Health Consultation

NATIONAL GYPSUM CEMENT KILN DUST PILE,
ALPENA (ALPENA COUNTY), MICHIGAN.

Prepared by the
Michigan Department of Community Health

JUNE 11, 2009

Prepared under a Cooperative Agreement with the
U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Agency for Toxic Substances and Disease Registry
Division of Health Assessment and Consultation
Atlanta, Georgia 30333

Health Consultation: A Note of Explanation

A health consultation is a verbal or written response from ATSDR or ATSDR's Cooperative Agreement Partners to a specific request for information about health risks related to a specific site, a chemical release, or the presence of hazardous material. In order to prevent or mitigate exposures, a consultation may lead to specific actions, such as restricting use of or replacing water supplies; intensifying environmental sampling; restricting site access; or removing the contaminated material.

In addition, consultations may recommend additional public health actions, such as conducting health surveillance activities to evaluate exposure or trends in adverse health outcomes; conducting biological indicators of exposure studies to assess exposure; and providing health education for health care providers and community members. This concludes the health consultation process for this site, unless additional information is obtained by ATSDR or ATSDR's Cooperative Agreement Partner which, in the Agency's opinion, indicates a need to revise or append the conclusions previously issued.

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Acronyms and Abbreviations

ACVB	Alpena Convention & Visitors Bureau
ATSDR	Agency for Toxic Substances and Disease Registry
AWTP	Alpena Water Treatment Plant
BBL	Blasland, Bouck, and Lee, Inc
CKD	cement kiln dust
CoA	City of Alpena
DLZ	DLZ Michigan, Incorporated
EPA	Environmental Protection Agency
g	gram
GC	groundwater contact
GMLLP	Google Maps Latitude, Longitude Popup
GSI	groundwater surface water interface
HNV	human noncancer value for drinking water
IDW	industrial drinking water
IoM	Institute of Medicine
IRI	Interim Response Investigation
IRIA	Interim Response Investigative Action
kg	kilogram
L	liter
MDCH	Michigan Department of Community Health
MDEQ	Michigan Department of Environmental Quality
MFCMP	Michigan Fish Consumption Monitoring Program
MI	Michigan
MRL	minimal risk levels
MSU	Michigan State University
ND	not detected
NS	not sampled
NT	not tested
ppm	parts per million
RCRA	Resource Conservation and Recovery Act
RDW	residential drinking water
RfD	reference dose
RRD	Remediation and Redevelopment Division
TBNMS	Thunder Bay National Marine Sanctuary
U.S.	United States
USGS	United States Geological Service
µg	microgram
µg/L	micrograms per liter

Summary

The National Gypsum Cement Kiln Dust (CKD) pile (site) is located along Thunder Bay, Lake Huron in the City of Alpena (Alpena County), Michigan. The pile is waste from cement production, CKD, which was dumped at the site, beginning in the 1950s. The CKD pile extended offshore, into the bottom land of Thunder Bay. The cement waste contains metals and other inorganic contaminants that have leached into the groundwater beneath the pile, which has discharged into Thunder Bay and have leached directly into Thunder Bay surface water from direct contact with CKD in areas under the pile that were once part of the bay. Surface water within Thunder Bay is the source water for Alpena's drinking water.

Although contaminants from the site are entering Thunder Bay, many of the contaminants are not detectable, or are at concentrations below acceptable limits in the public water supply. The main contaminants from the CKD pile (antimony, arsenic, cadmium, mercury [inorganic], thallium, lead, and copper) are not detectible in the source water from the Alpena Water Treatment Plant. Sodium and sulfate levels are much lower (around 50 to 175 times lower, respectively) in water from the water treatment plant compared to groundwater samples collected from the CKD pile. The Michigan Department of Community Health (MDCH) concludes that drinking the City of Alpena public water supply will not harm people's health.

One of the contaminants, mercury, is converted to methylmercury in the environment and can build up in fish. People that eat the fish from Thunder Bay may be exposed to this form of mercury. Fish from Thunder Bay and the Thunder Bay River have been sampled between 1986 to 2007. Of the fish tested, only seven walleye and one channel catfish had levels of mercury that are greater than or equal to the screening value for consumption restrictions. Currently, there are no consumption restrictions on fish from Thunder Bay due to mercury. MDCH concludes that eating fish from Thunder Bay will not harm people's health.

Groundwater with elevated pH levels, from under the CKD pile, is venting into Thunder Bay. However, locations and size of the venting groundwater areas, when venting occurs, and the exact pH are unknown with open water conditions. Elevated pH, up to 12.14, has been measured in the surface water offshore of the CKD pile, when the bay was covered in ice. People who have direct contact with water with a high pH may have irritation or burns at the area of contact. It is unknown if swimmers, divers, and people that could be walking along the shoreline have been or will be in the area or ever encounter localized areas of high pH water in Thunder Bay near the CKD pile. MDCH cannot currently conclude whether people have had, are having, or will have direct contact with venting groundwater in Thunder Bay and so cannot conclude whether there is harm to people's health.

Purpose and Health Issues

The Michigan Department of Environmental Quality (MDEQ) requested an evaluation of exposure and public health implications of the National Gypsum Cement Kiln Dust (CKD) pile (site) in the City of Alpena, Alpena County, Michigan. Areas of high pH and elevated inorganic contaminants have been identified in the ground and surface water under and around the CKD pile.

This health consultation evaluates the National Gypsum CKD pile in the City of Alpena. Multiple contaminants are present in the CKD material and have leached into the ground and surface water surrounding the pile. This includes areas of high pH in Thunder Bay water. Direct contact with material containing high pH can cause skin or eye irritation and even burns.

Background

The National Gypsum Cement Kiln Dust (CKD) pile is in the City of Alpena, Alpena County, Michigan (Figure 1). It is located along Thunder Bay, on the west shore of Lake Huron. This pile began in the 1950s as a dumpsite for CKD, a by-product of cement production. It covers over 80 acres and rises as high as 59 feet above the lake level. The CKD pile stretches 5,400 feet along the shore. To the south of the pile is Thunder Bay. LaFarge Corporation cement plant is to the west. Both Thunder Bay and LaFarge property are on the eastern side of the pile. A road, Ford Avenue, and a railroad right-of-way are on the northern border of the pile. The LaFarge rock quarry is on the other side of the road and railroad. This quarry is currently in use. The quarry surface water outfall, which drains into Thunder Bay, is to the east of the CKD pile. The Thunder Bay River discharges southwest of the site into Thunder Bay.

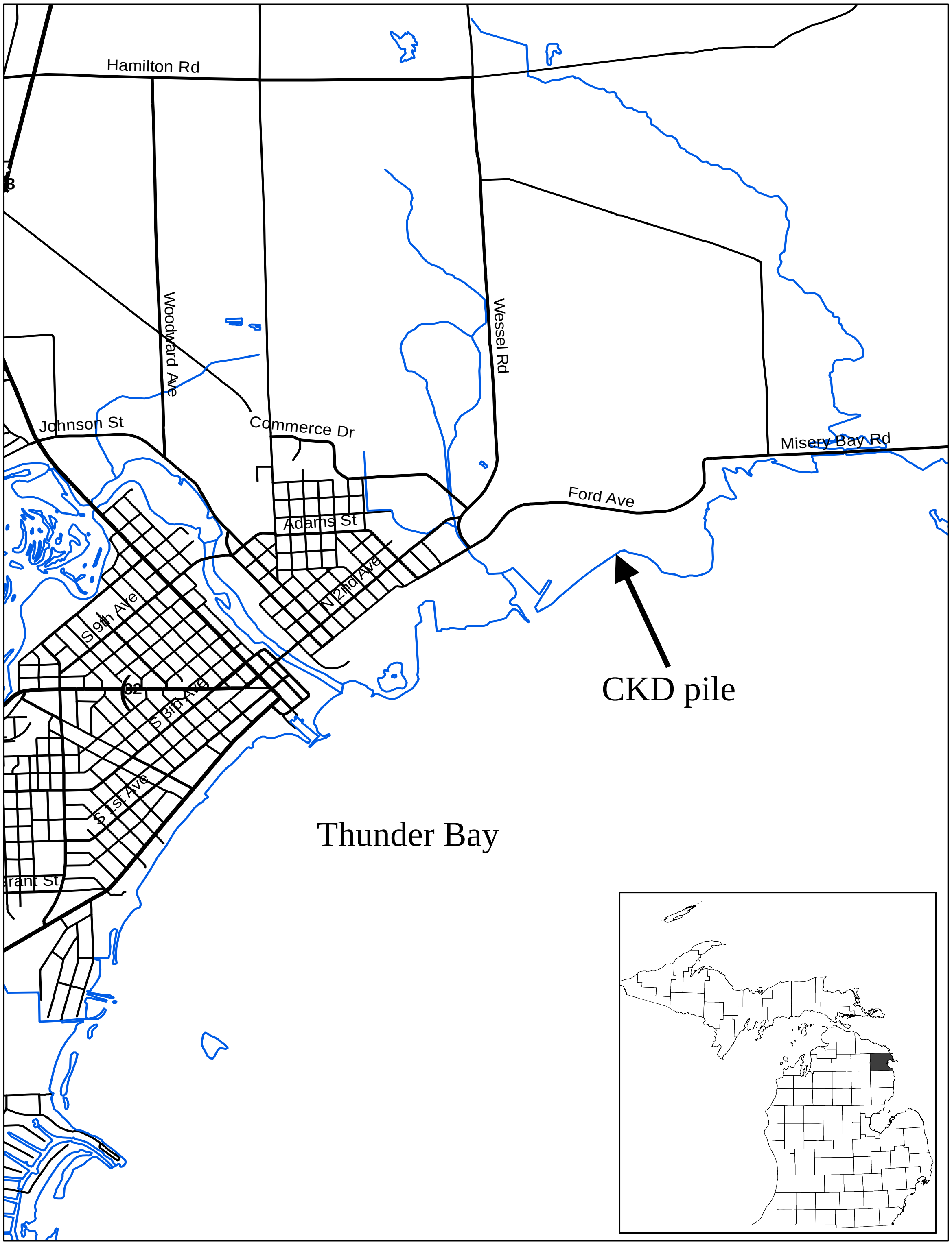
The City of Alpena has over 11,000 residents and visitors (CoA 1998). There are numerous beaches and recreational water usages (ACVB 2006) of Thunder Bay and other areas of Lake Huron. One recreational use of Thunder Bay is the National Marine Sanctuary. This Sanctuary contains a Shipwreck Cemetery. People can take a diving or snorkel tour of wrecked ships in the waters of Thunder Bay and Lake Huron (TBNMS 2008). Several of the wrecked ships (the Rend, Shamrock, and OT Flint) are in Thunder Bay, within five miles of the shore of the CKD pile. One shipwreck, the Rend (bow), is within one mile (0.47-0.65 miles) of the shore along the CKD pile. (Distance, using latitude and longitude, was calculated using the Great Circle Calculator by Williams [1997].) People touring the Rend wreckage, by diving or snorkeling, may go even closer to the CKD pile. Table 1 provides latitude and longitude of four locations at the edge of the CKD pile along Thunder Bay and of the closest shipwrecks in Thunder Bay to the CKD pile.

Table 1: Decimal latitudes and longitudes of the National Gypsum CKD pile in Alpena (Alpena County), MI along the shore and of several shipwrecks in Thunder Bay.

Location	Latitude (decimal)	Longitude (decimal)
CKD 1 (west shore) [a]	45.069762	-83.40065
CKD 2 (center shore) [a]	45.069278	-83.395243
CKD 3 (east shore) [a]	45.069156	-83.391724
CKD 4 (west shore) [a]	45.070672	-83.398848
Rend - bow [b]	45.062366	-83.392583
Shamrock - stern [b]	45.051283	-83.43405
OT Flint [b]	45.026133	-83.347383

[a] = location from GMLLP (2008)
[b] = location from mooring buoy coordinates from the TBNMS (2008)

Figure 1: National Gypsum CKD pile in Alpena (Alpena County), Michigan.



Since the early 1990s, there have been several investigations of the surface water and groundwater under and around the CKD pile. Elevated pH has consistently been present in the both surface and groundwater around the pile as well as elevated levels of metals in the groundwater, surface water, and sediment. In 1993, sampling by the Michigan Department of Environmental Quality (MDEQ) found heavy metals in the surface water and CKD pile.

Prior to installation of a clay cover by the owners, erosion channels were apparent in the CKD pile from runoff (Figure 2). CKD material followed the erosion channels and discharged into the lake. Historically, CKD leachate discharged into the surface water with runoff. Wind and melting ice deposited CKD material in Thunder Bay, and on the land surrounding the CKD pile. The clay cover appears to be an effective barrier (DLZ 2007).

Figure 2: Erosion channels on the National Gypsum CKD pile in Alpena (Alpena County), Michigan before cover installation.

(Pictures are from MSU [2009].)

Discussion

<u>Environmental Contamination</u>

Geological and hydrogeological investigations

Under contract with MDEQ, DLZ Michigan, Incorporated (DLZ) investigated site geology and hydrogeology. The CKD pile thickness averages approximately 32 feet. The northern edge of the site has no CKD material and the center of the pile has a maximum thickness of 67 feet. A layer of material underneath the CKD material, composed of sand, silt, clay, and gravel, ranged in thickness from three to 40 feet (average of 31 feet). DLZ categorized this layer as former lake bottom sediments. Due to the elevation of Lake Huron, around 577 mean sea level, some of the CKD material and most of the layer beneath the CKD material are below the lake level and may therefore be saturated (DLZ 2007A).

Blasland, Bouck, and Lee, Inc (BBL), hired by the property owner, previously concluded that the clay layer under the CKD pile formed an aquiclude. An aquiclude is a complete barrier to water movement, in this case preventing water from moving from the CKD pile to the bedrock. In a later investigation, DLZ determined that the clay layer between the CKD and bedrock is not an aquiclude, but an aquitard. An aquitard is an intermittent barrier, which means it allows water to move from the CKD pile to the bedrock and is present in some areas but absent in others. The bedrock layer is mainly below the lake level, 16-80 feet below grade, and is composed of limestone (DLZ 2007A).

Hydrogeological information, which was similar for shallow and bedrock monitor wells, indicated the groundwater flow associated with the CKD pile was southwesterly towards Thunder Bay. A groundwater divide is present, but variable, between the quarry and CKD pile. Water north of the divide flows toward the quarry and water south of the divide flows toward Lake Huron. DLZ determined that the water draining from the quarry to Lake Huron, or changes in water movement in the area, might alter the function and location of the groundwater divide (DLZ 2007A).

Groundwater investigations

In 2005, DLZ installed and extensively sampled thirty-eight monitor wells at fifteen locations on the CKD pile and along the shoreline. Groundwater samples were collected from the new monitor wells, which were at a shallow depth either in the saturated CKD or just beneath the CKD, an intermediate depth right on top of the bedrock, or deep, seven feet into the bedrock. The monitor wells were installed to assess leaching of contaminants from the pile, and to monitor the groundwater surface water interface (GSI) along the shoreline. Sampling from off-site wells consisted of two LaFarge monitor wells and one off-site background well (DLZ 2007A). (A description of earlier site activities is located in Appendix 1 and contaminant levels in off-site background well are in Appendix 2.)

Groundwater samples from eighteen monitor wells had a pH greater than 8.5. Wells screened within the CKD also had elevated levels of mercury, vanadium, aluminum, chloride, and sulfate (DLZ 2007A).

Most contaminant levels were compared against MDEQ's human noncancer value for drinking water (HNV), if available, or the Residential Drinking Water (RDW) criteria, both protective of human health. (See Table 8 in Appendix 2 for the MDEQ criteria values that were compared to the contaminant levels.) Drinking water values were selected because groundwater and any potential runoff flowed into Thunder Bay. The Great Lakes are protected as human drinking water sources and levels of contamination must comply with values protective of human health. Lake Huron is the municipal water source for the City of Alpena and Alpena Township. The intake is located in Thunder Bay, south of the CKD pile, on the south side of the City of Alpena. Only two contaminants, mercury and chloride, were not compared to human health protective drinking water values. Mercury levels in the various samples were compared to the GSI criteria, which are protective of people who may eat fish containing mercury, in the form of methylmercury. The GSI criterion identifies the groundwater concentration of a chemical that is protective of a surface water body to which the groundwater vents, such as a stream, pond, or lake (MDEQ 2004). All contaminants, except pH in certain samples, are below the MDEQ Groundwater Contact (GC) criteria that are protective of dermal contact with contaminants in groundwater.

Table 2 presents a list of contaminants in the groundwater within and below the CKD pile. Aluminum, antimony, arsenic, cadmium, chromium (III), copper, lead, mercury (total), thallium, vanadium, sodium, manganese, chloride, and sulfate levels and pH were elevated at several different monitor wells over different sampling events. In the last two sampling events, chromium (III), copper, and manganese were below MDEQ criteria, while thallium was not tested. Bromide, potassium, and calcium do not have established criteria, but these levels are greater than levels measured from the off-site background well (Off-site background well values are in Appendix 2, Tables 9 and 10.). Barium, beryllium, nickel, selenium, silver, zinc, phosphorous (total), and magnesium were below MDEQ criteria in almost all samples. Barium, selenium, and magnesium each had one exceedence of applicable criteria in 111 samples.

Table 2: Contaminants (in micrograms [µg]/liter [L]) present in groundwater at the National Gypsum CKD pile, Alpena (Alpena County), MI.

Contaminants (in µg/L) above criteria					
Contaminant	Highest level (8/1999 up to 8/2002) (number of exceedences) (DLZ 2003A)	Highest Level (removed wells; 8/2005) (number of exceedences) (DLZ 2007A)	Highest level (installed wells; 10/2005) (number of exceedences) (DLZ 2007A)	Highest level (8/2007) (number of exceedences) (DLZ 2007B)	Highest level (4/2008) (number of exceedences) (DLZ 2008)
Aluminum	**70,300 (97/111)**	**3,300,000 (42/42)**	**170,000 (28/38)**	**11,000 (23/38)**	**4,800 (24/40)**
Antimony	**20 (24/111)**	**15 (1/42)**	**13 (1/38)**	**16 (5/38)**	**11 (1/40)**
Arsenic	**470 (36/111)**	**220 (28/42)**	**170 (15/38)**	**170 (5/38)**	**130 (6/40)**
Cadmium	**220 (58/111)**	**20 (12/42)**	**11 (7/38)**	**14 (10/38)**	**8.1 (9/40)**
Chromium (III)	**1,500 (16/111)**	**1,300 (11/42)**	**220 (1/38)**	74	59
Copper	**3,700 (2/111)**	**4,400 (4/42)**	310	51	33
Lead	**180 (26/111)**	**410 (24/42)**	**110 (3/38)**	**41 (3/38)**	**19 (1/40)**
Mercury (total)	**3.5 (104/106)**	**0.98 (41/42)**	**1.1 (24/38)**	**1.0 (22/38)**	**0.82 (22/40)**
Thallium	**6.5 (8/111)**	**18 (3/42)**	**2.2 (1/38)**	NT	NT
Vanadium	**2,000 (31/111)**	**740 (14/42)**	**550 (8/38)**	**650 (7/38)**	**720 (6/40)**
pH	**13.96 (92/114)**	**14.00 (18/42)**	**13.17 (18/38)**	**13.17 (16/38)**	**13.13 (18/40)**
Sodium	**740,000 (59/111)**	**450,000 (12/42)**	**473,000 (16/38)**	**470,000 (16/38)**	**424,000 (16/40)**
Manganese	**3,500 (3/111)**	**3,400 (2/13)**	**2,000 (1/38)**	560 (0/38)	740
Chloride	**680,000 (29/111)**	**533,000 (4/42)**	**564,000 (8/38)**	**574,000 (25/38)**	**484,000 (24/40)**
Sulfate	**5,800,000 (82/111)**	**4,260,000 (36/42)**	**4,440,000 (28/38)**	**4,360,000 (32/38)**	**3,160,000 (32/40)**

Table 2 continued

Contaminants (in μg/L) with no criteria					
Contaminant	Highest level (8/1999 up to 8/2002) (DLZ 2003A)	Highest Level (removed wells; 8/2005) (DLZ 2007A)	Highest level (installed wells; 10/2005) (DLZ 2007A)	Highest level (8/2007) (DLZ 2007B)	Highest level (4/2008) (DLZ 2008)
Bromide	5,200	3,800	3,200	NT	NT
Potassium	12,000,000	6,490,000	6,110,000	6,260,000	5,610,000
Calcium	3,500,000	3,800,000	475,000	333,000	396,000

Contaminants (in μg/L) below criteria[a]					
Contaminant	Highest level (8/1999 up to 8/2002) (number of exceedences) (DLZ 2003A)	Highest Level (removed wells; 8/2005) (DLZ 2007A)	Highest level (installed wells; 10/2005) (DLZ 2007A)	Highest level (8/2007) (DLZ 2007B)	Highest level (4/2008) (DLZ 2008)
Barium	**3,600 (1/111)**	1,800	740	350	270
Beryllium	7.9	4.2	<10	1.4	<10
Nickel	1,200	970	340	330	250
Selenium	**580 (1/111)**	61	71	26	50
Silver	51	31	0.52	1.1	0.47
Zinc	940	1,200	730	81	67
Phosphorous (total)	3,700	26,000	5,000	NT	NT
Magnesium	**480,000 (1/111)**	250,000	71,000	76,000	80,000

a = Based on all of the data (eight years of sampling and over 250 samples collected), barium, selenium, and magnesium are considered to be below criteria.

NT = not tested

Samples from 24 GSI monitor wells, collected in August 2007, had levels of multiple contaminants exceeding criteria, including lead, and mercury levels exceeding the GSI criteria. Samples from the 14 CKD pile area monitor wells had levels of multiple contaminants exceeding criteria. Table 2 includes results from the August 2007 sampling event (page 11). Contaminant levels decreased from the October 2005 sampling event for most of the contaminants, including those that were already below MDEQ criteria. However, pH exceeded the RDW criteria for a majority of the samples. Both the off-site background and LaFarge monitor wells were also sampled (DLZ 2007B). (See Appendix 2, Table 9 for the contaminant levels in the off-site background well and Table 10 for contaminant levels in the LaFarge monitor wells.)

In April 2008, groundwater was sampled again. The highest levels of the contaminants are included in Table 2. Groundwater levels of aluminum, antimony, arsenic, cadmium, lead, mercury (total), vanadium, sodium, chloride, and sulfate along with pH had exceedences of criteria. Potassium and calcium levels, which have no criteria, were greater than historical levels measured from the off-site background well. Although many of the contaminants were over criteria, a majority of them decreased compared to the August 2007 sampling data (DLZ 2008).

Groundwater pH was higher than the RDW (pH greater than 8.5), the GSI (pH greater than 9.0), and even the Groundwater Contact (GC) (pH greater than 12.0) criteria. pH has remained consistently high at the site over the years of these sampling events. Mercury also exceeded the GSI (0.0013 micrograms per liter [μg/L]) criteria and remains consistently high. The highest mercury value measured was 3.5 μg/L between 1999 and 2002 and values have remained between non-detect and 1.1 μg/L from 2005 to 2008.

Surface water investigations

DLZ collected winter surface water samples on March 11 and 12, 2003, to investigate if groundwater under the CKD pile was venting into surface water. Sampling occurred while Thunder Bay still had an ice cover to obtain relatively unmixed samples. Collections of surface water occurred at 10 locations, all 16 to 93 feet from the revetment wall/shoreline and 0.25 feet above the lake bottom (DLZ 2003B).

Table 3 presents the results from the surface water sampling in 2003. Aluminum, antimony, arsenic, cadmium, lead, mercury (total), thallium, sodium, chloride, and sulfate levels along with pH were higher than the MDEQ criteria values for surface water protected for human drinking water use. Bromide, potassium, and calcium levels were similar to, though slightly lower than, the levels measured in the groundwater. Barium, beryllium, chromium (III), copper, nickel, selenium, silver, zinc, phosphorous (total), magnesium, manganese, and vanadium levels were below applicable criteria.

Table 3: Contaminants (in μg/L) present in the winter surface water, under ice, offshore of the National Gypsum CKD pile, Alpena (Alpena County), MI.

Contaminants (in μg/L) above criteria	
Contaminant	Highest level measured in winter surface water (3/2003) (number of exceedences) (DLZ 2003B)
Aluminum	**25,000 (10/11)**
Antimony	**4.8 (1/11)**
Arsenic	**64 (1/11)**
Cadmium	**6.5 (2/11)**
Lead	**140 (3/11)**
Mercury (total)	**0.431 (10/10)**
Thallium	**5.1 (2/11)**
pH	**12.14 (16/20)**
Sodium	**315,000 (2/11)**
Chloride	**457,000 (4/11)**
Sulfate	**2,990,000 (4/11)**

Table 3 continued

Contaminants (in µg/L) with no criteria	
Contaminant	Highest level measured in winter surface water (3/2003) (DLZ 2003B)
Bromide	2,400
Potassium	4,400,000
Calcium	225,000

Contaminants (in µg/L) below criteria	
Contaminant	Highest level measured in winter surface water (3/2003) (DLZ 2003B)
Barium	170
Beryllium	ND
Chromium (III)	28
Copper	55
Nickel	130
Selenium	43
Silver	ND
Zinc	160
Phosphorous (total)	500
Manganese	200
Magnesium	31,300
Vanadium	150

ND = not found above detection level

During a sampling event in August 2007, DLZ collected surface water samples at the foot of the revetment wall. All of the surface water samples had slightly elevated pH, just above the RDW criteria of 8.5, between 8.97 and 9.07 (DLZ 2007B).

Surface water samples were collected again in April 2008 for pH measurements. The pH of the surface water ranged from 8.15 to 9.00 (six of 46 samples were above 8.5) (DLZ 2008).

DLZ also calculated mercury surface water discharges for 2002, before the clay cover, and 2005, after the cover was in place. For 2002, the surface water discharge was estimated at 6,022 gallons of water per day with 13,380 µg mercury discharged per day. After installation of the clay cover, surface water discharge was estimated at 4,215 gallons of water per day with 4,436 µg mercury discharged per day (DLZ 2007A).

DLZ found that the clay cover, while being an effective barrier between runoff water and the contaminants, only caused a slight improvement to the groundwater quality. The continued impact to groundwater is due to metals and other contaminants leaching from the CKD, which is at or below the lake level. Additionally, DLZ stated that the CKD at and beneath the lake levels would be a continuing source of contaminants although less contamination may occur over time if the cover is effective (DLZ 2007A).

Fish from in and around Thunder Bay

Fish from Thunder Bay have been collected periodically since 1986, and measured for contaminants including mercury, as part of the Michigan Fish Contaminant Monitoring Program (MFCMP). In 2007, several additional fish, 9-spine stickleback, round goby, and smelt, were also collected. Almost all fish, from 1986 to 2007, have total mercury levels below the current mercury screening level for restricted consumption (0.5 parts per million [ppm]). Seven walleye, collected both before and after cover instillation, and one channel catfish had total mercury at or above 0.5 ppm. Table 4 presents the average, range, and number of fish collected (sample size) for every fish species caught in Thunder Bay from 1986 to 2007. Samples are divided into two groups, 2001 or earlier and after 2002. The years for the groups were chosen to obtain groups of fish collected before (2001 and before) and after (2002 to 2007) cover installation on the CKD pile. The levels of mercury in fish species have not changed much since the cover installation. Along with the contribution of mercury from the CKD pile, mercury is deposited into Thunder Bay from the atmosphere. All waterbodies in Michigan have mercury deposition from various global and local sources and the mercury that is deposited can end up in the fish.

Table 4: Total mercury levels (in ppm) of fish from Thunder Bay or Thunder Bay River, Lake Huron from 1986 to 2007.

	Samples from 2001 or before			Samples from 2002 to 2007		
Fish	Average (ppm)	Range (ppm)	Sample size	Average (ppm)	Range (ppm)	Sample size
Alewife	0.050	0.04-0.06	2	0.095	0.081-0.108	2
Brown Trout	0.122	0.06-0.17	45	NS	NS	NS
Carp	0.129	0.01-0.41	85	0.198	0.08-0.391	20
Channel Catfish	0.257	0.09-0.51	3	NS	NS	NS
Chub	0.060	0.04-0.08	4	NS	NS	NS
Lake Trout	0.154	0.08-0.28	67	0.189	0.079-0.38	38
Lake Whitefish	0.077	0.04-0.17	35	0.105	0.033-0.179	10
Spottail Shiner	0.030	0.03-0.03	3	NS	NS	NS
Walleye	0.232	0.06-0.82	74	0.253	0.076-0.794	20
Yellow Perch	0.023	0.02-0.03	10	NS	NS	NS
9-spine stickleback	NS	NS	NS	0.040	0.036-0.042	3
Round goby	NS	NS	NS	0.032	0.026-0.036	4
Smelt	NS	NS	NS	0.025	0.015-0.039	3

Data from the MFCMP was obtained from Joe Bohr, MDEQ.
NS = not sampled (no fish collected)

Exposure Pathways Analysis

An exposure pathway contains five elements: (1) the contaminant source, (2) contamination of environmental media, (3) an exposure point, (4) a human exposure route, and (5) potentially exposed populations. An exposure pathway is complete if there is a high probability or evidence that all five elements are present. Table 5 describes human exposure to pH and inorganic contaminants from the CKD pile. CKD material is no longer present in the air, due to installation of the clay cover, therefore, inhalation as an exposure route was not considered.

Table 5: Exposure pathway for human exposure to contaminants around the National Gypsum CKD pile, Alpena (Alpena County), Michigan.

Source	Environmental Medium	Exposure Point	Exposure Route	Exposed Population	Time Frame	Status
High pH material in CKD pile	Runoff (from surface and groundwater) from the CKD pile with high pH	Thunder Bay, Lake Huron	Dermal	Individuals performing recreational activities in Thunder Bay	Past Present Future	Potential Potential Potential
	Runoff (from surface and groundwater) from the CKD pile with high pH	Public water (Thunder Bay as the source)	Ingestion	Individuals drinking the public water supply	Past Present Future	Potential Potential Potential
	Groundwater below the CKD pile with high pH	Groundwater on and around the site	Dermal, ingestion	Individuals using groundwater on and around the site	Past Present Future	Potential Eliminated Eliminated
Metals and other inorganic contaminants in the CKD pile	CKD material in Thunder Bay and runoff (from surface and groundwater) from the CKD pile	Sediment and water in Thunder Bay, Lake Huron	Dermal	Individuals performing recreational activities in Thunder Bay	Past Present Future	Potential Potential Potential
	CKD material in Thunder Bay and runoff (from surface and groundwater) from the CKD pile	Public water (Thunder Bay as the source)	Ingestion	Individuals drinking the public water supply	Past Present Future	Potential Potential Potential
	Groundwater below the CKD pile	CKD pile material	Dermal, ingestion	Individuals using groundwater on and around the site	Past Present Future	Potential Eliminated Eliminated
Mercury in the CKD pile and groundwater under the pile	Sediment/water in Thunder Bay (conversion to methylmercury)	Fish	Ingestion	Individuals eating fish from Thunder Bay and Lake Huron	Past Present Future	Complete Complete Potential

Since no one is currently drinking groundwater from the site, those exposure pathways have been eliminated. Pathways where Thunder Bay is the exposure point are included because the groundwater vents into Thunder Bay. Even though exposure pathways are marked as complete or potential, people may not have any adverse effects or harm from any past, present, or future exposure. For example, any contaminants that have discharged into Thunder Bay, the source of the public drinking water supply for the City of Alpena, may not be present in the public drinking water. Additionally, although people may be in contact with metals or inorganic contaminants in the water of Thunder Bay, levels are below the GC criteria and do not pose a danger to human health. Contact with water having elevated pH will be discussed in a later section.

Public water supplies are regularly screened for numerous contaminants. Antimony, arsenic, cadmium, lead, mercury, and thallium were not detected in the public drinking water supply, according to the 2007 Annual Water Quality Report (AWTP 2007), so people are not exposed to elevated levels of these contaminants. It is also possible that other contaminants in Thunder Bay, from the CKD pile, are diluted below levels that would be of concern for a drinking water source. Amounts of contaminants that remain in Thunder Bay or the public drinking water could be much lower than levels measured in the groundwater. People exposed to any of the contaminants remaining in the public drinking water supply are not automatically harmed or have adverse effects from this possible exposure. Several of the metals and inorganic contaminants are required for the human body to function normally, mentioned below in the following section, and cells in the body have ways of removing the excess amounts. Additionally, although people are exposed to mercury, as methylmercury, by eating fish in and around Thunder Bay, the levels of mercury are not expected to cause health effects. The 2008 Michigan Family Fish Consumption Guide does not have any mercury-based restrictions on consumption of fish in and around Thunder Bay.

Toxicological Evaluation

General toxicological information was included for contaminants that are not measured in the public water supply. Levels of these contaminants in the public water supply are not available. Groundwater levels were related to potential health effects solely to provide a general discussion of health effects. April 2008 groundwater sampling data was used as it is more recent than the March 2003 surface water samples. However, this does not mean that people are exposed to these contaminants. Actual levels of these contaminants in the public water supply will typically be lower as compared to contaminant levels in both the surface water of Thunder Bay and the groundwater venting from the CKD pile. Even though possible health effects are mentioned, people may not have health effects or even be exposed to contaminant levels high enough to cause possible health effects.

Aluminum

Aluminum is the most abundant metal in the earth's crust. It does not accumulate in plants or animals and does not readily dissolve in water. Natural water concentrations are usually below 100 μg/L, although they can be as high as 400-1,000 μg/L (ATSDR 2006). The EPA has set a secondary maximum contaminant level for aluminum to 200 μg/L for aesthetic reasons (color) (EPA 1999).

The estimated dietary intake of aluminum is 100-120 μg per kilogram per day (μg/kg/day). People taking buffered analgesics, antacids, or anti-ulcer products may have an aluminum intake of 2,000 up to 71,000 μg/kg/day (ATSDR 2006). Aluminum is a food additive, used as an emulsifying, anti-caking, and leavening agent (Saiyed and Yokel 2005). Aluminum is present in white cake, biscuit, pancake, and waffle mix (31,000-57,000 μg of aluminum per serving) as well as cheese (from frozen pizza, as a topping and in the crust, and processed American cheese, 8,900-16,000 μg aluminum per serving) (Saiyed and Yokel 2005).

Even if people do consume these levels of aluminum, the body retains very little. Only 0.1-0.6% of the amount consumed is absorbed and an even smaller amount (0.07-0.39%) is absorbed from drinking water. Absorbed aluminum is excreted in urine (ATSDR 2006).

Excessive aluminum ingestion could cause musculoskeletal effects, such as joint pain and osteomalacia (bone softening). In animals, the nervous system is a sensitive target and gestational or lactational exposure to aluminum impaired the development of the fetus's nervous system. People with impaired renal functions may have decreased urinary excretion of aluminum. This could cause these individuals to exhibit more symptoms associated with excess aluminum ingestion. The uremic population (those with altered or reduced kidney function) is also at risk for aluminum related dementia (ATSDR 2006).

Levels of aluminum in the groundwater (April 2008) were as high as 4,800 µg/L and 24 out of 40 samples exceeded criteria. As a 70 kg (about 155 lbs) person has an estimated intake of 7,000-14,000 µg/day, and daily intakes can range up to 4,970,000 µg/day, it is unlikely that people will consume enough water to have any health effects at the current aluminum levels (maximum of 4,800 µg/L). ATSDR has set an oral chronic minimal risk level (MRL) for aluminum at 1,000 µg/kg/day, which is equivalent to an intake of 70,000 µg/day for a 70 kg person (ATSDR 2008). Additionally, water with aluminum levels above 200 µg/L could be discolored, which may provide a deterrent to drinking.

Vanadium

Vanadium has no known function in the human body, but people consume vanadium in mushrooms, shellfish, black pepper, parsley, and dill seed (IoM 2002). People eat around 10-20 µg vanadium/day, mostly from food. Drinking water can contain 0.2-100 µg/L, with an average of 4.3 µg/L. Most samples (91%) have less than 10 µg/L but most have approximately 1.0 µg/L. People are typically exposed to vanadium by drinking vanadium-contaminated water (ATSDR 1992).

Vanadium is not well absorbed by the gastrointestinal tract or through the skin. Children may absorb more vanadium as compared to adults. Health effects in humans after ingesting vanadium have included cramping, diarrhea, nausea, vomiting, and changes in the blood, such as a change in white blood cell count (ATSDR 1992).

Levels of vanadium in the groundwater at the site have decreased over time, but six of 40 samples in April 2008 still exceeded criteria. The maximum level of vanadium was 720 µg/L. Surface water, sampled in April 2003, did not exceed criteria for vanadium, so it is possible that current surface water would still be below criteria. A person drinking 2 L per day of water containing vanadium, at 720 µg/L, would ingest 1,440 µg/day, which is far more than is typically consumed. This vanadium intake may cause health effects although human health effects from ingestion of vanadium are not well known. ATSDR has set an intermediate oral MRL at 3.0 µg/kg/day (ATSDR 2008). A 70 kg person could have a daily intake of 210 µg/day for up to one year and would not be expected to have any health effects. The maximum level of vanadium in the groundwater, 720 µg/L, results in a possible intake of 1,440 µg/day, which is almost seven times higher than the daily intake for a 70 kg person.

pH

pH values provide an indication of how acidic or basic liquids are. Liquids that are too acidic or basic can irritate people's skin on contact. Acidic household items are vinegar (pH = 2.2) and orange juice (pH = 3.7). Household items that are basic are baking soda (pH = 8.3), milk of magnesia (pH = 10.5), and lye (pH = 13.0). The EPA has listed a high pH in water as causing a slippery feel, soda taste, and capable of leaving deposits (EPA 1999).

Cement, and CKD material, contains calcium oxide (quicklime), which can form calcium hydroxide after addition of water (Alam et al. 2007). The resulting calcium hydroxide can give wet cement a pH of 12 or greater. As cement dries, the pH may rise to around 14.0 (Mehta et al. 2002; Keles et al. 2008).

Exposure to high pH can range from irritating to corrosive to skin, eyes, and mucus membranes. Intermittent exposure can result in minimal irritation or discomfort, due to healing that can occur between exposures. Prolonged exposure can result in irreversible tissue damage, and depending on the pH, irreversible damage could occur after one exposure. Substances with a pH greater than 11.5 are known to be corrosive and can produce irreversible damage to skin, eyes, and mucus membranes after one exposure (EPA 1998).

Over half of the samples collected since 1999 have had a pH higher than 8.5. Maximum pHs have ranged from 13.13 to 14.00. Water with this high of pH is not suitable to drink. It is likely that contact with this water would cause damage to skin, eyes, or mucus membranes. Surface water offshore of the pile, sampled in April 2003, had a maximum pH of 12.14 and 16 out of 20 samples had a pH higher than 8.5. Water with a high pH may be discolored or have an odor that could deter people from touching, drinking, or swimming through it.

Chloride

Chloride plays a role in maintaining the fluid around cells in the body and maintaining the proper water levels in the serum (blood), along with sodium. The maximum level of daily chloride intake in people without hypertension depends on age. The range of the adequate intake for chloride is 180,000 to 2,300,000 μg/day, depending on age. The upper limit of chloride consumption that is considered safe ranges from 2,300,000 to 3,600,000 μg/L. A possible health effect of consuming chloride levels above this range, primarily along with sodium, is hypertension (IoM 2004).

The EPA secondary maximum contaminant level for chloride is 250,000 μg/L. Water containing chloride above this level can have a salty taste (EPA 1999).

Over half of the samples of the groundwater, from the April 2008 sampling, had chloride levels above criteria. The maximum chloride levels have been consistent over time (484,000 µg/L from the April 2008 sampling). The levels are well above MDEQ's GSI criteria and are about double both the MDEQ's RDW criteria and the EPA's secondary maximum contaminant level. Surface water also had a maximum chloride level that was similar to the maximum groundwater chloride level. It is likely that the public water supply has lower levels of chloride compared to both the surface and groundwater.

Water with high chloride levels has a salty taste, which may prevent people from drinking it. People drinking 2 L of water with 484,000 µg/L chloride would ingest 968,000 µg/day of chloride. If people manage to drink the water once, it is unlikely they would have lasting health effects. People with kidneys functioning at less than the necessary level may have trouble filtering out the excess chloride. People that already have hypertension may have a further increase in their blood pressure due to the excess chloride.

Bromide

Bromide is present in coastal water and groundwater in certain areas of the United States. For example, Texas has bromide in the groundwater from the use of brine in crude oil extraction (Richardson et al. 1999). The highest bromide levels in the U.S., reported by Richardson et al. (1999), were 3,000 µg/L. Bromide is water-soluble and easily absorbed from the intestinal tract (Ryan 1999).

Different bromide salts have historically been used as seizure control medication (Emancipator and Kroll 1990). Ingestion of large amounts of bromide salts is irritating and causes vomiting, as the small intestine rapidly absorbs small amounts of bromide. Bromide levels can reach toxic concentrations when bromide intake increases (Bowers and Onoroski 1990). Classic symptoms of brominism are related to alteration in central nervous system functioning, including headaches, irritability, fatigue, slurred speech, ataxia, emotional instability, tremors, and hallucinations, with an acne-like rash in some cases (Horowitz 1997).

Brominism occurs in people with high levels of serum bromide (March et al. 2002). However, different people can tolerate different concentrations of bromide. Some people may show symptoms of brominism with serum levels below the lowest therapeutic concentration (400,000 µg/L), and other people can tolerate high levels near (2,500,000 µg/L) without any symptoms of toxicity (Bowers and Onoroski 1990).

There are no criteria for bromide. The maximum levels of bromide in the groundwater ranged from 3,200 to 5,200 µg/L. These levels are well below low therapeutic doses of bromide, and are between a hundred and a thousand times lower than serum levels from people taking bromide medications. It is unlikely that health effects would occur in people drinking water with these levels of bromide. However, if health effects did occur, irritation of the digestive system and/or vomiting would be the most likely health effects.

Potassium

Potassium is the most abundant positively charged ion in human cells. It is necessary for the normal functioning of cells. Recently, the National Academy of Sciences published a report that stated the dietary intake of potassium was as low as half, in Americans adults, of the adequate daily intake (4,700,000 µg) (IoM 2005). Health effects can occur at both low and high serum potassium, called hypokalemia and hyperkalemia, respectively.

Hyperkalemia occurs in people with high serum potassium. Kidneys normally remove excess potassium. Most cases of hyperkalemia are due to kidney disorders that reduce the excretion of potassium. Symptoms of hyperkalemia are nausea, irregular heartbeat, and possibly a slow, weak, or absent pulse (Medline 2007).

There is no upper limit on the daily intake set for potassium because there is no evidence chronic excess intakes of potassium can occur in apparently healthy individuals. Hyperkalemia can occur in individual with chronic renal insufficiency (kidney disease) or diabetes. People taking potassium sparing diuretics or drugs for cardiovascular disease might need to consume less than the recommended adequate intake (IoM 2004).

Potassium levels have been decreasing over the years, but there are no criteria. The maximum level in the April 2008 sampling was 5,610,000 µg/L. Even though this level is high, for people with normal functioning kidneys there should be no health effects. People that have kidney disease, diabetes, or are taking potassium sparing diuretics or drugs for cardiovascular disease may have symptoms of hyperkalemia.

Calcium

Calcium is required for teeth and bone formation, along with muscle contracting and blood clotting. Recommended intakes are 1,000,000 µg/day or higher for people over 9 years of age. The upper limit on the daily intake is 2,500,000 µg/day for people older than 1 year old. People can obtain calcium from eating milk, cheese, yogurt, corn tortillas, Chinese cabbage, broccoli, kale, and calcium-set tofu (IoM 2002).

Excess calcium can result in kidney stones, hypercalcemia, milk alkali syndrome, or renal insufficiency (kidney disease) (IoM 2002). Hypercalcemia is having elevated levels of serum calcium. This can be due to kidney disorders, ingesting massive amounts of calcium (dietary), primary hyperparathyroidism, or adrenal gland failure (Medline 2008).

Hypercalcemia can cause a variety of symptoms. Gastrointestinal symptoms include constipation, nausea, pain, and vomiting. Kidney effects can be flank pain, frequent thirst and/or urination, and kidney stones. Other symptoms are muscle twitches/atrophy, apathy, coma, dementia, depression, irritability, memory loss, and bone pain (Medline 2008).

There are no criteria for calcium. Maximum levels in the groundwater have been decreasing over the years. The April 2008 sampling had a maximum level of 396,000 µg/L. A person drinking 2 L of water with 396,000 µg/L of calcium would have around 30% of the upper limit of calcium intake for the day. For a majority of the population, the kidneys remove excess calcium without any health effects resulting. Sensitive people may develop kidney stones or have reduced kidney function from excess calcium.

Children’s Health Considerations

Children could be at greater risk as compared to adults from certain kinds of exposure to hazardous substances. Children play outdoors and sometimes engage in hand-to-mouth behaviors that increase their exposure potential. Children are shorter than are adults; this means they breathe dust, soil, and vapors close to the ground. A child’s lower body weight and higher intake rate results in a greater dose of hazardous substance per unit of body weight. If toxic exposure levels are high enough during critical growth stages, the developing body systems of children can sustain permanent damage.

Certain contaminants of concern, such as lead and mercury, at this site produce greater adverse effects in children as compared to adults. Children have both increased absorption and increased susceptibility to these contaminants. Children are also more sensitive to effects of methylmercury in fish as compared to adults. Although levels of six contaminants are high in the groundwater of the CKD pile, they are not present in the public water supply (AWTP 2005; AWTP 2007). These chemicals are antimony, arsenic, cadmium, lead, mercury (inorganic), and thallium. Additionally, fish from the Thunder Bay area have no consumption advisories due to mercury contamination.

This site may be attractive to young trespassers due to the multiple monitor wellheads present and the revetment wall made of rocks, which they may want to climb. Warning signs present at the site might not deter children. Differences in water taste or color, resulting from aluminum, chloride, sulfate, or pH, may be more of a deterrent to adults than to children. Children swimming offshore may not notice or be concerned about moving through discolored water or stinging sensations due to areas of high pH. This could result in eye or skin irritation or damage if they remain in water with high pH for too long.

Conclusions

MDCH cannot currently conclude whether people have had, are having, or will have direct contact with venting groundwater in Thunder Bay and so cannot conclude whether there is harm to people's health. The reason for this is although groundwater with high pH is venting into Thunder Bay, the location and size of the areas and the exact pH levels are unknown with open water conditions. A shipwreck, part of Thunder Bay National Marine Sanctuary, is within one mile of the CKD pile. People walking along the shoreline might get close to the pile, as people in Michigan are allowed to walk on private property up to the high water mark. If swimmers, divers, and people walking along the shoreline are ever in these areas, they may encounter localized areas of high pH in Thunder Bay near the CKD pile. MDCH does not anticipate receiving information on the usage of the area as no agency is collecting that information.

MDCH concludes that mercury exposure from eating fish from Thunder Bay will not harm people's health. Currently, there are no mercury-based consumption advisories for fish in or around Thunder Bay.

MDCH concludes that, in relation to the contaminants at the National Gypsum CKD pile, drinking the City of Alpena public water supply will not harm people's health. The reason for this is people have not been drinking harmful levels of the inorganic contaminants in the water. Although the surface water from Thunder Bay is the source water for the public water supply, the water treatment plant regularly screens water for many of the contaminants present at this site.

Recommendations

Water sampling of ground and surface water surrounding the CKD pile should continue to monitor the status of the site.

Warning signs near the CKD pile should be maintained.

Fish sampling and testing for mercury, as well as regular screening for other contaminants should continue.

The City of Alpena public water supply should continue to be monitored.

Public Health Action Plan

1. DLZ, contractors for MDEQ, plan to monitor the water for at least three more years. If the data collected suggest different public health implications than concluded here, MDCH will update this health consultation.

2. The local health department will periodically confirm the continued presence of the warning signs near the CKD pile.

3. The MDEQ Fish Contaminant Monitoring Program will continue to check fish from the Thunder Bay area for mercury and MDCH will issue consumption advisories as necessary.

4. The Alpena Water Treatment Plant will continue to screen the public water supply yearly for many of the contaminants.

If any citizen has additional information or health concerns regarding this public health consultation, please contact the MDCH Division of Environmental Health at 1-800-648-6942. ATSDR and MDCH remain available for further consultation on this site.

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Certification

This Health Consultation was prepared by the Michigan Department of Community Health under a cooperative agreement with the Agency for Toxic Substances and Disease Registry (ATSDR). It is in accordance with approved methodology and procedures. Editorial review was completed by the cooperative agreement partner.

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The Division of Health Assessment and Consultation, ATSDR, has reviewed this public health consultation and concurs with the findings.

Team Leader, CAPEB, DHAC, ATSDR

Appendix 1: Historical site activities at the National Gypsum CKD pile in Alpena (Alpena County), Michigan, from 1996 to 2003.

In 1996, DLZ conducted an investigation into the CKD pile, surface water, groundwater, and air. High levels of metals were in the CKD material, surface water, and groundwater. High pH, greater than 8.0, was measured in both the surface water and groundwater under the pile. Air monitoring revealed that CKD material was present in the air around the pile. These results were reported in the 1996 Final Technical Memorandum #1, Interim Response Investigative Action (IRIA) (DLZ 2003A).

DLZ conducted a more in-depth investigation, on behalf of the MDEQ and reported in the Final Technical Memorandum #2, Interim Response Investigation (IRI) (June 2001), of the CKD material and the groundwater under it. DLZ determined that the groundwater flow under the pile was to the south and east, heading into Lake Huron. DLZ verified the presence of a groundwater divide, identified by the property owner's contractors (Blasland, Bouck, and Lee, Inc [BBL]), between the northern edge of the CKD pile and the southern edge of the LaFarge quarry. Groundwater north of the divide flowed toward the quarry and south of the divide flowed toward Lake Huron. However, DLZ noted that this divide could shift depending on the conditions present at the site (DLZ 2003A).

The pH of the groundwater and CKD material was elevated. Half of the solid CKD material samples (10 of 20 samples) exceeded the Resource Conservation and Recovery Act (RCRA) corrosivity criteria (pH greater than or equal to 12.5) with a range of 10.5 to 12.9. Groundwater pH beneath the pile was primarily between 11.08 and 12.10. Two samples had normal values, 7.49 and 7.73. DLZ concluded that the CKD pile was affecting groundwater pH at the site. Additional groundwater sampling from on-site monitor wells found a pH ranging from 6.28 to 14.00 and mercury levels from 0.0014 to 2.6 μg/L. By comparing the concentrations of metals from background and upgradient wells to downgradient wells, DLZ determined that CKD leachate was in groundwater (DLZ 2003A). (See Appendix 2, Tables 9 and 10 for levels of metals in those wells.)

Inorganic chemical concentrations were higher in deeper portions of the pile, compared to areas within two feet of the top of the pile. Six samples of surface water, taken off shore of the pile, near discolored water, found pH values of 8.63 to 12.03 and mercury concentrations ranging from less than 0.0067 to 0.026 μg/L (DLZ 2003A).

In 2002, the property owners re-graded the CKD pile, added a clay cover, and revetment wall along the lakeshore. Prior to that action, DLZ decommissioned and disassembled on-site monitor wells, on-site pizometers, and removed any other state-owned structures. DLZ also confirmed the groundwater flow and the presence of the groundwater divide (DLZ 2003A).

Groundwater under the pile flowed toward Lake Huron. The groundwater divide was located between the quarry and the CKD pile. Groundwater from under the quarry flowed toward the quarry. DLZ did note that the divide shifted in response to pumping conditions at the quarry and groundwater recharge during their activities. DLZ collected groundwater samples during this investigation (August 5-14, 2002) (DLZ 2003A).

The off-site background monitor well had a pH of 6.69 with the field pH of monitor wells on the site ranging from 6.69 to 13.50. Twelve of the wells had a pH greater than 9.0 and seven of the wells had a pH greater than 12.5. The high pH in the groundwater allows more ions and total dissolved solids to be in the water. Data on specific conductance, which measures how well water can conduct an electrical current, indicated that there was increase conductivity in the water. Increased conductivity in water indicates that there may be more ions present, which may mean that there is a pH plume present (DLZ 2003A).

DLZ concluded that there was “no evidence to suggest that pH encountered at the base of the CKD pile is being reduced or attenuated.” In addition, DLZ noted that the pH plume might expand with increased rainfall. Total mercury was present in all wells above GSI criteria (DLZ 2003A).

DLZ collected winter surface water on March 11 and 12, 2003 to investigate if groundwater under the CKD pile was venting into surface water. Sampling occurred while Thunder Bay still had an ice cover to obtain relatively unmixed samples. Collections of surface water occurred at 10 locations, all 16 to 93 feet from the revetment wall/shoreline and 0.25 feet above the lake bottom (DLZ 2003B).

DLZ sent samples to two different laboratories, Trace Analytical Laboratories, Inc and Frontier Geosciences Inc, for measurement of total mercury levels. Trace Analytical quantitated total mercury in all previous samples, but did not have the capability to measure methylmercury. Frontier Geosciences was able to measure methylmercury, as well as total mercury, in the samples. To determine of the two labs resulted in comparable measurements, both laboratories analyzed split samples (a sample divided in half and sent to two different laboratories for analysis). That allowed a comparison of total mercury measured at both laboratories and confirmed whether there could be a comparison of historical values to future values.

Total mercury measured 0.00267 to 0.431 μg/L from Frontier Geosciences and 0.0036 to 0.500 μg/L by Trace Analytical. Mercury values from the two laboratories were indeed comparable. All total mercury values were above the GSI criteria value of 0.0013 μg/L. Table 6 presents total mercury and methylmercury levels from surface water sampled March 11-12, 2003. Methylmercury levels were 0.000025-0.00128 μg/L and the pH was greater than 9.0 at seven of the ten locations. Table 7 presents the field pH readings taken from surface water sampled on March 11-12, 2003. Based on these data, DLZ concluded that groundwater is venting beneath the CKD pile into Thunder Bay, possibly near the eastern end of the revetment wall (DLZ 2003B).

Table 6: Mercury levels in surface water samples from Thunder Bay next to the National Gypsum CKD pile, Alpena (Alpena County), Michigan. Samples were collected March 11-12, 2003.

	Mercury levels in surface water (DLZ 2003B)		
	Trace labs	Frontier Geosciences	
Sample	Total mercury (µg/L)	Total mercury (µg/L)	Methylmercury (µg/L)
1	**0.018**	**0.0156**	0.00048
2	**0.017**	**0.0182**	0.00042
3	**0.0036**	**0.00267**	<0.000025
4	**0.012**	**0.0113**	0.000076
5	**0.020**	**0.0124**	0.000152
6	**0.500**	**0.431**	0.00128
7A	**0.170**	**0.158**	0.000663
7B	**0.060**	**0.0588**	0.000527
8	**0.140**	**0.220**	0.000151
9	**0.0045**	**0.00387**	0.000033

Bold values exceed GSI criteria for total mercury (0.0013 µg/L)

Table 7: pH in surface water samples from Thunder Bay next to the National Gypsum CKD pile, Alpena (Alpena County), Michigan. Samples were collected March 11-12, 2003.

Surface water pH (DLZ 2003B)		
Sample	Field pH	
1	**9.83**	**9.6**
2	**10.75**	**10.67**
3	8.27	8.45
4	**10.81**	**10.77**
5	**8.8**	**9.1**
6	**11.97**	**12.14**
7A	**11.84**	**11.95**
7B	**11.01**	**10.87**
8	**9.47**	**9.89**
9	7.2	7.18

Bold exceeds RDW criteria (less than 6.5 or greater than 8.5)

Appendix 2: Criteria compared against and contaminants present in the background wells for the National Gypsum CKD pile in Alpena (Alpena County), Michigan.

Table 8: Contaminants present at the National Gypsum CKD pile in Alpena (Alpena County), Michigan, with applicable MDEQ criteria.

Contaminant	MDEQ criteria (µg/L)
Aluminum	50 (RDW)
Antimony	1.7 (HNV)
Arsenic	50 (HNV)
Barium	1,900 (HNV)
Beryllium	160 (HNV)
Bromide	--
Cadmium	2.5 (HNV)
Chromium	120 (HNV)
Copper	470 (HNV)
Lead	14 (HNV)
Mercury (total)	0.0013 (GSI)
Nickel	2,600 (HNV)
Selenium	120 (HNV)
Silver	130 (HNV)
Thallium	1.2 (HNV)
Vanadium	220 (HNV)
Zinc	3,300 (HNV)
pH	6.5 to 8.5 (RDW)
Calcium	--
Chloride	50,000 (GSI)
Magnesium	400,000 (RDW)
Manganese	1,300 (HNV)
Phosphorous (total)	63,000 (RDW)
Potassium	--
Sodium	120,000 (RDW)
Sulfate	250,000 (RDW)

RDW = Residential Drinking Water (MDEQ 2006)
HNV = Human noncancer value for drinking water (MDEQ 2008)
GSI = Groundwater Surface Water Interface (MDEQ 2006)
-- = No criteria

Table 9: Historical contaminant levels in the off-site background monitor well for the National Gypsum CKD pile in Alpena (Alpena County), Michigan.

	Off-site Background well sampling events (DLZ 2007A; DLZ 2008)									
Contaminant (µg/L)	7/2/97	8/23/99	11/15/99	2/14/00	5/15/00	9/18/01	8/10/02	10/6/05	4/15/08	Highest level
Aluminum	**--**	**140**	**--**	**240**	**--**	**180**	**228**	**110**	**--**	**240**
Antimony	**--**	**--**	**--**	**--**	**--**	**--**	**--**	<1	**--**	<1
Arsenic	--	--	--	--	--	--	1.6	<1	--	1.6
Barium	--	--	--	--	--	--	37	20	20	37
Beryllium	**--**	**--**	**--**	**--**	**--**	**--**	**--**	<1	**--**	<1
Bromide	NT	--	--	--	--	--	--	<60	NT	<60
Cadmium	--	--	--	--	--	--	--	<0.2	--	<0.2
Chromium (III)	--	--	--	--	--	--	--	<1	--	<1
Copper	--	--	--	--	--	--	1.2	<1	--	1.2
Lead	--	--	--	--	--	--	--	4.1	8.5	8.5
Mercury (total)	--	**0.00803**	**0.00864**	**0.00294**	**0.00244**	**0.012**	**0.0054**	**0.012**	**0.0016**	**0.012**
Nickel	--	--	--	--	--	--	2.2	<2.0	2.5	2.5
Selenium	--	--	--	--	--	--	--	<1	--	<1
Silver	--	--	--	2.8	--	--	--	<0.2	--	2.8
Thallium	**--**	**--**	**--**	**--**	**--**	**--**	**--**	**<2**	NT	**<2**
Vanadium	NT	--	--	--	--	--	--	<2	--	<2
Zinc	NT	--	--	--	--	--	--	<10	--	<10
pH	7.4	7.5	8.1	6.68	7.92	6.37	6.69	6.43	6.56	8.1
Potassium	--	1,200	1,400	830	1,200	2,600	2,100	1,100	600	2,600
Sodium	1,400	1,900	2,200	2,900	3,400	2,100	2,000	1,100	7,500	7,500
Calcium	NT	27,000	36,000	39,000	37,000	34,000	36,700	25,300	44,200	44,200
Magnesium	NT	5,200	6,600	7,900	7,000	7,000	7,800	5,900	5,600	7,900

Table 9 continued

Contaminant (μg/L)	7/2/97	8/23/99	11/15/99	2/14/00	5/15/00	9/18/01	8/10/02	10/6/05	4/15/08	Highest level
Manganese	--	120	100	100	--	87	516	220	14	516
Phosphorous (total)	NT	270	15	17	8	23	--	30	NT	270
Chloride	NT	--	2,000	2,300	7,200	--	32,000	3,000	7,000	32,000
Sulfate	NT	2,900	3,000	2,500	61,000	1,400	--	Interference	7000	61,000

-- = Not detected
NT = Not tested
Bold exceeds criteria

Table 10: Levels of contaminants present in LaFarge background wells near the National Gypsum CKD pile in Alpena (Alpena County), Michigan.

LaFarge wells (DLZ 2007A)		
Contaminant	Well A Level in µg/L	Well B Level in µg/L
Aluminum	<50	**58**
Antimony	<1	**2.5**
Arsenic	<1	2.9
Barium	71	120
Beryllium	<1	<1
Bromide	210	240
Cadmium	<0.2	0.23
Chromium (III)	<1	<1
Copper	2.1	2.3
Lead	<1	<1
Mercury (total)	0.0007	**0.0022**
Nickel	5.4	7.1
Selenium	<1	<1
Silver	<0.2	<0.2
Thallium	<2	<2
Vanadium	<2	<2
Zinc	<10	10
pH	6.67	6.68
Potassium	130,000	77,000
Sodium	83,300	88,100
Calcium	183,000	330,000
Magnesium	21,200	42,000
Manganese	320	200
Phosphorous (total)	40	70
Chloride	**146,000**	**173,000**
Sulfate	237,000	**263,000**

Bold exceeds criteria