identifiable on a Michigan Department of Public Health (MDPH) site visit by a large visible amount of lime that had been put into the lagoon to abate the odor caused by PCA effluent.

In 1956, an industrial supply well located approximately 2,200 feet south of lagoon 3 on the PCA site found black water. The well was drilled deeper, beyond the black water. While seeking a location for a municipal well in 1976, workers for the Village of East Lake, north of the site, drilled a test well west of the lagoons. The test well contained black water, so the Village abandoned the test well and placed their municipal well elsewhere.

The wastes in the lagoons seeped into an underlying shallow aquifer, resulting in highly discolored, black, contaminated groundwater. Hydrogeological investigations performed by the company have established that groundwater contamination from the lagoons moves west toward Manistee Lake. No residential wells in the area have been affected. The presence of heavy metals (lead, chromium, and arsenic) in the groundwater and the lagoon sediments formed a basis for including the PCA site on the NPL. The site was proposed for the NPL on December 30, 1982, and placed on the list on September 8, 1983. PCA and the U.S. EPA

¹ ATSDR 1995 Quotation References:

1. Smithe, R.J. History of PCA Lagoons. June 1, 1985.
2. Michigan Department of Public Health, for ATSDR. Preliminary Health Assessment for Packaging Corporation of America. March 10, 1989.
3. Fishbeck, Thompson, Carr & Huber. Remedial Investigation Report, Packaging Corporation of America. April 1991.
4. Fishbeck, Thompson, Carr & Huber. Feasibility Study, Packaging Corporation of America, Draft. February 1992.
5. Camp Dresser & McKee and Battelle Great Lakes Environmental Center. Report: Packaging Corporation of America/Manistee Lake Site. August 13, 1993.
6. U.S. Environmental Protection Agency. Declaration for the Record of Decision, Groundwater Operable Unit, Packaging Corporation of America Site. September 24, 1993.



signed a Consent Order for a Remedial Investigation and Feasibility Study (RI/FS) in May 1985.

The Michigan Department of Public Health (MDPH), working under a cooperative agreement with the Agency for Toxic Substances and Disease Registry (ATSDR), prepared a Preliminary Health Assessment (PHA) for the PCA site on March 10, 1989. The PHA concluded that the site was of potential public health concern because of possible exposure to contaminants in groundwater. The PHA cited the following possible receptors for the contaminated groundwater: Manistee Lake, the Martin Marietta Plant and its supply wells, and private wells in Stronach and East Lake. Surface water in Manistee Lake was considered to be of greatest concern. The PHA recommended further monitoring of the groundwater. No health effects studies were recommended, since there was no indication in the data analyzed for the PHA that human exposure had actually occurred (2).

The final report on the RI of the site was issued in April 1991 (3). A draft FS was released in February 1992 (4). An MDNR contractor released a draft study of the potential impact of the PCA groundwater contamination plume on Manistee Lake in December 1992 (5). On September 24, 1993, the U.S. EPA signed a Record of Decision (ROD) for the Groundwater Operable Unit at the site, stating that no remedial action was necessary, but the groundwater at and near the site and fish and sediment in the lake would be monitored (6).

Figure 19 shows the numbered lagoons and spray areas per the ATSDR 1995 quotation.

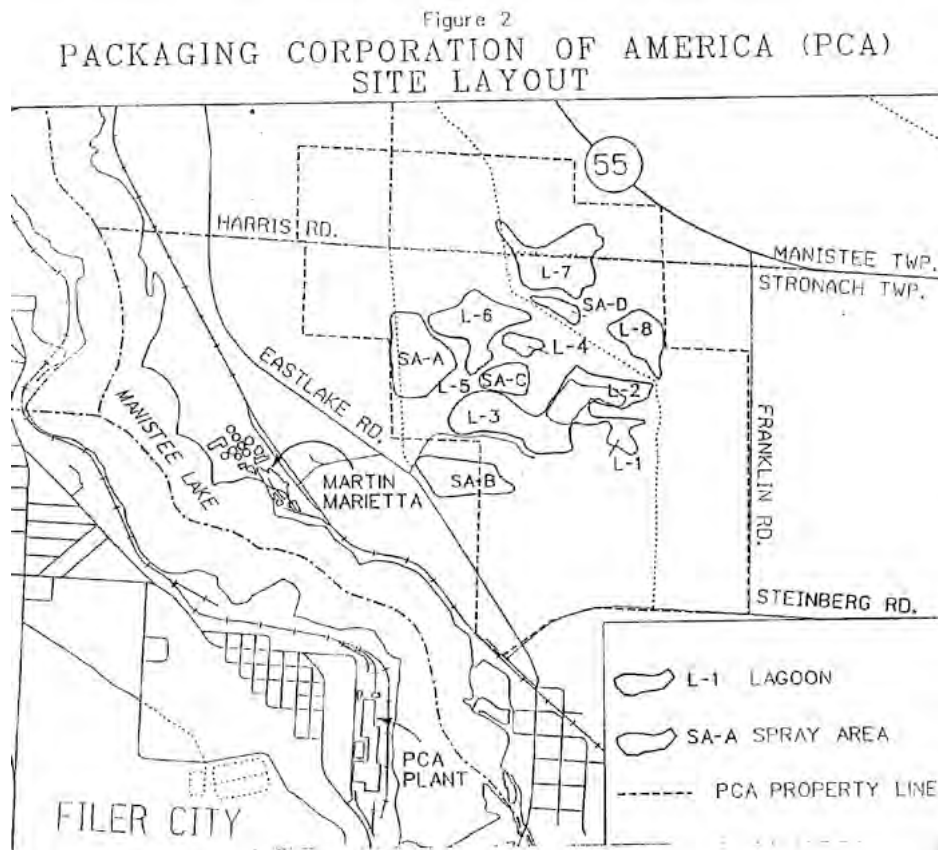


Figure 19 Numbered PCA Lagoons and Spray Areas per the ATSDR 1995 Report



Based on the USEPA Hazard Ranking System (HRS) scores, Scorecard.org depicts the PCA Lagoon site's hazard levels to be extremely high, as shown in Figure 20.

EPA [Hazard Ranking System](#) scores for PACKAGING CORP. OF AMERICA:

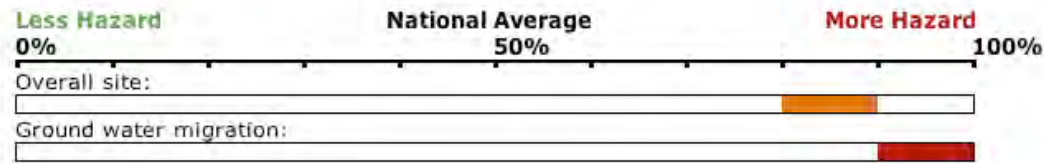


Figure 20 Depiction of HRS Scores for the PCA Superfund Site (www.scorecard.org)

Although a ROD was issued by USEPA for the PCA lagoon Superfund Site, there was evidently some controversy about this “No Action” (USEPA, 1993) ROD, some of which included disagreement with this decision by personnel at the Michigan Department of Natural Resources (MDNR)/Michigan Department of Environmental Quality (MDEQ). Upon reviewing only the information available in the public record for the PCA Superfund Site, the author of this report has the following concerns regarding this “No Action” approach and believes that further investigation is warranted unless these issues have been addressed:

1. The sheer volume of materials discharged should have resulted in significant groundwater mounding and the radial distribution of the wastes in all directions around the lagoons, not just in the predominant groundwater flow direction.
2. An assessment of contaminants that were originally in the waste materials (for example arsenic and chromium) versus those that were natively present in the soils and aquifer materials and released by the major shift in geochemical equilibria exerted by the waste materials.
3. The potential processes of contaminant adsorption with slow desorption from aquifer material and soil surfaces and slow diffusive processes from aquifer pore spaces do not seem to be mentioned. These could serve as long-term sources.
4. The generation of colloidal particles and their impact on contaminant behavior is not addressed.
5. It is unclear whether the model used adequately accounted for subsurface variability, i.e., beyond simple flow from the shallow aquifer to Lake Manistee. Such variability could include:
 - a. Discontinuities in the clay layer underlying the shallow aquifer that might allow contaminant movement into the deeper aquifer (particularly in the less investigated northerly and easterly directions)
 - b. Sinking of the contaminant plume due to its higher density (possible lake underflow)
 - c. The processes of adsorption/desorption, diffusion from pore spaces, colloidal transport



6. The risk assessment (RA) appears inadequate from the point of view of addressing all the necessary variables. It appears to have only addressed human exposure in the downgradient direction (and even this seems superficially done based on what is presented). RA should also have also included overall ecosystem and cultural impacts. Risks upgradient from the lagoon site don't seem to be considered even though mounding and radial distribution of the contaminants is almost certain to have occurred. A declining population for the area was apparently a major factor in the RA and a very poor factor to use based on human migration patterns in Michigan (generally northward with periodic large increases on weekends and during the summer) and the potential for the area to be developed for recreation and tourism (which has occurred and is increasing).

It is the author's opinion that this site and the information/conclusions upon which the ROD was based should be reconsidered by the appropriate entities including LRBOI, USEPA and MDEQ. Recent information indicates the MDEQ is re-evaluating this site.

b) PCA Industrial Location and Current Operations

Table 2 indicates a plethora of contaminants of potential concern associated with the operations at PCA. None of these appear to be listed for required monitoring in the PCA NPDES permit for discharges to water but discharges to both water and air are occurring, based on the data available in the TRI (Figure 21). Table 6 and Figures 22 through 31 depict the discharges and transfers for individual types of contaminants as reported in the PCA TRI reports for the years 1987 through 2002. Figure 21 shows that for the period from 1994 through 2002 releases by PCA to the air averaged about 400,000 lbs per year. Acetaldehyde appears to have been a major constituent of these air emissions (Figure 22), along with methanol (Fig 28) and periodic emissions of hydrochloric acid (Figure 25), phenol (Figure 30), and sulfuric acid (Figure 31). During this period decreases in air emissions seem to correspond somewhat with increases in releases to water (Figure 21) that consisted largely of nitrate compounds (Figure 29), with the exception of 2001 that shows an overall reduction in reported values. 2002 shows a return to the average reporting range for this facility.

In addition to major air and water releases (in terms of pounds) smaller but potentially significant (in terms of health effects) emissions also occurred, such as 39 lbs of lead to the air and 605 lbs to the water for the combined years 2001 and 2002 (Table 6) whereas no previous lead releases had been reported. Although not particularly toxic, manganese releases also occurred during 2002 whereas there had been no previous reporting. Sulfuric (28,564 lbs) and hydrochloric (194,316 lbs) acids were released to the air in 2002 after 10 to 11 years where they had not been reported. Many materials in the highly colored plumes from the PCA discharge pipes (Figure 32) in Lake Michigan (early discharges were to Manistee Lake), perhaps do not require TRI reporting or NPDES monitoring. It is known, however, that such pulp mill effluents can exert estrogenic effects (due to the presence of plant phytoestrogens) on aquatic organisms, particularly fish, which have shown female egg proteins in males, reduced levels of endogenous hormones in both males and females, gonad tissue pathologies, and the presence of combined ovarian and testicular features (ovotestes) on fish (Pait and Nelson, 2002).



Table 6 TRI Individual Chemical Releases for PCA, 1987 to 2002 (lbs except for Dioxin = grams)

Year	ACETALDEHYDE (AIR FUG)	ACETALDEHYDE (AIR STACK)	ACETALDEHYDE (DISP NON METALS)	ACETALDEHYDE (WATER)	AMMONIA (AIR FUG)	AMMONIA (DISP NON METALS)	AMMONIA (WATER)	CHLORINE (AIR FUG)	CHLORINE (AIR STACK)	CHLORINE (WATER)
1987	0	0	0	0	250	2,473	5,361	250	0	355
1988	0	0	0	0	250	3,578	126	250	0	399
1989	0	0	0	0	250	5,733	482	250	0	296
1990	0	0	0	0	250	0	483	250	0	257
1991	0	0	0	0	517	0	2,858	7	0	510
1992	0	0	0	0	516	47,590	3,962	7	0	96
1993	0	0	0	0	516	71,365	5,543	7	0	192
1994	1,831	15,540	0	607	518	0	374	6	6	148
1995	1,721	76,467	0	571	1,000	5,601	625	5	0	3,313
1996	1,711	82,502	5	568	512	10,505	1,208	5	0	90
1997	1,697	93,067	2	558	503	2,180	429	6	0	107
1998	1,631	82,089	0	541	502	0	592	5	0	0
1999	1,418	75,784	0	430	501	0	768	1	0	0
2000	1,441	73,567	0	337	500	0	364	0	0	0
2001	1,402	37,910	0	425	500	0	491	0	0	0
2002	1,622	36,764	11	422	500	603	378	0	0	0

Year	LEAD COMPOUNDS (AIR STACK)	LEAD COMPOUNDS (DISP NON METALS)	LEAD COMPOUNDS (WATER)	MANGANESE COMPOUNDS (AIR STACK)	MANGANESE COMPOUNDS (DISP NON METALS)	MANGANESE COMPOUNDS (WATER)	METHANOL (AIR FUG)	METHANOL (AIR STACK)	METHANOL (DISP NON METALS)	METHANOL (WATER)
1987	0	0	0	0	0	0	0	0	0	0
1988	0	0	0	0	0	0	0	0	0	0
1989	0	0	0	0	0	0	0	0	0	0
1990	0	0	0	0	0	0	0	0	0	0
1991	0	0	0	0	0	0	0	0	0	0
1992	0	0	0	0	0	0	0	0	0	0
1993	0	0	0	0	0	0	0	0	0	0
1994	0	0	0	0	0	0	412	548,971	40	4,120
1995	0	0	0	0	0	0	288	296,151	0	2,882
1996	0	0	0	0	0	0	264	309,255	22	2,621
1997	0	0	0	0	0	0	276	347,495	8	2,762
1998	0	0	0	0	0	0	249	305,536	0	2,492
1999	0	0	0	0	0	0	239	282,091	0	476
2000	0	0	0	0	0	0	248	274,847	0	390
2001	6	0	305	0	0	0	980	162,821	0	382
2002	33	1,938	300	36	17,193	3,594	993	175,078	312	390

Year	NITRATE COMPOUNDS (DISP NON METALS)	NITRATE COMPOUNDS (WATER)	PHENOL (AIR STACK)	PHENOL (DISP NON METALS)	PHENOL (WATER)	POLYCHLOR- INATED BIPHENYLS (OTH DISP)	SULFURIC ACID (AIR STACK)	HYDROCHLORI C ACID (AIR STACK)	DIOXIN AND DIOXIN-LIKE (AIR STACK)	DIOXIN AND DIOXIN-LIKE (DISP NON METALS)
1987	0	0	0	0	0	0	0	0	0	0
1988	0	0	0	0	0	1	0	70,902	0	0
1989	0	0	0	0	0	0	0	159,461	0	0
1990	0	0	0	0	0	0	55,131	209,617	0	0
1991	0	0	0	0	0	0	0	47,653	0	0
1992	0	0	0	0	0	0	0	0	0	0
1993	0	0	0	0	0	0	0	0	0	0
1994	0	0	681	0	3,695	0	0	0	0	0
1995	0	0	0	0	36	0	0	0	0	0
1996	0	0	37	0	39	0	0	0	0	0
1997	97	31,169	35	0	37	0	0	0	0	0
1998	0	31,893	38	0	37	0	0	0	0	0
1999	0	59,307	22,400	0	0	0	0	0	0	0
2000	0	205,114	28,133	0	0	0	0	0	0	0
2001	0	120,445	13,520	0	0	0	0	0	0	0
2002	462	69,296	18,633	4	0	0	28,564	194,316	0	0

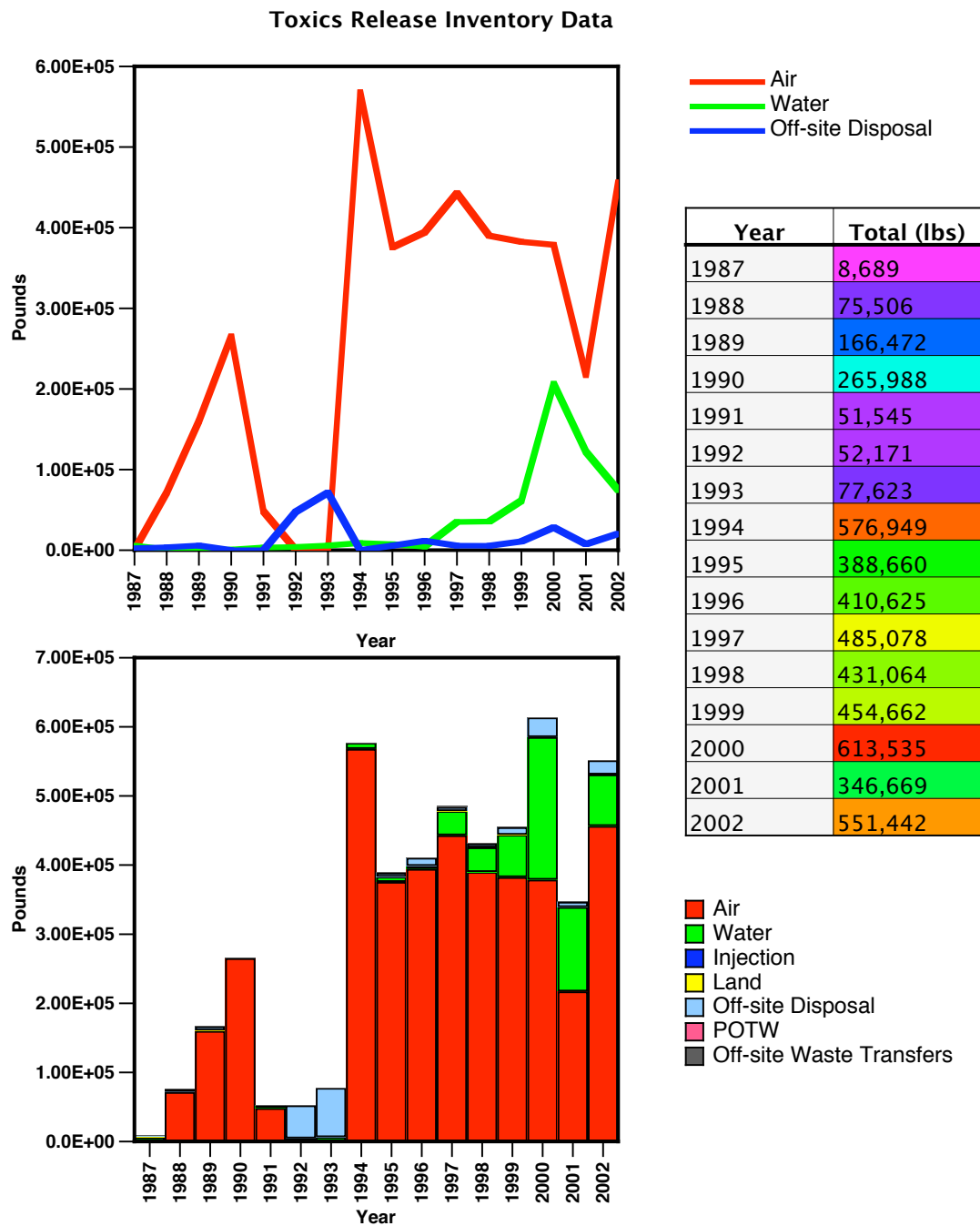


Figure 21 Toxic Release Inventory Data for PCA

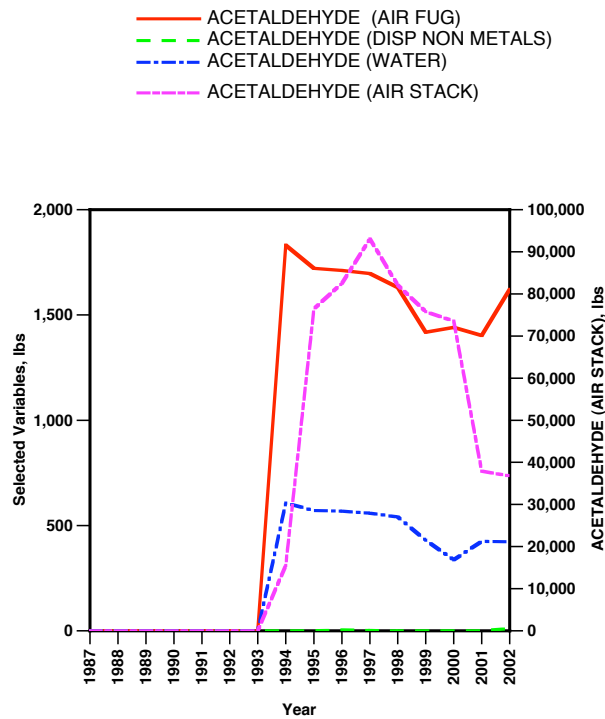


Figure 22 PCA TRI Report Values for Acetaldehyde

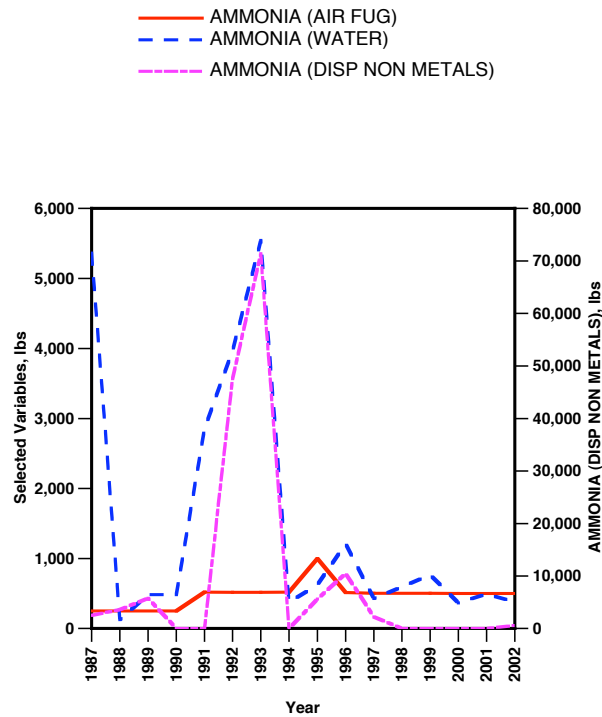


Figure 23 PCA TRI Report Values for Ammonia

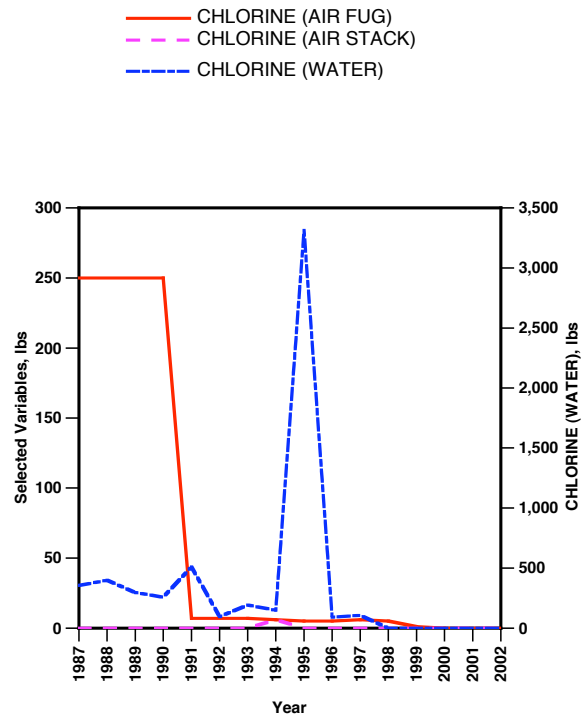


Figure 24 PCA TRI Report Values for Chlorine

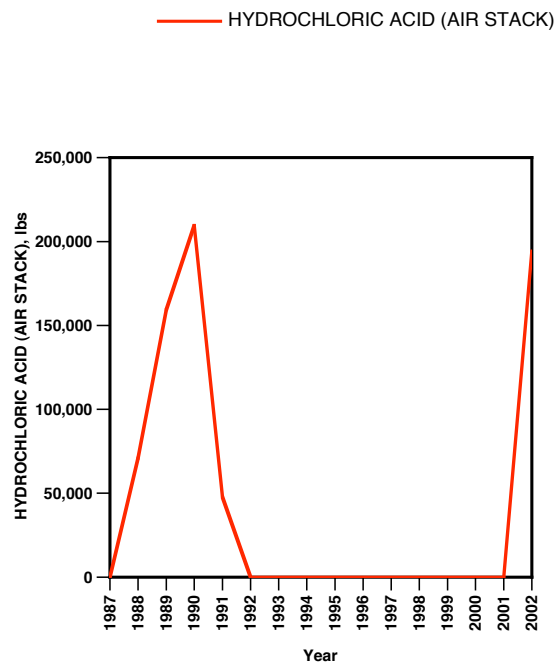


Figure 25 PCA TRI Report Values for Hydrochloric Acid

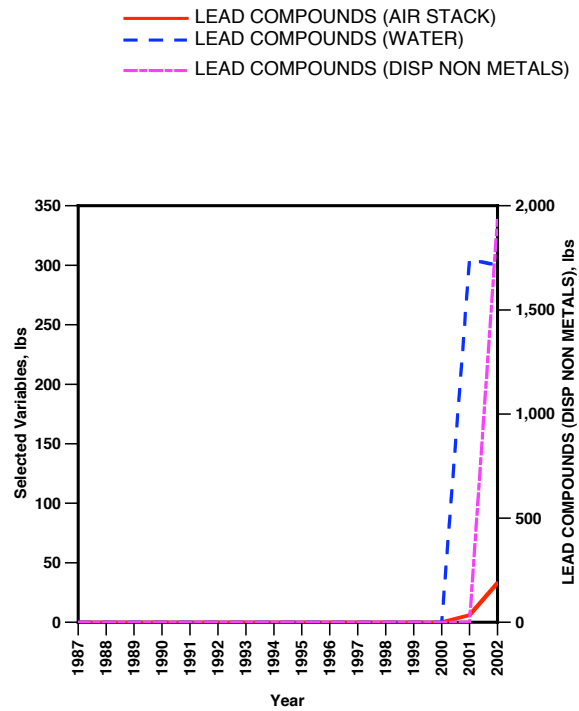


Figure 26 PCA TRI Report Values for Lead Compounds

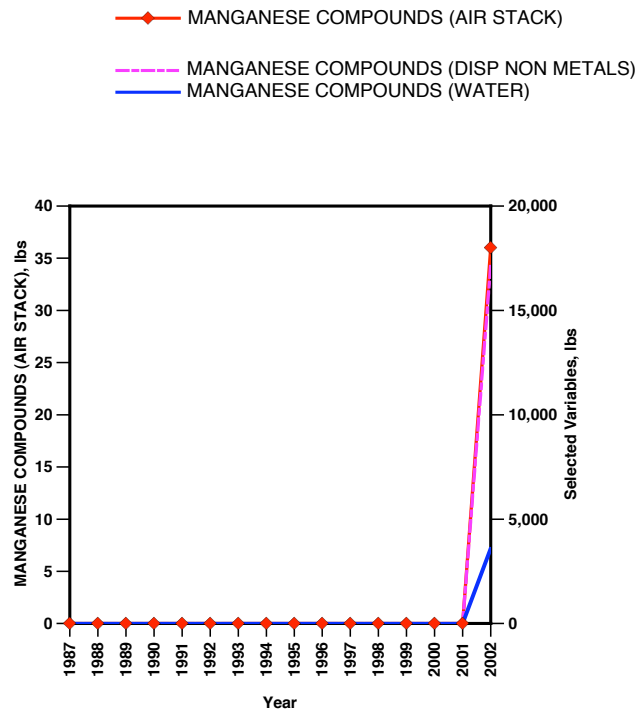


Figure 27 PCA TRI Report Values for Manganese Compounds

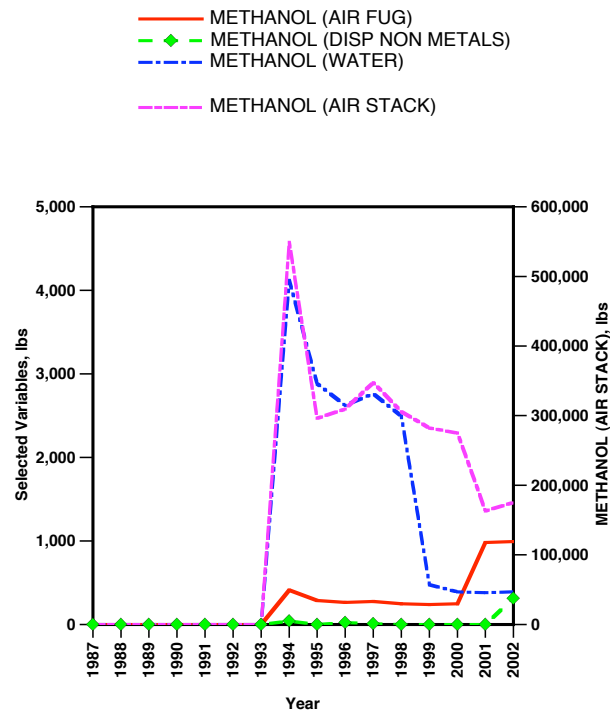


Figure 28 PCA TRI Report Values for Methanol

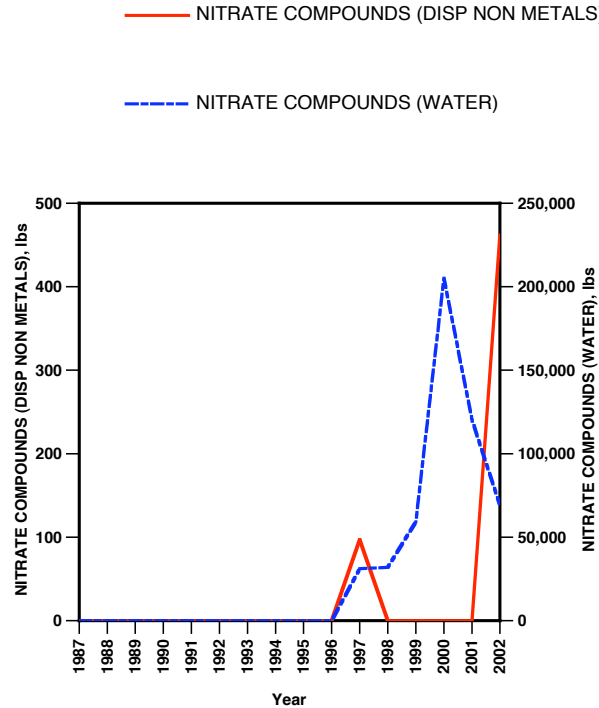


Figure 29 PCA TRI Values for Nitrate Compounds

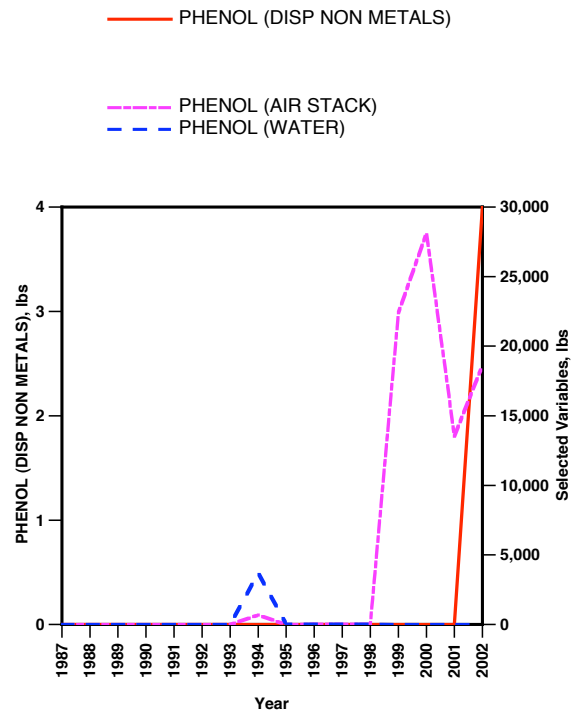


Figure 30 PCA TRI Report Values for Phenol

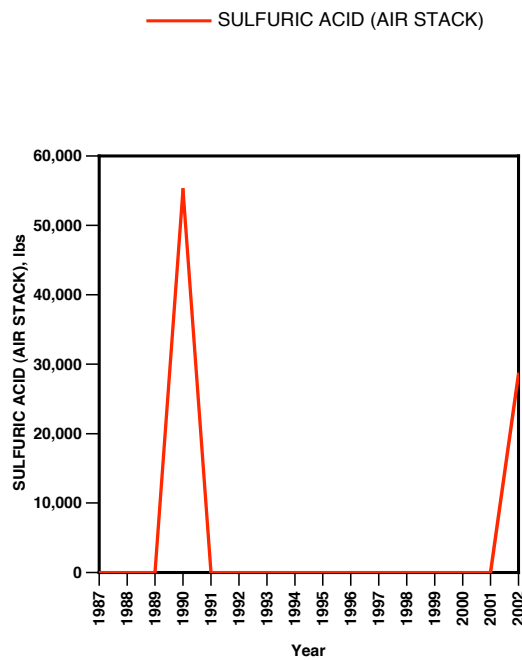


Figure 31 PCA TRI Values for Sulfuric Acid



Figure 32 Plume from PCA Discharge into Lake Michigan (Traverse City Record Eagle, 2004)

Because of the type and quantity of releases to the environment from the PCA site in Filer City, MI, Scorecard.org has rated the facility to be among the dirtiest/worst facilities in the United States. Figure 33 illustrates their scoring.

2001 Rankings: Major Chemical Releases or Waste Generation at This Facility

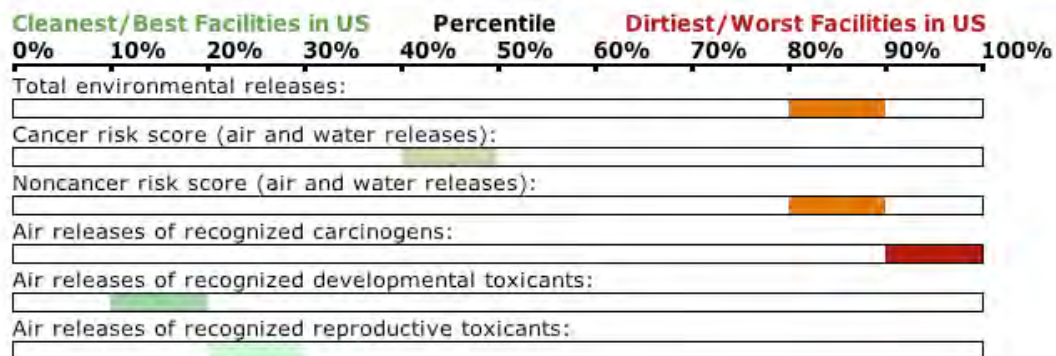


Figure 33 Scorecard.org 2001 Rankings for PCA, Filer City MI

Rengo Oil Co. Manistee

John E. Rengo & Company are listed in the category of “Gasoline and Oil Services” in the Manistee Lake area (Kaleva, MI) in the “Classified Buyers' Guide Of The City Of Manistee, Michigan 1928, R.L. Polk & Co., Publishers - Detroit, Mich.” Following World War 2, Robert Rengo and his brother Ray founded Rengo Brothers Oil Company. This company managed Phillips 66 throughout West Michigan and both owned and supplied about 10 gas stations until they sold their gas station business in the 1980s (<http://www.cnac.org/rengo01.htm>) to WESCO (<http://www.gowesco.com/history.htm>). Note: Wesco states the purchase from Rengo was 15 stores.



Table 2 indicates that the Rengo contaminants are typical of petroleum contaminants from leaking underground gasoline storage tanks. The Rengo Oil site at 217 Filer St. (now Cypress Street) is the current Cypress St. Wesco station, previously a Total Gas station. This location had serious leaking tank problems about 18 years ago. There were numerous neighborhood complaints about gas vapors entering residences through the floor drains; many older homes in Manistee had floor drains directly connected to the city sewer with no traps. The Michigan State Police Fire Marshall and the Michigan Department of Natural Resources made them leak test the tanks and remove the bad ones (personal communication). The 240 Arthur Street site used to be a large bulk storage facility that sat next to the CSX railroad tracks. It was closed a number of years ago and the tanks removed because Rengo Oil failed to provide adequate diking and spill protection and didn't want to invest any more money into it. Rengo opened a mini-mart gas station directly in front of this facility.

The 217 Filer St. location is listed as an archived Superfund site and the 240 Arthur St. location is included in the Part 201 of the Natural Resources and Environmental Protection Act. Other than routine monitoring of the extant Wesco station there is no environmental activity currently at these sites.

Sweetwater Crafts

Sweetwater Crafts began operations in Manistee, MI at 100 S. Glocheski Dr. (Figure 34) in 1987 (NLRB, 1990) manufacturing fiberglass parts for boats, including showers, galleys, radar arches, dive platforms, fish tanks and hatches.

Little contaminant information is available about this site other than from the Toxics Release Inventory for the years 1988 and 1989 for air emission releases of styrene in amounts of 17,000 and 8900 lbs, respectively. During 1988 Sweetwater disposed of 33,000 lbs. of styrene to Harland's Disposal Service, 3890 Camp Rd., Manistee, MI. They disposed of 12,000 lbs of styrene at Harland's in 1989.

Sweetwater Crafts is now doing business as Oak Grove International, manufacturing fiberglass caskets, burial containers for ashes etc. Before that it was Enduroglass, making fiberglass body components for automobiles. Prior to that it was Sweetwater, which took over operations from the Century Boat Company that used the facility as their final assembly for their 19, 22, 25, 27, and 28 ft cabin cruisers. It has been rumored that Century Boat had at least one acetone spill and one ruptured resin line that spilled quite a bit of material but there seems to be no environmental reports or confirmation of these incidents.



SWEETWATER CRAFTS
100 S. GLOCHESKI DR.
MANISTEE MI 496603301
Latitude: 44.256933 Longitude: -86.325062

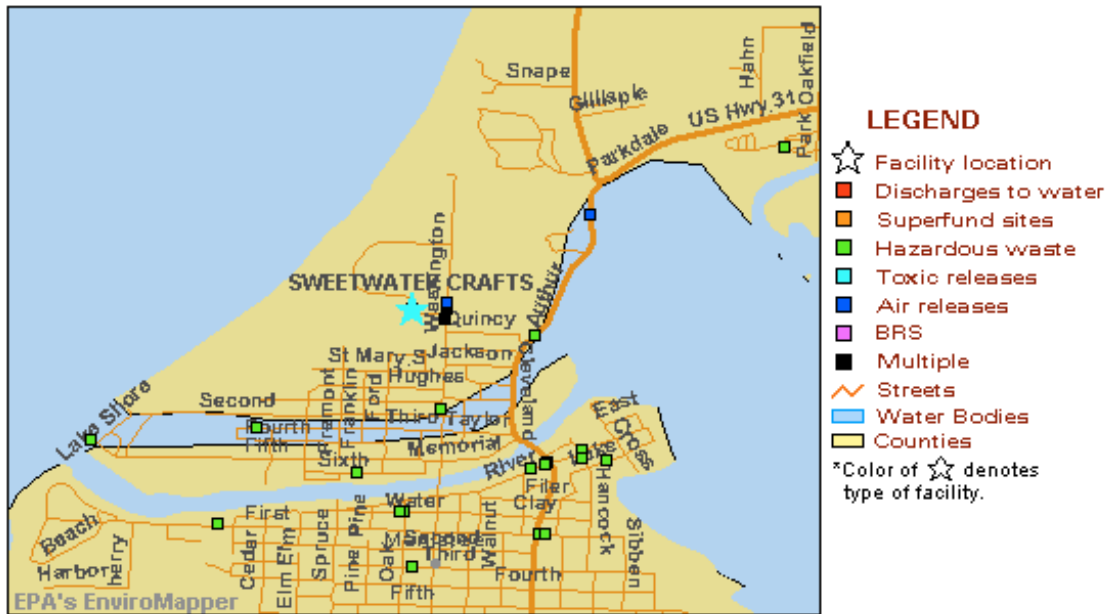


Figure 34 Location of Sweetwater Crafts

T.E.S. Filer City Station

The T.E.S. Filer City Station is a 60 MW coal-fueled cogeneration electric power plant that is also capable of generating 100,000 lbs/hr of 600 psi industrial process steam located in Filer City, MI, along the shoreline of Manistee Lake (Figure 35). CMS Generation operates the plant and owns 50% of the operation; Tondue Energy Systems owns the other 50% (<http://www.csrwire.com/article.cgi/572.html>). The plant began operations in June 1990. Its electricity is sold under a 35-year contract to Consumers Power Company while the steam it generates is sold to Packaging Corporation of America for use in their nearby paper mill (<http://www.tonduecorp.com/experience.html-filer>).

In addition to burning coal (approximately 750 tons/day) the facility also burns waste wood (120 tons/day) and was licensed in 2001 to burn tire chips at a rate of 96 tons/day (<http://www.record-eagle.com/2001/apr/15burn.htm>). It uses standard stoker boilers and dry gas scrubbers with a high-pressure extraction turbine and is operated by 31 full time employees (<http://www.tonduecorp.com/experience.html-filer>). Although the facility has been reported at a Manistee City Council meeting to be the largest emitter of dioxin in the state of Michigan (<http://www.ci.manistee.mi.us/Minutes/2004/05-18-04.pdf>), it has



previously been awarded the Clean Corporate Citizen designation by the state (<http://www.record-eagle.com/1999/dec/28filer.htm>).



Figure 35 Location of T.E.S. Filer City Station

To meet the needs of its operation, T.E.S. Filer City stores large quantities of coal outdoors on the edge of Manistee Lake. Coal piles on Manistee Lake are addressed in a later section of this report (T.E.S. Filer City coal storage is shown in Figure 47).

Based on a search of the USEPA's water discharge permits for Manistee County (http://www.epa.gov/enviro/html/pcs/pcs_query.html), there does not seem to be a NPDES permit listed for this power plant, even though large quantities of water are withdrawn and discharged to Manistee Lake for cooling purposes. Water usage for a three-year period is given in Table 7 (USEPA, 2002)

Table 7 T.E.S. Filer City Station Water Use

Calendar Year	2000	2001	2002
Actual Quantity gal/yr	30,454,797	23,914,080	23,928,213



The Toxics Release Inventory information for the T.E.S. facility is shown in Figure 36 and indicates no significant releases to water, but large releases occurring via air emissions and off-site disposal, even though no releases were reported prior to 1998.

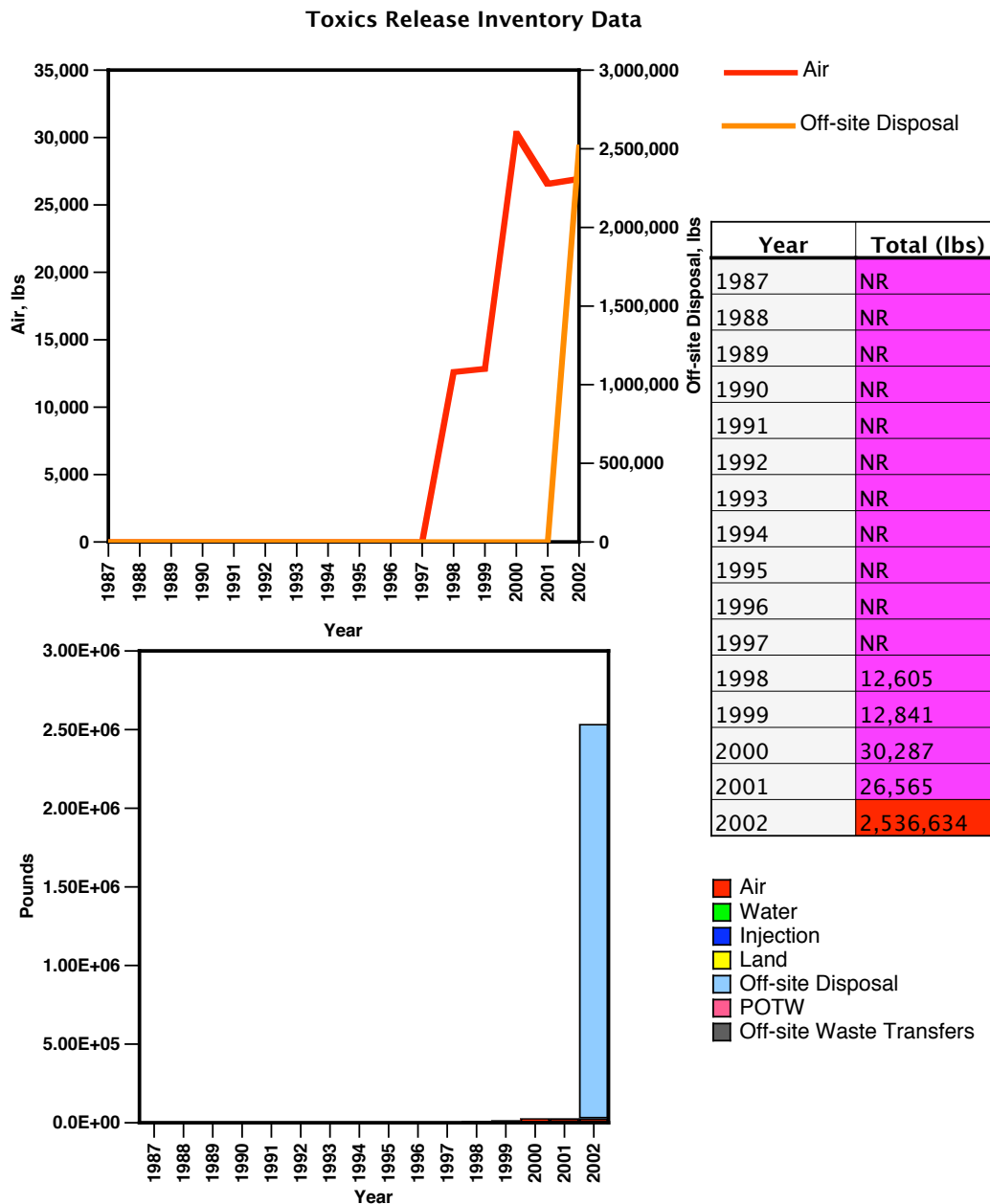


Figure 36 Toxic Release Inventory Data for T.E.S. Filer City Station



The TRI release data for individual components for the years 1998 through 2002 are illustrated in Table 8 and Figures 37 through 45. Data for the previous eight years of its operation were not reported by T.E.S. Filer or are, for some reason, not provided by USEPA in their database. This is an unfortunate lack of data that makes it much more difficult to evaluate and understand the environmental performance of this power plant and its total emissions over the course of its lifetime. Notable are several toxic metal and metalloid contaminants known to be released during coal combustion and ash management that are not listed in the releases or transfers for disposal from this facility. These would include arsenic, selenium, cadmium, and uranium to name a few.

Several of the Table 2 contaminants are of significant concern in the environment, in particular lead, mercury and chromium. These are important with regard to both air pollution and surface deposition that can contaminate land surfaces and bodies of water, such as Manistee Lake. Table 8 and the associated plots raise as many questions as they answer. A notable question is why there is so much variation across the years and between the variables (contaminants). For example, Cr was reported as emitted to air in all the years reported in the TRI but, suddenly, there are 20,216 lbs of Cr compounds disposed off-site in 2002 where there had been no reporting of this before (Figure 38). This does not correspond with a similar change in the emissions, so where did the Cr waste go during the previous years of operation? Cu, Ba, Pb, Mn and Zn show similar patterns and raise the same question. Dioxins were not reported until 2001 and 2002, with a total of 7 grams being released during that two-year period.

Mercury, a contaminant of extreme importance shows the odd pattern of no reported emissions in 1998 and 1999 followed by 19 lbs of elemental Hg in 2000 then 5 lbs of Hg compounds in 2001 and 131 lbs of Hg compounds in 2002 (Figure 42). One has to wonder how, assuming electrical generating needs did not radically decrease or emission controls increase during 2001, the emissions went from 19 lbs of elemental Hg to 5 lbs of Hg compounds. And why were both of these previous values so much lower than the 131 lb air release value for 2002? The Environmental Working Group (1998) reported estimated total mercury released and estimated mercury air pollution for 20 Michigan coal-burning power plants. T.E.S. Filer City Station was the only one of the 20 for which there was no estimate because “insufficient data precludes estimation of mercury emission from these plants.”

Consistently reported, along with having numerically consistent values, are the acidic emissions, HCl, H₂SO₄ and HF (Table 8, Figure 44), of the T.E.S. Filer City power plant. Based on these values the power plant has reported emitting approximately 61,000 lbs of acid and acid-forming compounds during the five-year period from 1998 through 2002.

It seems reasonable to assume that if the acidic emissions were reported for every year covered by the TRI reports that metals emissions should likewise have been reported. The plethora of missing years, missing metals and metal compound values for the reported years, and inconsistencies in the reported values are potentially indicative of a need to improve the means by which values are reported to the Toxics Release Inventory and to develop a system that allows the reported values to be better verified.

**Table 8 TES TRI Reported Release Values for Various Chemicals, 1998 through 2002. Values are in lbs Except for Dioxins in Grams.**

Year	BARIUM COMPOUNDS (AIR STACK)	BARIUM COMPOUNDS (DISP NON METALS)	CHROMIUM COMPOUNDS (AIR STACK)	CHROMIUM COMPOUNDS (DISP NON METALS)	COPPER COMPOUNDS (AIR STACK)	COPPER COMPOUNDS (DISP NON METALS)	DIOXIN AND DIOXIN-LIKE COMPOUNDS (AIR STACK)	HYDROCHLORIC ACID (AIR STACK)	HYDROGEN FLUORIDE (AIR STACK)
1998	0	0	61	0	0	0	0	8925	1080
1999	0	0	64	0	0	0	0	9088	1100
2000	1045	0	134	0	362	0		8885	1076
2001	942	0	120	0	311	0	3	7906	922
2002	929	153883	122	20216	313	51842	4	8081	929

Year	LEAD COMPOUNDS (AIR STACK)	LEAD COMPOUNDS (DISP NON METALS)	MANGANESE COMPOUNDS (AIR STACK)	MANGANESE COMPOUNDS (DISP NON METALS)	MERCURY (AIR STACK)	MERCURY COMPOUNDS (AIR STACK)	SULFURIC ACID (AIR STACK)	ZINC COMPOUNDS (AIR STACK)	ZINC COMPOUNDS (DISP NON METALS)
1998	0	0	115	0	0	0	2424	0	0
1999	0	0	121	0	0	0	2468	0	0
2000	47	0	272	0	19	0	2835	15612	0
2001	47	0	258	0	0	5	2622	13432	0
2002	48	7893	249	41242	0	131	2640	13489	2234629

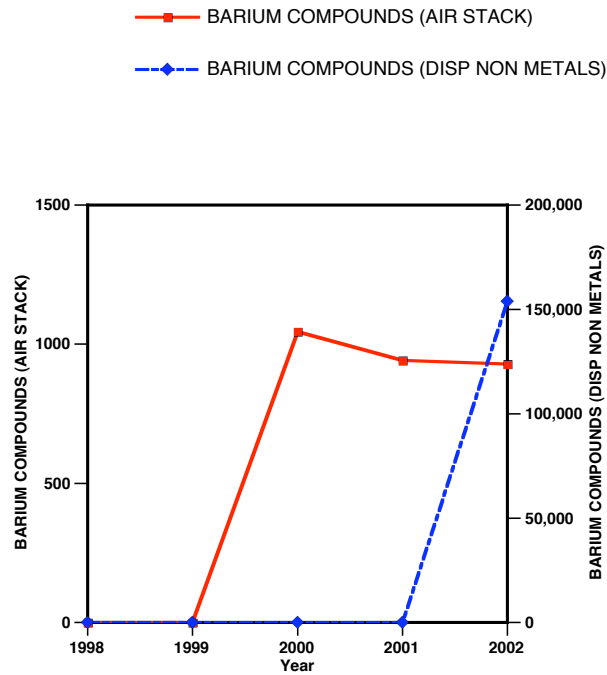


Figure 37 TES TRI Values for Barium Compounds, lbs

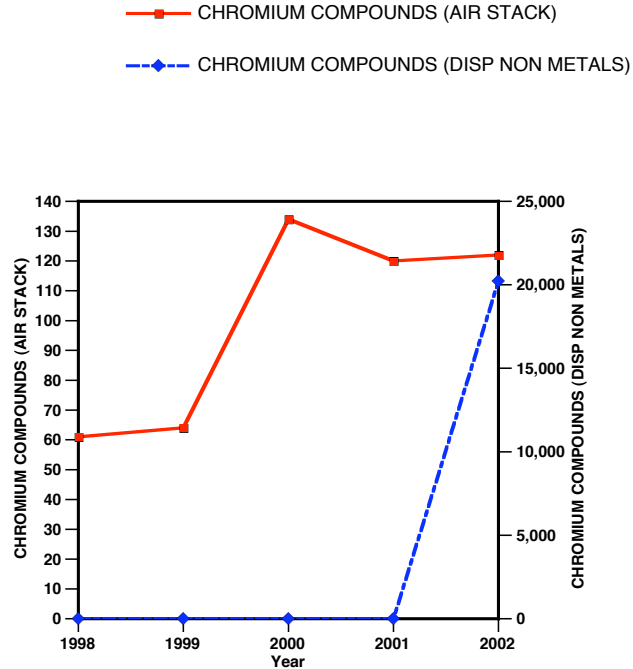


Figure 38 TES TRI Values for Chromium Compounds, lbs

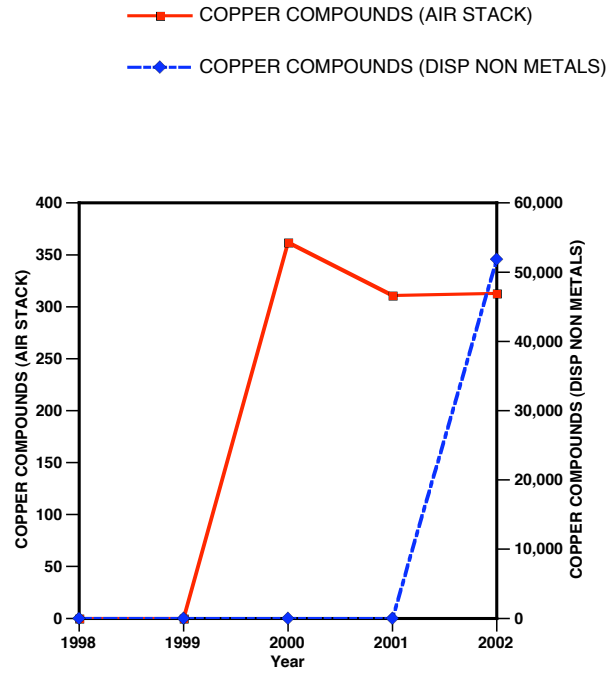


Figure 39 TES TRI Values for Copper Compounds, lbs

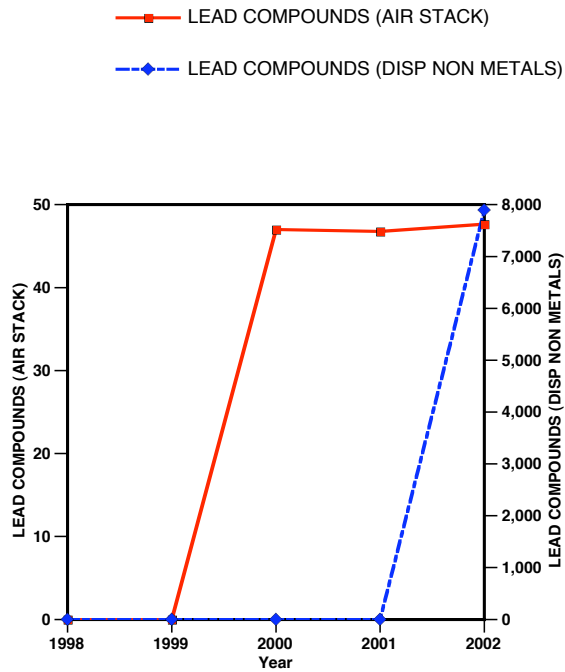


Figure 40 TES TRI Values for Lead Compounds, lbs

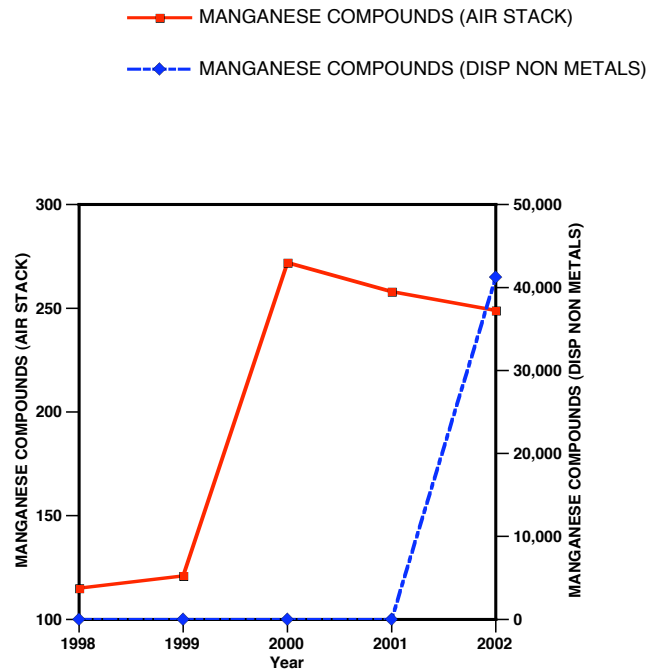


Figure 41 TES TRI Values for Manganese Compounds, lbs

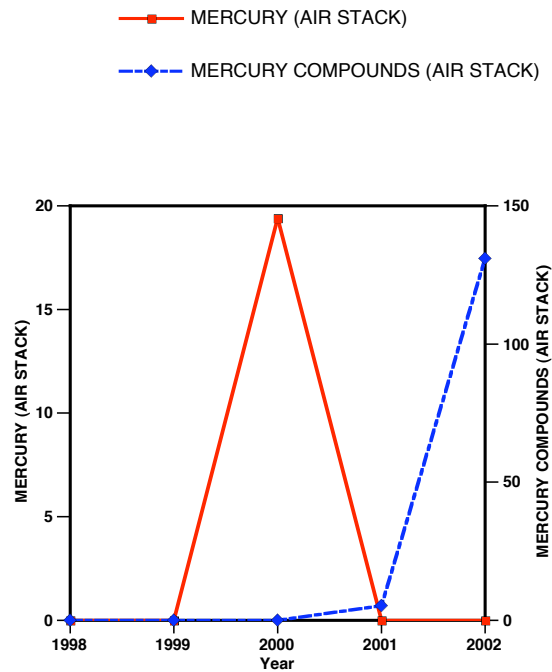


Figure 42 TES TRI Values for Mercury and Mercury Compounds, lbs

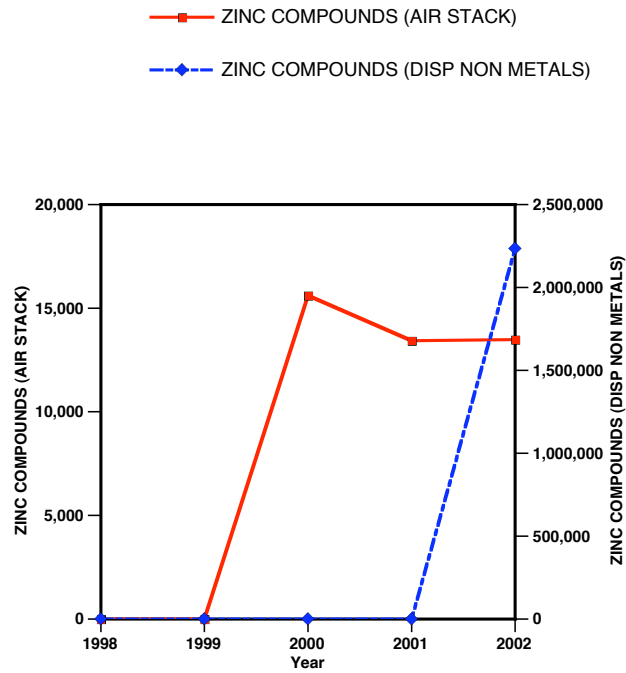


Figure 43 TES TRI Values for Zinc Compounds, lbs

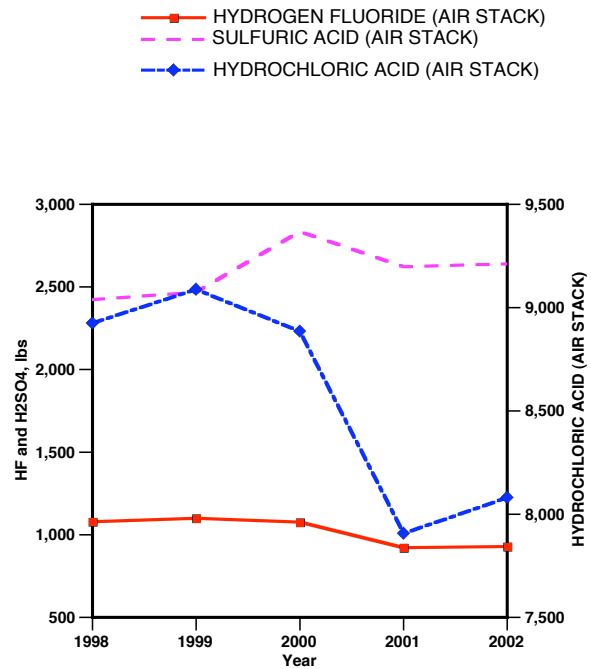


Figure 44 TES TRI Values for Acidic Compounds, lbs

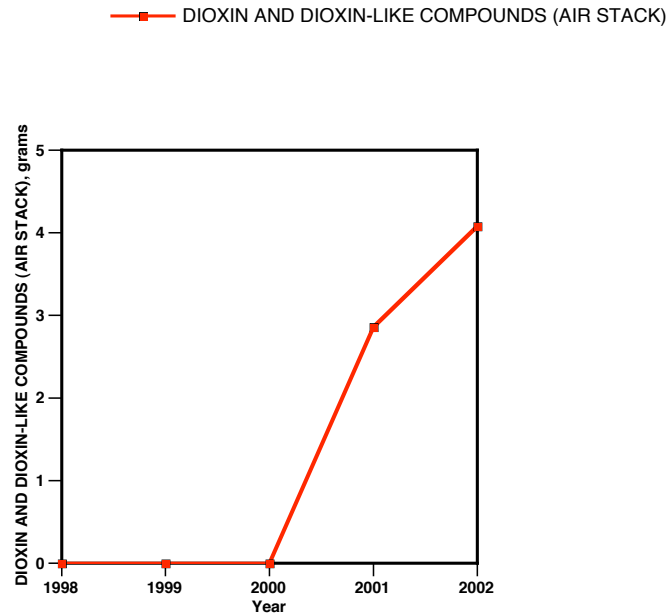


Figure 45 TES TRI Values for Dioxin and Dioxin-Like Compounds, grams

Figure 46 shows the ranking by Scorecard.org for the T.E.S. Filer City facility and they give the power plant their highest ranking for non-cancer risk and very high rankings for cancer risk and total environmental releases.

2001 Rankings: Major Chemical Releases or Waste Generation at This Facility

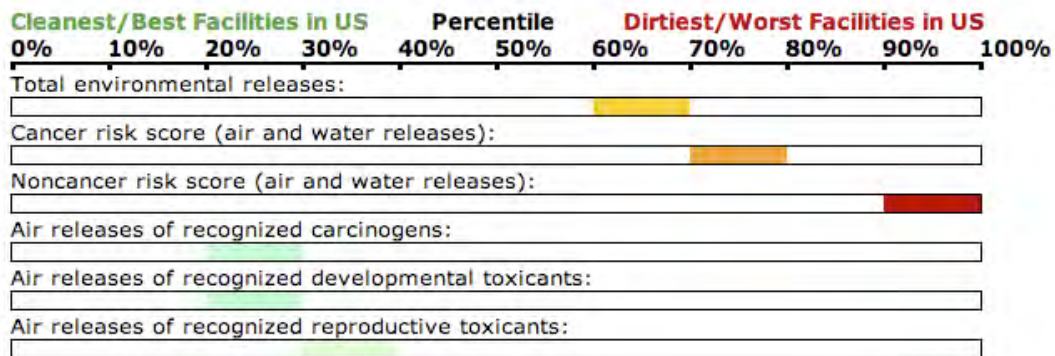


Figure 46 Scorecard.org Ranking for the T.E.S. Filer City Power Plant



Coal Storage Pile Sites (Various) Around Manistee Lake

At least four facilities burn coal to power their processes on the shores of Manistee Lake and four large open coal piles are maintained on the shoreline to store the coal. Three of these piles are in use and one other is supposedly abandoned. One of the three functioning piles is owned by Martin Marietta and is located on approximately 30 acres near the General Chemical property. This active coal pile is shown in the lower portion of Figure 47, where the shoreline bends to the west. Coal is trucked from this pile, beginning about 7:00 AM and ending in the late evening six days per week, to fuel the industrial processes at Martin Marietta on the opposite side of Lake Manistee. Another coal pile is located on Packaging Corporation of America shoreline property adjacent to the T.E.S. Filer Station power plant (Figure 48) and is used by both the power plant and for the operations at PCA. The site is reported to have a capacity of about 90,000 tons (<http://www.iwr.usace.army.mil/ndc/ports/pdf/ps/ps48.pdf>). The third actively used coal pile is located at and used by Morton Salt and Magnesia (Figure 49). The unused coal pile is on the General Chemical property and is shown in Figure 47 north of the Martin Marietta coal pile.



Figure 47 Martin Marietta (S) and General Chemical (N) Coal Piles

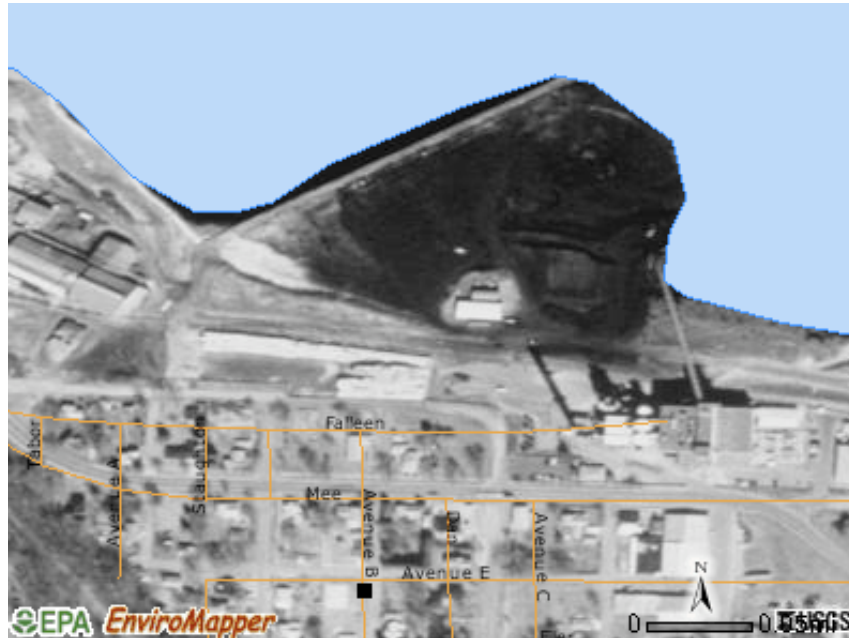


Figure 48 T.E.S. Filer City Station Coal Pile (PCA Property)



Figure 49 Morton Salt and Magnesia Coal Pile

Although coal is a potential contaminant because of its inherent constituents, such as various inorganic and organic compounds and metals, it is not regulated as a toxic substance. One issue long discussed about coal storage piles is the fugitive emissions of



dusts and gases into the air from the piles. Blackwood and Wachter (1978) estimated the emission of respirable particulates (< 7 micrometers) from coal storage piles to be 6.4 mg/kg/yr. They studied a 95,000 metric ton bituminous coal pile and determined it to have an emission rate of 601 kg/yr (1345 lbs/yr). This is a significant quantity of particulates being transported downwind of coal storage piles that can result in aesthetic issues (coal dust on houses, cars, etc.), health issues (respiration of particles) and the contamination of water bodies by particle settling into streams, rivers and lakes.

Other issues include direct contamination of groundwater by leachate from the coal piles, especially with older unlined piles, and erosion of the coal materials into surface water bodies where their contaminants can leach into the water. Coal piles stored directly on soil surfaces risk ground-water contamination when extremely acidic coal-pile leachates with elevated concentrations of heavy metals are being generated, especially when the soil material is coarse and has limited buffering capacity (Zelmanowitz et al., 1995). Available information indicates that none of the coal piles on the perimeter of Manistee Lake have either liners to prevent infiltration or dikes to prevent erosion into the lake.

The author of this report has identified the following coal constituents leached from coal storage piles and disposed coal ash to be of the most concern for water and groundwater (unpublished data). Table 9 lists these constituents in the evaluated order of concern (e.g., number 1 is of the most concern, number 14 the least):

Table 9 Coal Constituents of Concern

Ranking	Constituent
1	Sulfate (SO_4^{2-})
2	Selenium (Se)
3	Boron (B)
4	Arsenic (As)
5	Manganese (Mn)
6	Chromium (Cr)
7	Cadmium (Cd)
8	Nickel (Ni)
9	Iron (Fe)
10	Beryllium (Be)
11	Molybdenum (Mo)
12	Antimony (Sb)
13	Barium (Ba)
14	Lead (Pb)

It should be noted that the toxicity of the constituent is not the only consideration for this ranking but also such factors as the quantity in the coal and the mobility in groundwater systems. Notably absent from this list is mercury, primarily because of its usually very low concentration in coal and because its presence in water is thought to be primarily from atmospheric deposition after coal combustion.



Brine Leakage

In addition to the industries listed in Table 2 that extract chemical brines for calcium, magnesium, bromine, etc., there have been numerous historic abandoned and improperly plugged wells, as well as damaged pipelines, that have leaked dense salt solutions into Manistee Lake. Major constituents of these brines can include sodium chloride, calcium chloride, sodium sulfate, and magnesium, iodide, or bromide compounds (USEPA, 1999).

A layer of high conductivity water, approximately 5 ft thick, above the lakebed has been reported (Rediske et al., 2001). Divers have visually observed this density-driven stratification (personal communication) probably noting a difference in its refractive index relative to the surrounding water. There is also reported to be a fairly deep gelatinous layer in the uppermost sediments throughout portions of the lake (MDEQ, personal communication). It is possible that this is an impact on the lakebed sediments due to clay/soil dispersion because of the high sodium content of the overlying/infusing brine waters followed by aggregation and flocculation of the soil materials into a gelatinous mass. Because of the long history of the timber industry along Manistee Lake, there is also the possibility that these gelatinous materials are derived from cellulose, possibly a result of partial degradation by bacterial consortia in an anaerobic environment. More investigation is needed to understand these materials. Their origin and properties might have a significant impact on the complexation, biological availability, transport and fate of both metallic and organic contaminants of concern in this environment.

Salt well installation around Manistee Lake has been occurring since 1881 and chemical brine wells have been installed since 1927. Potentially more than 100 of these wells were installed for salt and oil. The location, design, construction, and abandonment condition was solely up to the owners, hence the locations and status of many of these wells was unknown (Childs, 1977). As of 1995 the Michigan Department of Natural Resources (DNR) was to spend \$400,000 to plug one abandoned well near Manistee and was studying many others to prevent contamination of drinking water around Manistee Lake. This was because natural gas developers planned to drill several deep injection wells in the Manistee Lake area for disposal of millions of gallons of brine that was a byproduct of Antrim development. The DNR was concerned that brine from the Antrim disposal wells could flow through the rock layers and migrate back to the surface through the old unplugged wells (MCLUC Reporter, 1995). The leaking brine wells along the lake have now been located and the majority plugged (MDEQ, personal communication).

In addition to leaking wells and pipes, in some geographical locations there is the potential for the contamination of drinking water aquifers by the re-injection of the spent brine into the formation from which the brine was originally pumped. This is probably not a problem in the Manistee Lake area because the lowermost drinking water strata is about 634 ft below ground surface and is separated from the re-injection zone by about 2000 ft of sedimentary rock strata (USEPA, 1999). The only concern would occur if there



were integrity problems with the casing and/or the surrounding cement (cemented from the injection zone to the surface around the annular space) along the length of the casing.

Part 4: Discussion of Contaminants and Sources

Review of Important Manistee Lake Contaminants

Several contaminants are implicated in the damage that has been done to the health of Manistee Lake. Based on toxicity to sediment-dwelling (benthic) organisms (Rediske et al., 2001) an exploratory data analysis (Powell, 2004) using stepwise regression found a few of these to probably have the most impact; in approximate order of significance:

As > Cr, hexane extractables, PAH > Hg, Se

For three of the four organism studies arsenic was the most significant predictor of organism mortality, or organism absence, in sediments. Chromium was the second most significant factor in two studies with hexane extractable materials the most significant factor in one study and the third most in another. PAH at very high concentrations seemed to account for abnormally high mortality/species loss in three samples from two studies that were outliers in the regressions. Mercury was the second most significant factor in one study and selenium the fourth most significant in the same study. Table 10 reproduces Table 23 from Powell (2004).

Table 10 Summary of Regression Model Results for the Biological Studies

Study	Significant Predictors	Outlier Locations	Model Fit (R ² value)	F-Ratio
<i>H. Azteca</i> % Mortality	As, Hg, Hexane Extractables, Se	12	97.7%	109
<i>C. Tentans</i> % Mortality	Hexane Extractables, Cr	13 (PAH)	81.7%	20.3
Organisms (total)	As, Cr		62.0%	11.6
Species #	As	12, 13 (PAH)	88.0%	32.8

Studies by Rediske et al., 2001, on the same datasets led them to state, “Sediment toxicity to amphipods and midges was observed at M-6 and M-13². These stations had the highest levels of hydrocarbon oils and PAH compounds,” and reached the conclusions that mortality was “related to the presence of elevated PAH compounds” and that “brine intrusion appeared to have a greater negative affect on taxa numbers (number of species) and abundance than did the HEM and PAH compounds. Although their ANOVA results “suggested that the brine-impacted sites as a group, had benthic invertebrate populations with a lower trophic status than benthos collected in the area influenced by the

² Note that M-13 was an outlier in the Powell (2004) stepwise regressions and the conclusion was that increased mortality in these samples was due to high PAH.



PCA/Martin Marietta groundwater plume,” the Powell (2004) analyses of the data show that there seems to be no real statistical discrimination between these two environmental milieus on the organism mortality and count studies. Nonetheless, both evaluations implicated PAH and hexane extractable materials (hydrocarbon oils) as having an impact. One difference between the two evaluations is that Rediske et al. (2001) discounted the importance of the metals based on published Probable Effects Concentrations (PEC), while Powell (2004) incorporated them into all the exploratory statistical analyses because of concerns about site- and biogeochemical-specific reactions and interactions.

Development of Industry Significant Contamination Factors

Table 11 lists the primary contaminants of concern and relates them to the industries listed in Table 2 (also historic industry, coal storage piles, or processes) that are either known to have discharged these chemicals, have reported their release, are licensed to discharge them (NPDES) or are known to release them under certain conditions (e.g., coal storage piles)³. This table is a tool for consideration of possible action plans and sampling. It is not an implication of liability or a conclusive indication of source but, rather, a starting point for focusing on further contaminant investigation and management, including the development of a sampling plan. It should be noted that other operations and processes, both major and minor, could result in some release of the contaminants listed. Also, merely being in the listing does not necessarily indicate that the industry released that component, only that the potential exists for that type of industry or process. For the purposes of this assessment, chemical release is only certain when the releases have been reported, the industry has listed it in their Toxic Release Inventory, or if the site has been investigated thoroughly for known problems, such as the PCA Superfund Site. Information from Table 2 is carried to Table 11 for those sites.

Table 11 Significant Contaminants and Potential Sources

Significant Contaminant	Potential Sources
Arsenic	Tannery*, MWWTP, PCA, Coal Piles
Chromium	Tannery*, Manistee Plating, MWWTP, M. Marietta, PCA, TES Filer, Coal Piles
Hexane Extractables (oil & grease, hydrocarbons)	Fablite, General Chemical, Harland's, MASBG, Manistee Forge, M. Marietta, Morton, Rengo
PAH	General Chemical, MASBG, Manistee Forge, M. Marietta, Morton, PCA, Rengo, Coal Piles, Coal combustion, All combustion processes (including coal)
Mercury	MWWTP, PCA, TES Filer, Coal Piles, Coal combustion
Selenium	MWWTP, Coal Piles, Coal combustion

*Arsenic if cattle/hides were arsenic dipped as an insecticide. Chromium possible but unlikely for the time period the known tannery operations were in place. Tannery = the old historic tanneries, MWWTP = Manistee Wastewater Treatment Plant, MASGB = Manistee Area School Bus Garage

³ Although pressure treated CCA wood (CCA = chromium, copper and arsenic) could potentially be implicated due to the historic lumber industry around Manistee Lake, this process has only been around for the past 70 years, beginning in effect after the end of the major timber industry in this area.



Fifteen industries or processes are listed in Table 11 as being possible sources for one or more of the six contaminants listed. Table 12 lists those potential 15 sources and the number of contaminants for which each appeared in Table 11.

Table 12 Potential Industrial Sources and Number of Associated Contaminants from Table 11

Industry or Process	Number of Significant Contaminants from Table 11
Tannery	2
MWWTP	4
PCA	4
Coal Storage Piles	5
Manistee Plating	1
M. Marietta	3
TES Filer	2
Fablite	1
General Chemical	2
Harland's	1
MASGB	2
Manistee Forge	2
Morton	2
Rengo	2
Coal Combustion	3
All combustion processes	1

Table 12 can be further refined by removing coal piles and coal combustion as separate processes and incorporating them into the totals for those industries that carry out these processes around Manistee Lake. To reiterate, these are:

- Four Coal Piles
 - General Chemical
 - PCA for both TES and PCA
 - Morton Salt
 - Martin Marietta
- Four Coal Burning Facilities
 - PCA
 - TES Filer City
 - Morton Salt
 - Martin Marietta

This incorporation process is slightly complicated by the details of the industry involved, so each of those in the list above will be briefly and separately addressed. Table 13 is the result and the value is considered a significant contaminant "Factor" rather than the raw



number of significant contaminants because some of the contaminants are duplicated in the factor, as explained below for the individual sites.

General Chemical-

General Chemical is currently an unused coal pile site, with no combustion. In Table 11 it is listed for only hexane extractables (oil and grease) and PAH. Adding coal piles to its impacts adds arsenic, chromium, mercury and selenium to its potential contaminant list. For purposes of scoring potential contaminant sources, it is necessary to also add PAH, even though General Chemical is already listed as a potential contributor of PAH to the environment. This is because the coal pile is an additional source of PAH, making a separate contribution from the PAH that might have resulted from its oil and grease contributions. This results in an increase in the number of significant contaminants from two (Table 12) to a factor of seven (Table 13). Because of the unknown nature of the subsurface at the site it is not clear whether the oil and grease is still contributing to environmental contamination of the lake, but this is an illustration of the need for assessing the studies that need to be done.

PCA-

PCA burns coal for its energy needs and maintains a coal pile for both its own use and that of T.E.S. Filer City. However, it also has the PCA Lagoon Superfund site that contributes a variety of contaminants. This results in two separate locations, both of which must be considered from the perspective of developing action plans and sampling approaches for source and site characterization and understanding whether additional contaminant management is necessary. Because of the coal pile and the coal combustion, PCA increases from four significant contaminants (Table 12) to a factor of 12 (Table 13), adding another source of arsenic and chromium and two more sources of PAH, mercury and selenium.

T.E.S. Filer City-

The coal pile for T.E.S. Filer City is with that of PCA on PCA property. In essence, any responsibility for the coal pile appears to be PCA's. The T.E.S. facility burns large quantities of coal and sells the electricity that is generated. Because of the burning of this coal this plant goes from two significant contaminants in Table 12 to a factor of 5 (Table 13), which seems to be very conservative considering the large amount of coal that is burned in this operation.

Morton Salt-

Morton salt maintains a coal pile and burns the coal for its processes. This results in the two significant contaminants of Table 12 becoming a factor of ten in Table 13, adding arsenic and chromium as well as two more sources each of PAH, mercury and selenium.

Martin Marietta-

Martin Marietta both maintains a coal pile and burns coal for its industrial processes. The three significant contaminants listed in Table 12 become a factor of 11 in Table 13 because of these processes. Potential sources of chromium are increased from one to two



and PAH increased from one to three. Arsenic is added along with two sources each of mercury and selenium.

Table 13 Significant Contaminant Factors for Industries After Integrating Coal Piles and Coal Combustion

Industry or Process	Significant Contaminant Factor (Coal Piles and Combustion Integrated)
Tannery	2
MWWTP	4
PCA	12
Manistee Plating	1
M. Marietta	11
TES Filer	5
Fablite	1
General Chemical	7
Harland's	1
MASGB	2
Manistee Forge	2
Morton	10
Rengo	2

Figure 50 graphically depicts the relative potential importance of these industries for contamination of Manistee Lake by contaminants deemed most statistically significant (Powell, 2004) based on the Significant Contamination Factor in Table 13.

Figure 50 shows that several of the industries have high scores, but there is a range of values from a score of one to a score of 12 with quite a few near the center of the range. Plotting the scores using a box and whiskers plot (Figure 51) shows that three industries have high scores that fall “outside the box.” The box contains the scores that fall between the first and third quartiles (Q_1 through Q_3). In this case, $\{Q_1 : Q_3\}$ includes the seven midrange scores. The whiskers extend to cover the 10th and 90th percentiles of the data range. Three industries are above the Q_3 value, PCA, Martin Marietta and Morton Salt, while General Chemical sits alone on the upper hinge of the box. PCA is actually a high outlier based on the 90th percentile whisker. This information could be useful for prioritizing site-related investigations.

Tables 11 through 13 and Figures 50 and 51 provide a basis for prioritizing action plan ideas and a sampling approach. Other aspects must also be given some consideration, at least with regard to the contamination of Manistee Lake specifically rather than general environmental contamination. Industry/process location relative to the Lake and its flowpath should be a very significant consideration. All of the industries with scores higher than two (Table 13) are situated directly along the flowpath of the lake, simplifying this issue.

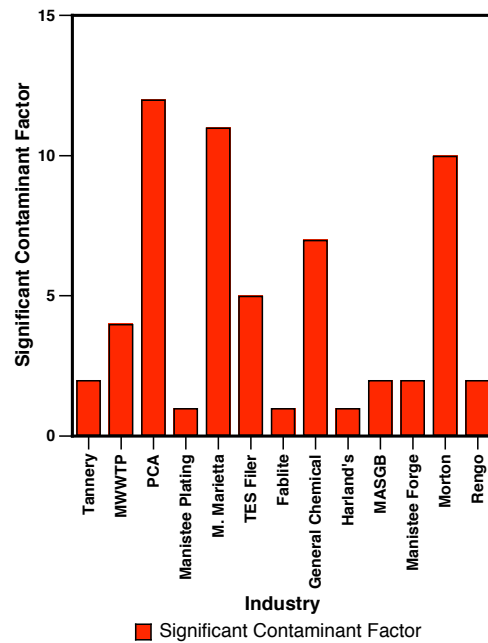


Figure 50 Bar Chart of Industries versus Significant Contaminant Factor

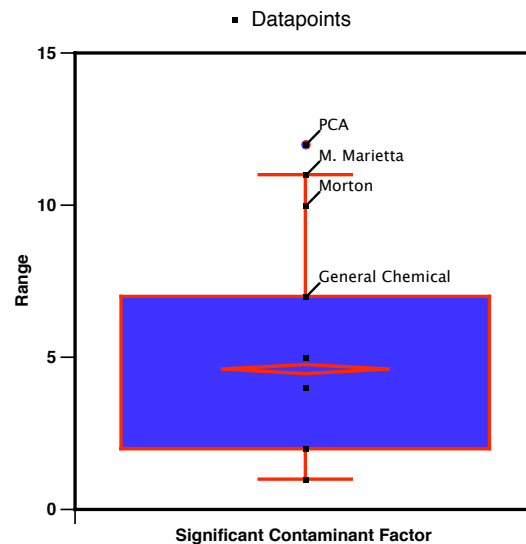


Figure 51 Box and Whisker Plot, Box {Q₁:Q₃}, Whiskers at 10th & 90th Percentiles



Part 5: Issues, Action Ideas and Action Plan Recommendations

Manistee Lake Issues to Be Addressed

The diagram in Figure 52 is the result of “mindmapping”, with conceptualization tools, the issues that need to be addressed with regard to Manistee Lake contamination. The final mindmap displayed lists a variety of issues in five major core issue categories to facilitate discussion and the development of “Action Ideas” for managing the issues. Figure 52 doesn’t necessarily address all possible issues but should delineate many of the major ones and serve as a point of departure for further detailed evaluations.

Action Ideas and Action Plan

The action ideas listed below are the result of brainstorming the issues of Figure 52 for potential solutions to the issues relevant to Manistee Lake and recording them, whether or not they are ideas that can be implemented immediately by the LRBOI, MDEQ, or USEPA. Figure 53 reverses the mindmap of Figure 52, moving the action ideas of this list into the categories where specific solutions to issues are needed (although there isn’t necessarily an exact 1:1 correspondence) and develops an action plan. It should also be noted that some of the ideas are relevant to multiple categories even though listed in only one and in many instances, additional linkages could be drawn.

1. Reassessment of release estimate calculations and actual monitoring rather than estimation whenever possible
2. No exemption from reporting to the TRI without an official notification as to why the report is not necessary that year.
3. More stream, lake, and air monitoring stations are needed.
4. An evaluation of whether industries are using the most current technologies, for example elemental chlorine free (ECF) or totally chlorine free (TCF) processes for PCA, should be done.
5. Lining and diking of the existing coal piles should be done. Leachate collection systems are needed. The coal pile spraying for stabilization should be evaluated.
6. The coal pile at General Chemical should be removed.
7. Better, more centralized maintenance of records, data and reports by all involved agencies & businesses should be implemented.
8. As a Tribal Sovereign Nation, the LRBOI could coordinate with the MDEQ and USEPA to serve as the focal point tribal reservation environmental issues, including Manistee Lake.
9. Educational materials, displays and lectures about Lake Manistee, its history and pollution aspects should be developed to help instill a community sense of pride for the lake.
10. Third party monitoring of the PCA lagoon plume should be done.
11. There should be LRBOI/consultant interaction with the MDEQ on the modeling, GIS and ongoing assessment of the PCA lagoon site situation. Estimates of total contaminant loading yet to enter Lake Manistee should be calculated.



12. Consider active remediation of the PCA Superfund plume based on the results of 3rd party monitoring and modeling/GIS results.
13. Conduct a survey to assess regional awareness of the Lake's condition and gauge thoughts about its future beneficial use.
14. Increase the awareness of cities around Manistee Lake regarding pollution concerns.
15. Obtain a regional agreement of city governments and county regarding future planning for the Lake's beneficial use.
16. Tribe/consultants/environmental organizations prepare a course on accessing and understanding environmental information for interested citizens and local political bodies, using Manistee Lake as the example case.
17. Voluntary reports or notifications provided by the industries when processes are changed that will or might impact contaminant loading, either positively or negatively⁴.
18. Sampling plans to increase understanding of the groundwater, lake water, and lake sediments should be developed and the sampling done.
19. Analytes should be selected and exploratory data analyses (EDA), ternary diagrams, etc., used in an attempt to identify the primary sources of the individual contaminants of concern as a precursor to remediation.
20. A complete risk assessment should be done that addresses not only human health but also the health of benthic organisms, fish, fish-feeding birds, and cultural impacts. Cultural impacts should include impacts to the indigenous peoples, their natural resources and customs, and to the impacts of the contaminated lake on tourism and the local economy.
21. A conceptual model of the lake and surrounding shoreline should be developed and routinely updated as additional or refined information becomes available.
22. Based on the results of sampling, the conceptual model, GIS, etc., a determination should be made as to whether "critically-contaminated" zones (e.g., very high As or PAH, etc.) can be remediated by sediment removal or in situ approaches to increase the rate of developing a healthy lake.

⁴ Perhaps develop some sort of "community good citizen" program that could acknowledge these voluntary notifications and reward the company with some sort of listing/certificate/acknowledgment of participation.

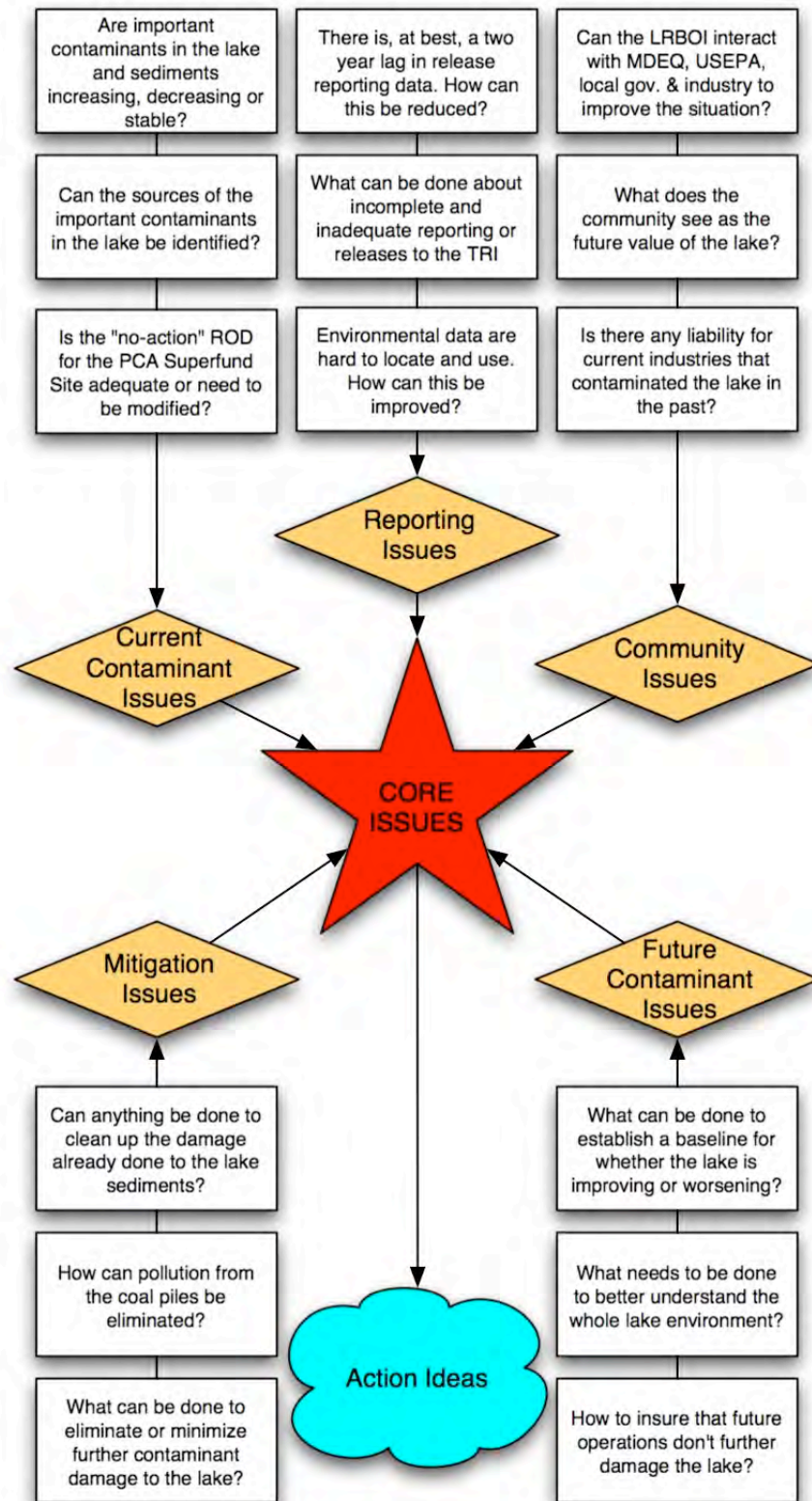


Figure 52 Categorization of Issues for the Formulation of Action Ideas

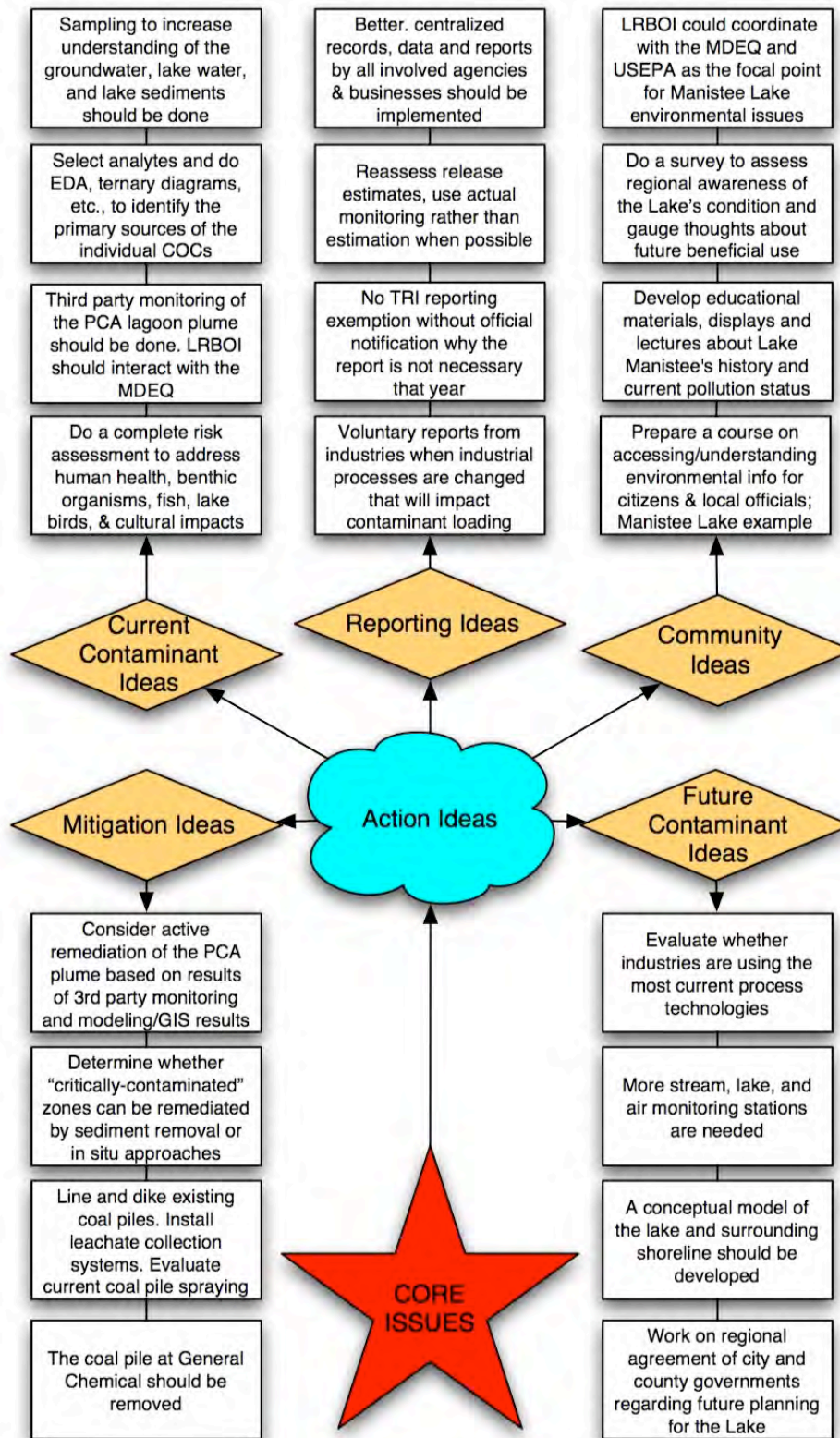


Figure 53 Action Plan Ideas to Address Manistee Lake Issues



Part 6: Sampling Concepts and Approach

Additional sampling is one of the primary needs that must be addressed in order to begin managing most of the Manistee Lake issues, hence a critical component of the action plan. Sampling data is needed as input for several other action ideas that could help deal with further items in the suite of issues but which require more information than is currently available.

In the case of Manistee Lake, sampling needs to be multi-component and multimedia. Also, sampling cannot be just for contaminants of concern but must also include constituents that allow an understanding of the geochemistry of the sampled milieu and provide input for geochemical speciation and transport and fate models. Monitoring such indicator parameters can yield valuable clues about contaminant behavior and its expected impacts.

Sampling Goals

Prior to conducting any sampling operation, the goals of the sampling need to be clearly defined. The following list includes important objectives for further sampling of Manistee Lake and its surroundings:

1. Further delineation of the overall knowledge of contaminants in the lake sediments.
2. Attempt to understand the sources and flow paths of at least the more important contaminants.
3. Understand the biogeochemistry of the lake bottom to understand the speciation (hence the toxicity, availability, etc.) of the contaminants.
4. Determine the impact of the coal piles on lake contamination.
5. Evaluate whether there are “hot spots” of critical contaminants that can be remediated.
6. Evaluate the extent to which the PCA plume (or other unknown plumes) continues to serve as a source of contaminants to the lake.
7. Initiate routine sampling to determine whether overall contamination is increasing or decreasing.
8. Generate input requirements for a risk assessment.
9. Provide input into various forms of modeling: GIS, transport and fate, geochemical speciation.
10. Development of an overall Manistee Lake conceptual model.

Sampling Agreement

Anytime an attempt is made to characterize a site through sampling, it seems that sampling sufficiently to achieve all goals and satisfy all interested parties is never possible. A classic example is when an industry wants to drill fewer wells and sample once per year while state regulators want many more wells and quarterly sampling. Although this example might not be entirely relevant to the case of Manistee Lake, it illustrates that it is important for all participants in the sampling program to understand



the approach and the limitations of that approach for achieving the overall project goals and their personal agendas with regard to the data that will be obtained. Compromises will be necessary. Money and time are usually the primary reasons for compromises in sampling. Additional complicating considerations can be property ownership issues, technological limitations, bad weather, equipment failure, and the unforeseen problems that always arise in field settings. If someone involved in the program has very specific data needs, then it is important that those needs be addressed in the early stages of the sampling design so that these issues don't impact their needs. Ultimately the sampling that will be done should be agreed upon by the participants and preferably, an agreement in principle should be signed by each of them. Probably the best approach to obtaining this agreement and collecting the requisite signatures is to develop written data quality objectives (DQOs) and a Quality Assurance Project Plan (QAPP) for the sampling program. USEPA provides guidance for the development of DQOs under the heading of Systematic Planning at <http://www.epa.gov/superfund/programs/dfa/systplan.htm> and provides a link to QAPP guidance at http://www.epa.gov/quality1/qa_docs.html.

Sampling Recommendations

Because of a relative paucity of information about Manistee Lake in general, the proposed sampling will adopt a fairly thorough approach, especially within Manistee Lake, in order to create a well-developed baseline understanding that can be further refined as time and finances allow.

Sampling Locations

Sampling is needed both on the shore and in the lake. Locations at and near the coal piles need to be emphasized as well as sampling around and in the PCA plume. Because of the shoreline sampling, property issues are likely to be an issue and permissions for sampling will be needed along with the usual permits for drilling, etc.

Manistee Lake Sampling Design and Locations

Sampling in the lake should include (at least) three vertical aqueous samples from the water column, with one at the surface, one at the sediment/water interface, and one midway between the two. Lake sediment samples should be collected immediately below, much as was done during the Rediske et al. (2001) study. All cores should be carefully described by a geologist/sedimentologist during and following collection.

Figure 54 is a subset of data presented in another report (Powell, 2004), incorporating only those contaminants shown in that report to have the most significant impact on the mortality of organisms. It shows Se, As, Cr, PAH, hexane extractables and mercury versus sampling location number and the mortality of two test species, *H. Azteca* and *C. Tentans*. Although high levels of contaminants and mortality are shown throughout Lake Manistee, with the exception of the control locations 1 and 14, there appear to be peaks and declines down the length of the lake. Peaks occur at locations 5 and 6, 10 and 11, and 13. The map of figure 55 is adapted from Figure 2.1 in Rediske et al. (2001). It is interesting to note in Figure 55 that these peak locations correspond exactly with the



immediate vicinity or directly downgradient of coal storage piles along Manistee Lake. These coal storage piles are labeled with “C” in Figure 55, with one label for each pile.

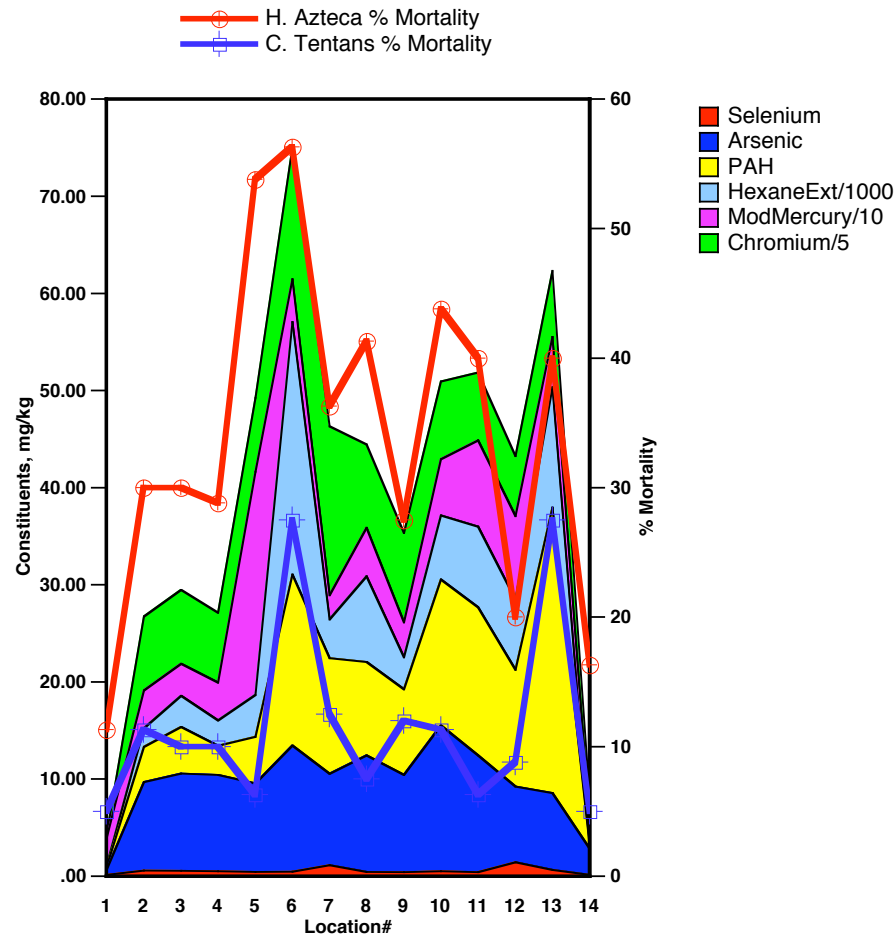


Figure 54 Significant Contaminants versus % Mortality and Location Number

Figure 55 also shows our proposed locations for sample collection in Manistee Lake. Because of the observations of contaminant peaks in Figure 54 and coal piles in Figure 55, sampling is somewhat focused around these locations. Sampling is also concentrated in the areas where it is believed the PCA Superfund lagoon plume discharges into the lake.

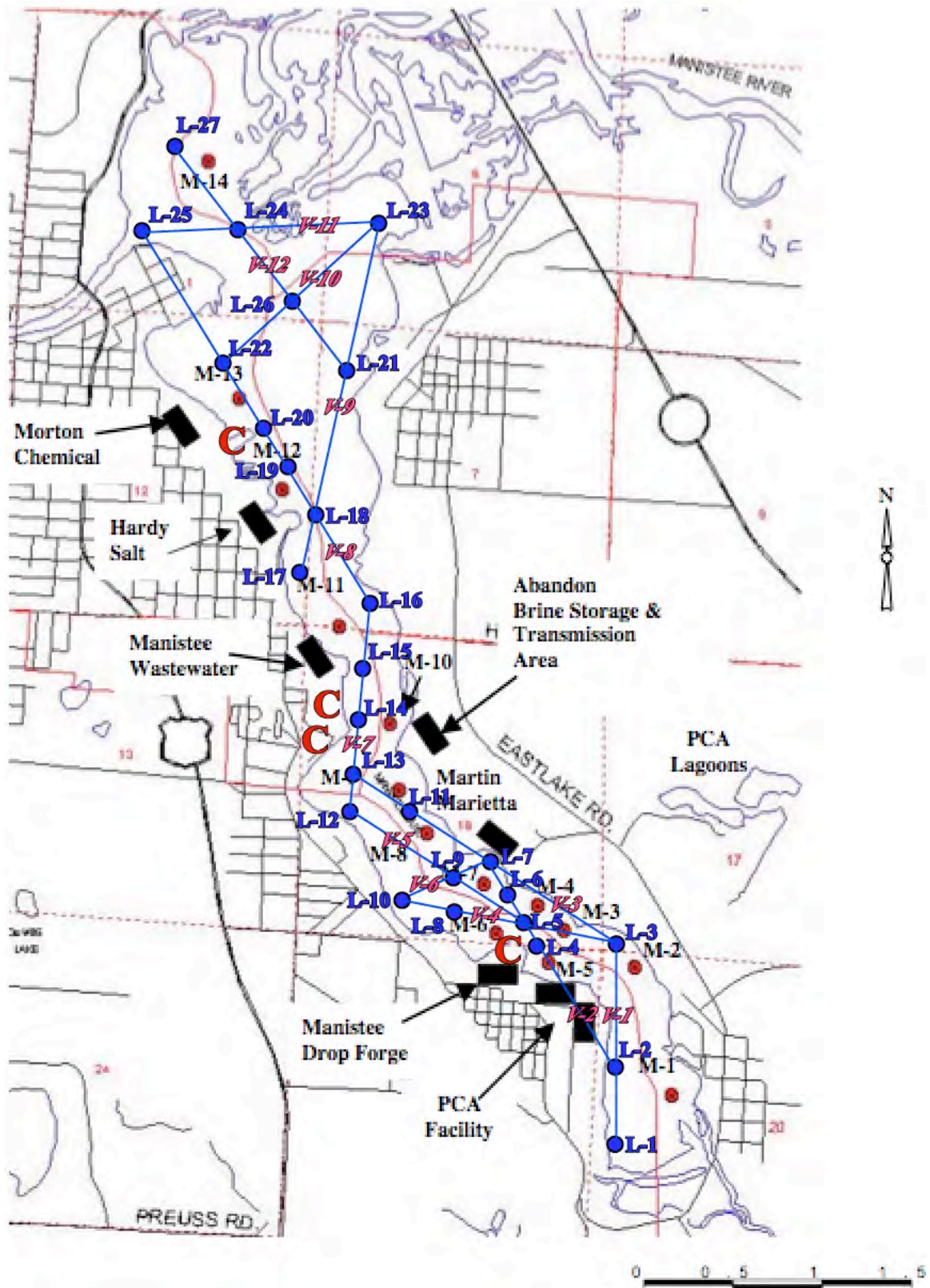


Figure 55 Map of Proposed Sampling Locations and Transect Vectors



Sampling in Manistee Lake is proposed for 27 new locations. These are labeled as L-1 through L-27 in Figure 55. This number of samples provides good lake coverage, especially in conjunction with the Rediske et al. (2001) studies (locations labeled “M-#” in the figure).

A new and slightly unusual approach is being proposed in this sampling design. The sampling locations have been established in a manner that defines 12 linear transects, or vectors, throughout the two-dimensional geometrical space that defines the surface of Manistee Lake. Many of these vectors begin upgradient to and end downgradient from a potential contamination source, such as a coal storage pile or the PCA plume discharge. In these cases certain chemical concentrations down the length of the vector might begin low (e.g., V-2:L-1) and end high (e.g., V-2:L-7). This could yield information about the contribution of the potential source to the downgradient contaminant loading of the lake.

Although the vectors are one-dimensional, samples are to be collected throughout the water column and into the sediments at each location; hence, each vector can be considered to represent a two-dimensional vertical plane. These are labeled V-1 through V-12 and each consists of a minimum of three and up to five sampling points to define the vector. Many of the sampling points help define more than one vector, allowing the observation of additional potential relationships. For example, L-3 and L-7 each lie on three vectors. The idea behind this is to better allow the resultant data for each sampling point to be evaluated specifically in relationship to the other sampling points in its line, in addition to inclusion in routine GIS and modeling⁵. This will be approached and considered in several ways:

1. The distances and depths can be considered as linear relationships and determination made as to whether chemical concentrations at these points are:
 - Unrelated to the distance/depth vector and source relationships
 - Related to input from potential contamination sources along the length of the vector but not necessarily to the other vector sampling points
 - Related in a linear fashion to the vector location (after considering potential input factors along the length)
 - Related in a nonlinear (but mathematically describable) way to its vector location (after considering potential input factors along the length)
2. The data will be evaluated using methods, particularly linear regressions, etc., in exploratory data analysis programs, such as DataDesk 6.2 (Data Description, 2003, <http://www.datadesk.com>) and Aabel 1.5.8 (Gigawiz, 2004, <http://www.gigawiz.com>).
3. Because appropriate geochemical data will be collected, data can be input into the equilibrium geochemical speciation model Minteq A2. This will increase

⁵ The author of this report is aware that the chemical relationships within these vectors will not necessarily be linear or possibly show any sort of predictable trend. However, some of them might (even if only in a subset of the points on a vector, for example, three or four out of five) and, if so, provide valuable information about the status of certain contaminants over a range of distance and transport time.



- understanding of the status of various contaminants (and other chemicals) in the sediments, e.g., the concentrations of the oxidation states of the various contaminant species and whether they are present in the dissolved phase or the solid phase as precipitates or adsorbed species. This can yield significant information about the transport of the contaminants and their bioavailability.
4. Sampling points along a vector (after considering potential input factors along the length) will be considered as though each is a batch reactor at various temporal states in an approach to equilibrium. That is, distance from a source or down the length of a vector is related to time, which is the basis for describing reaction rates. Should contaminant transformations along the length of the vector be consistent (with regard to species formation, adsorption, precipitation, etc.) then it should be possible to determine reaction rates for various significant contaminants introduced into the lake system. Most models for environmental reactions are reasonably described by pseudo-first order reaction kinetics of the form:

Equation 1 First Order Kinetic Equation Describing the Reaction $A \rightarrow B$

$$\log[A]_t = \log[A]_0 - \frac{kt}{2.303}$$

Where $[A]$ is the concentration of chemical species A at any time, t , 2.303 is the value that converts natural logarithms to base 10 logarithms, and k is the rate constant.

This approach is somewhat analogous to methods that have been used to calculate rates of natural attenuation of contaminants in groundwater.

5. The linear transects also form several triangles, allowing the concentrations to be integrated within the volumes defined by these triangles. These can then be plotted and “hot spots” observed for potential remediation consideration.
6. Information obtained from these evaluation procedures will be used to develop the geochemical portion of a conceptual model of Manistee Lake.

The proposed sampling locations can be refined as necessary during the preparation for the actual sampling and during development of the QAPP but major alterations in the overall geometry of their collection might require reconsideration of the data reduction approaches with a concomitant reduction in comprehension of the environment. During preparation for the actual sampling these locations should be identified using GPS coordinates and the actual sampling locations must be identified by GPS coordinates when sampling is conducted. When combined with the previously sampled locations from Rediske et al. (2001) these sampling locations and data reduction approaches should provide a very good overview of the geochemical status of Manistee Lake.

Shoreline Sampling

Sampling along the shoreline needs to include surface soils, vadose zone core, saturated zone core, and groundwater. Table 13, Figures 50, 51 and 54 provide guidance as to where some of this sampling needs to occur:

- Under and around the four coal piles maintained by



- General Chemical
 - PCA for both TES and PCA
 - Morton Salt, and
 - Martin Marietta
- Along the length and width of the PCA plume and within and around the old lagoons.⁶ This should include sampling/monitoring between the Martin Marietta facility and Lake Manistee along the most likely flowpaths toward the lake.
- Three uncontaminated upgradient locations should be sampled to establish good quality control on background chemical concentrations.

Additional sampling of soils and groundwater should be considered in the following areas:

- Between the Manistee Drop Forge facility and the lake
- Between Morton Salt and the lake and between the facility and its coal pile
- Between the Manistee Waste Water facility and the lake
- Around the old Martin Marietta plating facility

Phases for Sampling

Previous studies have sampled the sediments from Manistee Lake. For the proposed sampling the phases studied should be increased to include:

- Lake sediments (as per Rediske et al., 2001) from cores and ponar samples
- Interstitial waters from the collected lake sediment cores
- Overlying lake water column waters, and
- Vadose zone and groundwater in various locations along the shoreline of the lake.

Analytes

The Rediske et al. (2001) report presented a fairly thorough list of constituents of concern that were analyzed during their survey of the Manistee Lake sediments. These should be retained (to the extent possible considering the various phases to be sampled) for the proposed sampling study with the addition of the analysis of tannins and lignins and the geochemical indicator parameters that will be addressed later in this section. Their analytes included:

Arsenic, Cadmium, Lead, Selenium, Aluminum, Barium, Calcium, Chromium, Copper, Iron, Mercury, Magnesium, Manganese, Nickel, Zinc, Total Organic Carbon, USEPA Semivolatiles (Method 8270), and Resin Acids

⁶ This may be already satisfactorily done but, as of this writing, the author of this report has insufficient information to judge whether the plume has been adequately delineated, whether the locations immediately within and sufficiently upgradient from (or radial to) the lagoons have been characterized, whether constituents needed to understand and model system geochemistry are being collected, and whether preferred sampling approaches (i.e., low-flow rate purging and sampling) are being used. Personal communications with the MDEQ have indicated that additional effort is being made to understand the PCA lagoon plumes but it has not yet been possible to meet and go over all the details. This would need to be coordinated prior to finalizing any shoreline sampling plans.

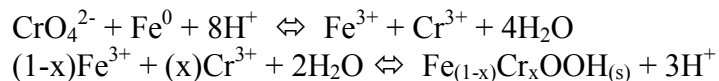


It is often not realized that it is as important to analyze for major geochemical parameters as it is to analyze for the contaminants of concern. This is because, in general, without understanding the geochemical environment in which the contaminants are present it is impossible to understand their toxicity, bioavailability, fate and transport. The chemistry of two contaminants of importance to organism mortality in Manistee Lake, chromium and arsenic, can be used to illustrate this fact while providing useful information about their toxicity and behavior.

Chromium Behavior

The behavior of chromium is less complicated than that of arsenic, having only two dominant oxidation states in aqueous systems, Cr(III) and Cr(VI) and relatively simple complex formation, but these two oxidation states represent extremely different mobilities and toxicities. Trivalent Cr(III) is relatively non-toxic and a micronutrient. It forms sparingly soluble hydroxide precipitates under conditions prevalent in most surficial aquifers and is also readily adsorbed by some minerals. Hexavalent chromium, Cr(VI), is a known carcinogen, which forms relatively soluble precipitates, resulting in the persistence of relatively high concentrations of dissolved Cr(VI) in affected aquifers (Palmer and Puls, 1994; Puls et al., 1995). Cr(VI) is usually speciated as chromate, CrO_4^{2-} , under typical ground water pH and Eh conditions. This results in a high degree of mobility for Cr(VI) because anions are not readily adsorbed to predominantly negatively-charged soil and aquifer materials. Treatments to remove Cr(VI) from groundwater typically use reduction to Cr(III) and precipitation of insoluble Cr(III) hydroxide precipitates (Powell et al., 1994; Powell et al., 1995). Equation 2 illustrates the reduction and removal of toxic and soluble chromate from solution by elemental iron and its incorporation into a far less toxic precipitated chromium iron hydroxide solid solution phase. Chromate can also be reduced and immobilized by the Fe(II) present on mineral surfaces in reducing environments (Palmer and Puls, 1994). Because of these oxidation state transitions it is important to determine the conditions under which samples containing chromium were collected because it makes all the difference in whether the element is toxic and whether it is mobile.

Equation 2 The Reduction and Precipitation of Chromate by Elemental Iron



Arsenic Behavior

The behavior and toxicity of arsenic in the natural environment is extremely complex and variable and depends upon the geochemistry where it is found. Figure 56 (Powell and Puls, 2000) illustrates the complexity of this toxic element. In the natural environment arsenic oxidation states include -3 (arsine), +3 (arsenites), +5 (arsenates), +1 (arsonium metals), and 0 (native arsenic), in order of decreasing toxicity (Welch et al., 1988).

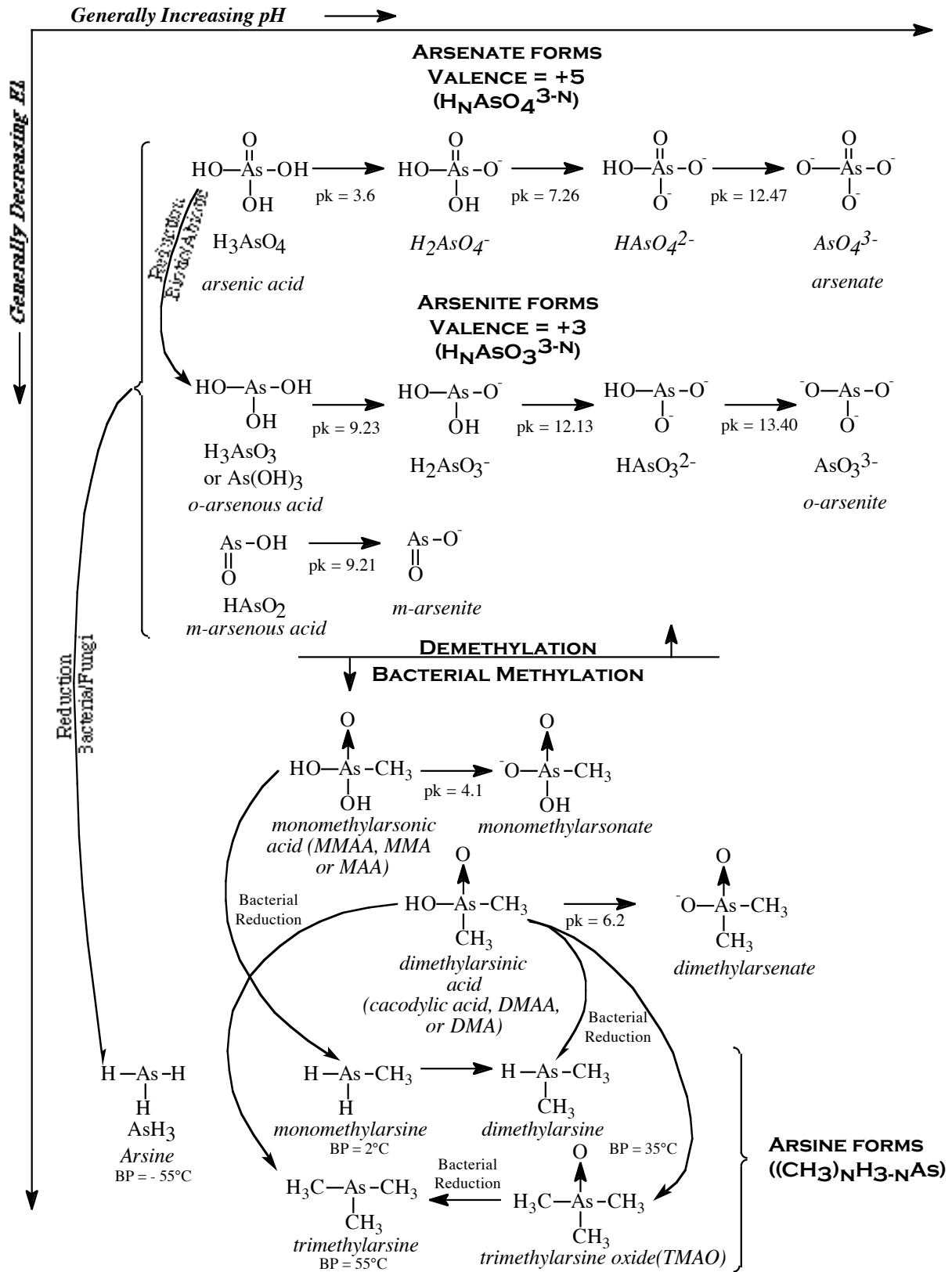


Figure 56 Speciation of Arsenic Under Various Conditions



The toxic effects of arsenic exposure depend upon the form of the arsenic, the concentration of arsenic in the body, and the period of exposure. In addition to acute arsenic poisoning, which can result in widespread damage to the organ systems and death, exposure to arsenic can cause gastrointestinal effects, respiratory effects, dermatologic effects, hematologic effects, hepatic effects, renal effects, cardiovascular effects, neurologic effects, mutagenic effects, and probably carcinogenesis (Morton and Dunnette, 1994).

Arsenite is usually considered to be more toxic than arsenate. Arsenite has been stated to be 25-60 times more toxic than arsenate by some sources (Korte and Fernando, 1991) due to its strong binding to thiol groups (Prasad, 1994). Others have stated that there really is no great toxicity difference between these species of inorganic arsenic (Yamauchi and Fowler, 1994) and both should be considered highly toxic. The biologically methylated As(V) species are less toxic by two orders of magnitude or more (Yamauchi and Fowler, 1994) than the inorganic species. There is general agreement that the toxicity of arsenic species follows the order, from most to least toxic, of:

arsines > inorganic arsenites > organic trivalent compounds (arsenoxides) >
inorganic arsenates > organic pentavalent compounds > arsonium compounds >
elemental arsenic (Eisler, 1994).

Whether or not arsenic is transported or bioavailable in subsurface systems depends on the speciation of the arsenic and its interactions with the organic, microbial and mineral phases of the soil, sediment or aquifer material. Major factors influencing the bioavailability of arsenic in the subsurface are pH and Eh, other reactive solution species such as Fe, Mn and S, competing anions such as PO_4^{3-} , and adsorptive/desorptive interactions with mineral phases, in particular with hydrous iron oxides, hydrous manganese oxides, phyllosilicate clay minerals, and calcite, as well as organic coatings, humic materials, and fulvic acids. Unfortunately, from an environmental perspective, the reactions and interactions of arsenic are very complex over the range of what can be considered “typical” or normal environmental conditions. This makes it difficult to predict arsenic transport and fate in soils and aquifers with any certainty except under conditions of both high Eh and pH, where arsenate should predominate (Figure 56) and will probably become immobilized. Because of these considerations, arsenic is a very good example of why it is necessary to measure several other constituents that serve as geochemical indicator parameters to allow understanding of the status of the arsenic in the environment.

Geochemical Indicator Parameters

It is important to determine constituents and parameters that provide information about the redox (oxidation-reduction) conditions, speciation state and complexation of the chemical constituents of interest, as illustrated for chromium and arsenic. This requires knowledge of the major constituents in the water collected and knowledge of certain of the minor constituents is also helpful. Table 14 lists parameters that are of critical importance to accurately measure in water collected from sediments and groundwater and some of those that are desirable. To the extent possible these constituents should also be



measured in surface waters. Several of these (DO, Eh, $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio) are difficult to nearly impossible to measure accurately in grab samples or batch containers open to the atmosphere and appropriate collection, such as low flow rate purging and sampling (Powell and Puls, 1997), for analysis of these values needs to be given consideration.

Table 14 Geochemical Indicators of Critical and Desirable Importance

Critical Parameters/Constituents	Desirable Constituents
pH	Na^+
Dissolved Oxygen (DO)	K^+
Oxidation Reduction Potential (Eh)	$\text{Fe}^{2+}/\text{Fe}^{3+}$
Sulfate (SO_4^{2-})	Mg^{2+}
Chloride (Cl^-)	Mn^{2+}
Carbonate/Bicarbonate ($\text{CO}_3^{2-}/\text{HCO}_3^-$)	Temperature
Alkalinity	
Calcium (Ca^{2+})	Turbidity
Conductance	Ammonia
TOC	

Many of the parameters listed in Table 14 are needed to run geochemical speciation programs such as MinteqA2 and PHREEQC, which allow predictions of speciation, precipitation, adsorption, and transport of the constituents of concern.

Sample Acquisition

Manistee Lake Sampling

The ASTM provides guidance on sampling lake sediments (ASTM, 1995). Sampling in Manistee Lake will be done from a boat-mounted coring/sampling rig. Further consideration needs to be given as to whether this rig will use a VibraCore core sampling device, as used by Rediske et al. (2001), a boat-mounted GeoProbe modification that allows the installation of screened water sampling points at depth in the sediment⁷ as was done along the shoreline of Lake Michigan (The Probing Times, 2004), or possibly both, so that both sediment cores and quality below-lake sediment water samples can be acquired. Otherwise the interstitial waters might have to be collected for analysis from the cores rather than as independent samples. A Ponar sampler for the acquisition of surface sediment grab samples should also be used. Water column lake samples above the selected core locations should be acquired using standard lake water collection methods. Flow rates at these locations should also be acquired.

Shoreline Sampling

Shoreline vadose zone and groundwater investigations and sampling should be done using direct push-tool technology such as the Geoprobe. This allows both the collection of core and the installation of either temporary water sampling points or permanent

⁷ Assuming Geoprobe considers sampling possible at this depth below the lake surface using their equipment mounted on a boat and whether the device configured in this way could be used to collect sediment core as well. This will need to be further investigated.



monitoring well installations. The ASTM provides guidance on the collection of both soil/aquifer material core samples (ASTM, 1998) and groundwater (ASTM, 2002) using such push tool technologies and information is also available from the companies that provide these devices.

Analytical Methods

Samples should be preserved, stored, transported, digested and analyzed using the standard methods that have been developed by numerous organizations such as ASTM, USGS and particularly the USEPA. These methods are readily available and most analytical laboratories are familiar with their application and use, so there is little value in re-listing them in this report. If an analysis is needed for which there is no standard approved method, a literature search should be done to locate the best method available for that analysis at that time. The methodology used for each analyte should be recorded, as should any planned divergence from the approved method and any errors that are observed. A complete .pdf list of USEPA methods, organized by analyte is available at <http://www.epa.gov/epahome/index/>. The laboratory chosen to conduct the analyses should be very familiar with the methods needed and all typical laboratory quality control procedures (replicates, blind samples, spikes, etc.) should be used.

Biological Studies

The biological studies, performed by Rediske et al. (2001), were very successful and included:

1. Total organism counts,
2. Species counts and
3. Toxicity studies that used 10-day survival tests for
 - a. the amphipod *Hyalella azteca* and
 - b. the dipteran *Chironomus tentans*.

These data were quite useful for observing toxicity trends versus contaminant concentration and carrying out exploratory data analyses to better understand the most highly impacted portions of Lake Manistee and the primary toxicants causing these impacts. It is highly recommended that these same organism studies be done for the sampling study proposed in this report.

Part 7: Contaminant Management Approaches

Because definitive proof of the source terms for the most important contaminants in Manistee Lake has not yet been developed, absolute statements about the best approaches for contaminant management are beyond the scope of this report. Clues to the likely sources are inherent in the presented data but further investigations, as described in the previous sections of this report, are needed. However, there are industrial practices around the lake that could be modified to reduce risk of further contamination and potentially exert a positive impact towards the gradual reduction of contaminant concentrations in the water column and sediments.



Coal Storage Piles

None of the coal storage piles along the shores of Manistee Lake appear to be constructed to modern standards, i.e., they are neither lined nor diked. As previously related in Part 6 of this report, Figure 54 shows a close correspondence between coal storage pile location, sediment contamination and organism toxicity. This correspondence could be due to erosion of the undiked coal piles into the lake, surface runoff of water from rainfall after percolation through the coal piles, and/or a result of percolation of water through the coal piles followed by infiltration into the vadose zone and finally into the groundwater where it discharges into the lake. Because of these potential problems it would be prudent to both line and dike these coal impoundments. Because the General Chemical site coal pile is unused it should be removed.

If there is a significant burden of coal pile materials extant on the bottom of Manistee Lake⁸, an evaluation is needed to determine which course of action is less damaging to the environment, a) dredging the materials up for removal or b) allowing them to remain in the lake. A number of issues would need to be considered:

1. The total mass and volume of the coal materials in the lake
2. The distribution area of the coal materials on the lake bottom
3. The contaminants remaining in the coal materials and their leachability
4. The toxicity of these contaminants
5. The location of sensitive fish habitats relative to the proposed dredging
6. Lake flow rate through the proposed dredging area (turbidity/contaminant distribution considerations).

PCA Superfund Site Plume (and other potential plumes)

Based on the findings of the sediment sampling study and the data previously evaluated from that study (Rediske et al., 2001 and Powell, 2004, respectively) and in this report it is fairly certain that the PCA Superfund Site contaminants have impacted Manistee Lake. It is the ongoing level of that impact that is uncertain at this point. Studies and GIS mapping are underway at the Michigan Department of Environmental Quality that should provide additional information about the extent of ongoing contamination from this source. In addition, this report recommends additional sampling of Manistee Lake in this area as well as an assessment by the author of sampling along the shoreline to determine whether additional sampling points in the groundwater would be beneficial.

Should it be determined that the PCA groundwater plume persists and will continue to persist as a long-term source of contaminants to Manistee Lake, there are remedial options that are available. Probably the best known of these remedial approaches are pump and treat (P&T) technologies but potentially the most effective for this scenario would be to use a permeable reactive barrier (PRB) across the plume. The treatable contaminants and advantages and disadvantages of these two remedial approaches have

⁸ Coal materials in certain areas on the bottom of Manistee Lake have been observed by divers (personal communication). The significance or extent of this observation is unknown to the author of this report.



been addressed (Powell et al., 1998; Powell and Powell, 1998; Powell and Puls, 2003), as has a comparison of the relative costs of the two approaches (Powell et al., 2002).

Salt and Chemical Brines

The effort by MDEQ and others to locate and cap/plug leaking brine wells and piping in the lake should be continued. The level of effort being exerted to address all land surface sources of salt (impoundments, dump sites, leaking pipes in current use, etc.) that might be impacting the lake by runoff or seepage into groundwater should be evaluated and an effort made to eliminate or at least monitor the impacts of these sources. Companies extracting these brine minerals should be encouraged to update equipment to avoid leaks and ruptures and to make an increased effort to account for the quantities of these materials pumped to the surface relative to the amounts incorporated into products and discarded. Adequate disposal and transfer records are needed⁹.

Airborne Lake Contaminants

Part 3 of this report inventories a number of industries that emit large quantities of airborne pollutants, many of which are likely to contribute to pollution in Manistee Lake. Foremost among these sources are the several industries that burn coal to power their own industrial processes (Morton Salt, Packaging Corporation of America, Martin Marietta) or to sell power to the electrical grid (T.E.S. Filer City Station).

A conservative estimate for the combined output (pounds) to the atmosphere of these four facilities during the period 1987 through 2002 is shown in Table 15.

Table 15 Reported Air Releases by Coal-Burning Facilities at Manistee Lake, 1987-2002, in pounds

Facility	Air Releases 1987-2002, lbs
Morton Salt	53,520
PCA	4,152,188
Martin Marietta	783
T.E.S. Filer	109,228
Total	4,315,719

This estimate of 4,315,719 pounds of total emissions is considered conservative by the author because these figures are summed from the TRI values reported by the industries themselves, in addition to the fact that in many instances there were periods of time with no reporting at all. Morton salt reported for the period 1987 through 1994 then did not report again until 2001 and 2002 (at which time emissions increased greatly). PCA reported to the TRI for this entire period for certain compounds but not for every chemical listed for every report. For example, lead compounds were not reported as released to the air until 2001, whereas fugitive ammonia was reported for the entire 16

⁹ Internal records of transfer and disposal may already be adequate. The author has not reviewed these sorts of materials and makes this recommendation in the event that one or more companies are not carrying out this type of recordkeeping.



years. Martin Marietta reported air emissions from 1987 through 1995 but there are no records in the TRI of reporting since that time. T.E.S. Filer City Station has reported since 1998 but shows no prior reporting of releases in the TRI. Reports submitted to the TRI by these industries need to be thorough, complete and cover every year of operation. This appears to be an area where important improvements are needed.

The primary observation to be made from these data is that there is a great deal of air pollution occurring in the vicinity of Manistee Lake as a result of emanations from coal-burning facilities. These emissions have been occurring at a very conservative mean rate of 269,732 lbs per year, some portion of which has impacted the water quality in Manistee Lake. Because of this and the apparent issues with the coal pile storage areas, it is the recommendation of this report that no additional coal-burning facilities be located in this vicinity until further study and air quality monitoring can be done and reporting improvements implemented.

In the context of helping to remediate the current polluted lake situation, industries that are using coal combustion in this area should be encouraged to implement the best technologies that are applicable to reducing their air emissions. Ideally these would be maximum achievable control technologies (MACT) but, at a minimum, best available control technologies (BACT) should be implemented.

Summary and Conclusions

Please refer to the Executive Summary section to avoid unnecessary repetition in this report.

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