CORRESPONDENCE/MEMORANDUM

State of Wisconsin

DATE: August 21, 2019

TO: File

FROM: Xiaochun Zhang

SUBJECT: Development of remedial action performance standards for arsenic cleanup at the Kewaunee Marsh Arsenic Contaminated Site

Summary

The purpose of this memo is to document a process of developing site specific arsenic remedial action performance standards (RAPS) or residual contaminant level (RCL) for the Kewaunee Marsh Arsenic Contaminated Site (KMASS). In the past, the site was also identified as Kewaunee Marsh Arsenic Spill Site. To clarify, from now on the site is referenced as Kewaunee Marsh Arsenic Contaminated Site (KMASS). Performance standards developed from the process as documented in this memo are recommended to be used for remedial option evaluation and selection of a remedial option for implementation in accordance with Wis. Admin Code ch. NR720. Applicable standards should support remedial actions to achieve goals for the site so that in the future

- arsenic in surface water (SW) at the site will meet surface water arsenic criteria in accordance with ch. NR 105
- arsenic in groundwater (GW) at the site will meet groundwater arsenic criteria in accordance with ch. NR 140
- arsenic in soil/sediment (SS) at the site will not exceed a level that may cause risks to human health and ecological system
- arsenic in SS at the site will not cause exceedance of water quality criteria for both SW and GW
- discharge of arsenic to the Kewaunee River is minimized or eliminated.
- overall quality of the marsh will be improved to support ecological function and recreational use in accordance with Wis. Admin Code chs. NR 103 and 104.

At present time, qualities of SW, GW, and SS are adversely impacted by high level of arsenic that originated from an accidental spill occurred maybe more than 80 years ago. The spilled material was a chemical product in granular form. It must be highly water soluble because arsenic has been detected high in SW, GW, and SS more than 1,000 ft downstream of the spill site and reached Kewaunee River. The impacted area covers over 15 acres. Infiltration of dissolved phase arsenic has also reached as deep as 20 ft in the marsh near the original spill area.

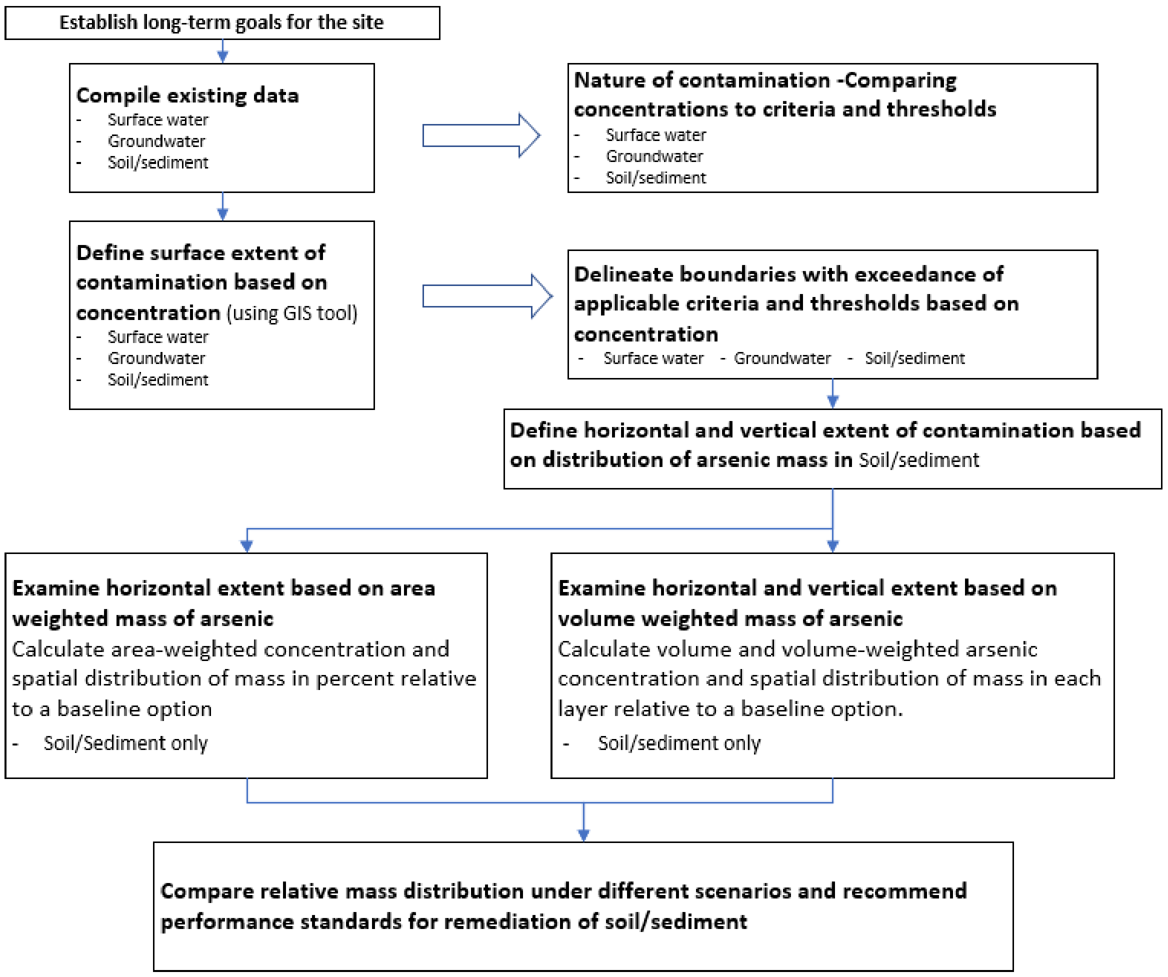
Arsenic is known carcinogen to human and is of great concern when present in surface water and groundwater. To protect public health and welfare, the present and prospective use of all surface waters for public and private water supplies, and the propagation of fish and aquatic life and wildlife, the Department has established surface water and groundwater criteria for arsenic as in chs. NR 105 and NR 140. Human cancer risk-based criteria are 13 ug/l and 40 ug/l of arsenic for the surface water within the marsh and in the Kewaunee River, respectively. Portion of the surface water present in the marsh may be subject to meet the criterion for the Kewaunee River because the area is constantly flooded, and the marsh water is inseparable from the river water. Although groundwater may be subject to meet arsenic criterion of 10 ug/l within the marsh, at the interface between the marsh and river the surface water standards may apply. Regardless the concentrations, on a basin scale, loading of arsenic from the site to the Kewaunee River should be minimized or eliminated because Lake Michigan, a drinking water supply source, has a background arsenic level already exceeding human cancer criterion of 0.2 ug/l. Any addition of arsenic from tributaries can further deteriorate the water quality in the lake. Sources of arsenic that contributes to surface water and groundwater that discharges to the Kewaunee River need to be addressed.

Various investigation and assessment have been conducted since 1994. Continuous detection of high concentrations of arsenic in SW and GW at present time is a result of large amount of mass of arsenic remaining in SS and associated aqueous phase. Although water is the driver in fate and transport of arsenic, mass of arsenic already integrated into the SS and associated aqueous phase is the continuing source to cause impact to the quality of SW and GW as well as discharge to the Kewaunee River and Lake Michigan. Highly contaminated SS and associated aqueous phase are the primary environmental medium for cleanup at the site. Without addressing arsenic contamination in SS, the water quality impairment and discharge of arsenic to the Kewaunee River will persist for a long time. In addition, the contaminated SS may pose direct risks to human health and ecosystem.

After being released to the environment, arsenic may undergo complex transformation that are controlled by physical, chemical, and biological conditions and subject to long distance transport. Specific to this site, the temporal and spatial distribution of arsenic in different forms are significantly affected by complicated marsh hydrologic condition. One such important hydrologic characteristic is that the contaminated area is located within the 100-yr floodplain of the Kewaunee River. The presence and depth of surface water in the marsh is not only precipitation and evapotranspiration dependent but also influenced by both the river flow and Lake Michigan water level. Therefore, redox potential in SS can change temporally and spatially. Groundwater at the site is in constant exchange with surface water within the site as well as between the marsh and Kewaunee River. Sometimes chemical concentrations measured in samples collected from wells in vadose zone is representative of concentrations in surface and pore water. Arsenic concentrations detected in the wells near the shore potentially represents water quality in a transition zone from GW to SW and is a measure of arsenic discharging to the river or in the river.

Development of RAPS based on concentration only without consideration of extent of contamination and distribution of arsenic mass is insufficient in general and more so for the site. Evaluation of quantity of arsenic and its distribution not only provides understanding of the center of contamination but also is an indirect evaluation of risks an area may pose to human and ecosystem. Also, it is a qualitive indicator of how long the contamination will persist in impacting the surface water. Without undergoing a full-scale risk assessment, the spatial extent of contamination, horizontally and vertically, can serve as surrogates for assessing exposure concerns. The larger an area with higher concentration is, the higher risk the area will pose to human health and the environment. The more mass of arsenic present in a specific area, the longer time the system will take to recover to environmentally sound condition. The closer an area with higher concentration to the Kewaunee River is, the more mass of arsenic discharge to the river. Therefore, site specific remedial action performance standards have been evaluated and developed following a process [Box 1] considering not only the spatial distribution of arsenic concentration but also the mass at the site. The RAPSs developed are meant for evaluation, selection, and implementation of remedial actions to achieve objectives within a reasonable time period so that the ultimate environmental goals for the site can be achieved in the future.

Box 1. Process of developing remedial action performance standards



Following the process as described in Box 1 and based on the data collected from three environmental media, SW, GW, and SS, between 1994 and 2018, conclusions are made as follows:

- water quality criteria have been frequently exceeded at the site
- arsenic concentration (C_{As}) of 20 mg/kg (ppm) in SS, is considered as the baseline threshold for evaluation. The numerical value was regarded as site specific residual contaminant level (RCL) derived from potential risks to human health via direct exposure pathway.
- with a few exceptions, the extent of SS contamination with arsenic concentration equals to or greater than 20 mg/kg ($C_{As}\geq20$ mg/kg) covers the extent where C_{As} in surface water and groundwater exceeded 40 ug/l (ppb) and 10 ug/l (ppb), respectively. Direct south of the existing fence had arsenic concentrations exceeding SW and GW criteria and resulted in extended area beyond the boundary of $C_{As}\geq20$ mg/kg in SS.
- area-wise, specifically, the surface area is
    - approximately 17 acres and 19 acres with C_{As} exceeding 40 ug/l and 13 ug/l in SW, respectively
    - approximately 15 acres with C_{As} exceeding 10 ug/l in GW
    - approximately 19 acres with C_{As} exceeding 20 mg/kg in SS
- when SW and GW criteria are met, the site will be protective to vegetation and wildlife. Applicable thresholds of 3-28 ug/l and 15-32 ug/l in SW for protection of vegetation and wildlife, respectively, were recommended by the US Fish and Wildlife Services (USFWS) and USEPA.
- when arsenic in SS is detected less than 50 mg/kg, the area will be protective of vegetation and wildlife as derived from the surface water thresholds recommend by the USFWS and USEPA.
- within each medium,
    - arsenic in SW has been detected greater than 1,000 ug/l in approximately 10 acres which is about 56% of the area bounded by $C_{As} \geq13$ ug/l (~19 acres).
    - arsenic in GW has been detected greater than 1,000 ug/l in approximately 5 acres which is about 37% of the area bounded by $C_{As} \geq10$ ug/l (~15 acres).
    - regardless of vertical location of samples, arsenic has been detected in SS greater than 1,000 mg/kg approximately in 4 acres, 500 mg/kg in 6 acres, 100 mg/kg in 11 acres, and 50 mg/kg in 13 acres, respectively. These areas are about 20%, 31%, 56%, and 68% of that bounded by $C_{As} \geq20$ mg/kg which covers about 19 acres.
- based on the surface extent of contamination, area with arsenic exceeding 100 mg/kg in SS is associated with the area where arsenic exceeded 1,000 ug/l in SW and 152 ug/l in GW with some exceptions in south and east of the fence.
- considering the area bounded by $C_{As} \geq 20$ mg/kg as the baseline for calculating arsenic mass in SS (**C20)**, the volume of contaminated SS is estimated to range from 65,000 to 87,000 cubic yards with a thickness varied from 6 inches to 23 feet. Assuming a bulk density of 0.5 g/cm^3 for SS in the entire site, a total of approximately 23,000 to 28,000 kg (23-28 tons) of arsenic may be present within the **C20** perimeter. About 59% out of the total mass is present in the top 2 ft and 98% in the top 10 ft, respectively. The

remainder 2% of mass is present deeper than 10 ft in a small area, approximately 0.2 to 0.3 acres, near the original spill site.

- although the depth of contamination may extend to 23 ft from the ground surface, arsenic concentrations exceeding 20 mg/kg were detected only in three samples in the interval of 18-20 ft and one sample in the interval of 20-23ft. These samples are located near the original spill site.
- analyses of area-weighted concentration and spatial distribution of mass revealed that out of 23,000-28,000 kg of arsenic potentially existing at the site, 70% of the mass is present in the area bounded by $C_{As} \geq 100$ mg/kg (scenario **C100**) and 76% in the area bounded by $C_{As} \geq 50$ mg/kg (scenario **C50**), respectively. Area-wise, the mass bounded by $C_{As} \geq 100$ and $C_{As} \geq 50$ mg/kg was 56% and 69% of that under the baseline scenario C**20**, respectively. The lower relative percent in area with higher proportion of mass is attributed to higher concentrations detected.
- further analyses based on volume-weighted concentration and spatial distribution of mass indicted that approximately 89 to 94% of arsenic mass under baseline (C**20**) can be addressed if performance standard for SS is set to $C_{As} = 50$ mg/kg (**C50**) and 85% to 89% if $C_{As} = 100$ mg/kg (**C100**).

As a result, it is concluded that the remedial action performance standards for the Kewaunee Marsh Arsenic Contaminated Site (KMASS) may vary from 20 to 100 mg/kg for different depth of the contaminated SS. Remedial options may be evaluated for four scenarios as 1) clean SS to 20 mg/kg (**C20**), the baseline option; 2) clean SS to 50 mg/kg (**C50**); 3) clean SS to 100 mg/kg (**C100**), and finally 4) a combination of using different scenarios of **C20, C50**, and **C100** for horizontal and vertical extent of contamination in SS. Application of different performance standards will also need to be combined with the type of technologies being evaluated when appropriate so that the most cost-effective remedial option or a combination of options can be selected for implementation.

Development of Remedial Action Performance Standards

Summary of Criteria and Thresholds Previously Applied to the Site

Cleanup of arsenic contamination in soil or sediment for the KMASS site needs to follow the processes established by the Department in accordance with the rules set forth in NR 700 series. Currently the rules only apply to soil but are often referenced for contaminated sediment management. At the site, since 1994 terms of “sediment” and “soil” have been interchangeable to describe the solid and associated aqueous phases. For convenience purpose, this document will not differentiate these two media but use a combined term as “soil and sediment” (SS) and manage SS following NR 700.

Historically, in addition to site assessment, two remedial actions have been implemented at the site. One action was the placement of a vegetative cap and installation of a chain-link fence in 1996 and the other was the pilot in-situ treatment at a limited area in 2011. These two actions collectively are considered as interim actions in this document. These actions as well as site assessment were conducted following performance standards mostly derived from human cancer risk via direct contact exposure, groundwater quality standard for protection of public health, characterization of hazardous waste, and surface water quality standards for protection of fish and aquatic life. Table 1 summarizes the applicable standards and thresholds that were applied or referenced in previous site assessment, remedial option evaluation, and implementation of the interim actions. Some of the criteria and thresholds applied to the site are further explained below; however, the thresholds for protection of vegetation and wildlife will be discussed in next section.

- To protect surface water quality in the Kewaunee River adjacent to the site, the groundwater discharging to the river was required not to exceed 925 ug/L and 680 ug/L of arsenic for protecting fish and aquatic life. The numeric values were derived from evaluation against acute and chronic toxicity criteria of 339.8 ug/L and 148 ug/l in surface water of the Kewaunee River, respectively, in accordance with NR 105 Wis. Adm. Code, 1997. The performance standards were established in 2000 and further evaluated in 2018 and 2019 by the Department's water quality program (Shields 2019). The most recent evaluation has concluded that arsenic in surface water within the marsh and adjacent to the river should not exceed human cancer risk-based criteria of 40 ug/l and 13.3 ug/l, respectively. However, there is no specific dividing line established to clearly define which part of surface water in the marsh needs to meet numerical criterion of 13.3 ug/l applicable to the Kewaunee River. Also, the evaluation recommended that "*remedial actions shall be taken to minimize the discharge of arsenic from the Kewaunee Marsh arsenic spill site that may contribute or result in concentrations of arsenic in the Kewaunee River near the confluence with Lake Michigan at levels above 0.2 µg/L. Adaptive management may be acceptable to implement technology based remedial options at present time with post remediation surface water quality monitoring near the river mouth*."

- To protect the groundwater, the arsenic enforcement standard (ES) of 10 ug/l in accordance with ch. NR140 was recognized. In the earlier evaluation, concentrations of 50 ug/l (STS, 2004) and 170 ug/l were also referenced (Appendix C, RMT 2010).

- To limit arsenic exposure to human and wildlife through direct contact with SS, cleanup objective was established for arsenic level at 20 mg/kg. This numerical value was derived from general residual contaminant levels (RCL) of 0.039 mg/kg for non-industrial land use. It was a result of calculation with assumptions of an excess cancer risk of 1×10^{-6} for a trespassing adolescent via ingestion of arsenic contaminated soil (STS, 2004 and Victor, 2018) in accordance with the Wis. Admin. Code ch. NR720.

- To meet then groundwater standard of 50 ug/l, consulting firm STS evaluated arsenic in pore water and associated bulk SS samples and concluded that if arsenic concentration (C_{As}) exceeds ≥400 mg/kg, groundwater criterion will be exceeded (STS, 2004). The analyses were later determined invalid because the linear regression of arsenic concentrations in solid phase and pore water was incorrectly evaluated (Victor, 2018).

- To identify the extent of SS that is defined as potentially hazardous waste, concentration of arsenic in leachate exceeding 5 mg/L was referenced. The benchmark was based on Toxicity Characteristic Leaching Procedure (TCLP) or screening Synthetic Precipitation Leaching Procedure (SPLP) in accordance with ch. NR 661 and 40 CFR Part 261. Based on site specific samples, RMT (2006 and 2010) concluded that if arsenic concentration in SS is greater than 1,000 mg/kg, the leachate from TCLP test would exceed 5 mg/l and the materials would be characterized as hazardous waste. Therefore, area with arsenic in SS detected greater than 1,000 mg/kg might need to be treated so the materials can be disposed of at a WDNR-licensed solid waste (Subtitle D) landfill if removal was the selected remedial option.

  However, the delineated spatial extent of 1,000 mg/kg was not aimed for implementation of in-situ remediation, rather a target level of 2,000 mg/kg was used as the threshold. The stated reason was that in five years, only the area with arsenic exceeding 2,000 mg/kg would be "future hot spot". The prediction was based on assumptions that arsenic level at the site decreases with a half-life of about 4-5 years. SS with arsenic concentration of 1,000 mg/kg would no longer be characterized as hazardous waste in 4-5 years based on the estimated natural attenuation rate. Therefore, only the area with arsenic concentration greater than 2,000 mg/kg would be characterized as hazardous waste after 4-5 years. As a result, arsenic concentration of 2,000 mg/kg was established as remedial action target level for delineation of an area for in-situ treatment (TRC, 2010). At the same time, the consultant acknowledged that the natural attenuation rate might contain high uncertainties and the assumptions were only applicable to marsh materials not the ballast solids present along the railroad tracks. During implementation of the in-situ treatment, the actual dose of chemicals was evaluated to meet the SPLP leachate arsenic concentration of 148 ug/l from samples collected from the targeted area.

  Re-evaluation of the attenuation trend as part of the current development of RASP indicated that the estimated attenuation rate may be biased high due to many factors including: 1) no consideration of arsenic transport and 2) no consideration of influence of water content. As discussed in Appendix A, it was found that in most cases samples used for comparison in temporal trend were collected not in line with the SW transport direction. To better evaluate the trend, the difference of arsenic concentrations in samples from different timeline should be treated as a vector. Samples collected from later years should be located either at the same location or downstream from the previous year because downstream transport is a significant pathway implied in the attenuation rate. However, based on the documentation, paired samples chosen for temporal trend evaluation were geographically located in direction opposite to the flow direction in most cases, although geolocation of the samples may carry high uncertainties. The decreasing rate is believed to be slower than the reported if location of samples were considered for analyses.

  Besides the influence of relative location of samples, variation of water content in samples collected in different years can also affect arsenic in SS samples as discussed in Appendix A. Site specific data show that higher water content is positively related to higher arsenic concentrations in some SS samples.

Nevertheless, even if concentration of arsenic in SS is decreasing at the site, the mechanisms may include volatilization, discharging to the Kewaunee River, infiltration from surface to deeper SS, and uptake by vegetation and wildlife. Transfer from one environment to another at the site is an environmental concern, particularly if substantial amount of arsenic volatilizes from the marsh to the air because the air born arsenic is more toxic to human and public is using the rail-trail adjacent to the site.

- To treat the materials with arsenic concentration $C_{As} \geq$ 2,000 mg/kg in-situ, chemical dose was evaluated to achieve a site-specific arsenic cleanup criterion of 148 ug/l in leachate from SPLP. However, higher individual concentration, up to 5 mg/l, was acceptable in performance verification process. According to TRC (2010), "*modifications to the numeric treatment goal were allowed*" and "*achievement of SPLP arsenic concentration below the hazardous waste criteria (5 mg/L), met the remedial objectives for the in-situ treatment. Therefore, the effectiveness of the full scale remedy was determined to be sufficient by TRC and the WDNR.*"

Related to the interim actions, site specific RCL of 20 mg/kg and arsenic concentration of 148 ug/l in SPLP were applied. The vegetative cap consists of woodchip overlain a geotextile sheet and polystyrene foam panels in some ponded area over a total of 4-acre area and the chain-link fence covers a 15-acre area. The extent of the action (Fig.1) was determined based on the site-specific RCL of 20 mg/kg, although not all areas with exceedance was covered or fenced in, particularly on the east side, maybe partially due to high water level at the time.

The extent of 2011 in-situ remedial action for approximately 0.2 acres was defined based on the 148 ug/l in leachate of SPLP which was associated with concentration of 2,000 mg/kg in SS according to data collected prior to 2010. Laboratory bench tests achieved the goal of 148 ug/l in SPLP leachate of testing samples. Information regarding the remediation can be found in the report by TRC (2011) and briefly summarized in Appendix A of this memo. Unfortunately, results from post remediation monitoring showed that arsenic concentration in GW within and immediately downstream of the treated area did not meet the criterion of 148 ug/l but with higher concentrations in a range of 12-380 mg/l in samples collected between Nov. 2011 and May 2017.

Proposed long-term remediation goals for the Site

The long-term remediation goals for the KMASS are determined to improve environmental quality in the marsh to support ecological function and recreational use set forth in Wis. Admin Code chs. NR103, 104, 105, and 140 and to minimize arsenic loading to the Kewaunee River. Specifically, the site should be managed to achieve that

- arsenic in surface water (SW) at the site will meet surface water arsenic criteria in accordance with ch. NR 105
- arsenic in groundwater (GW) at the site will meet groundwater arsenic criteria in accordance with ch. NR 140
- arsenic in soil/sediment (SS) at the site will not exceed a level that may cause risks to human health and ecological system

- arsenic in SS at the site will not cause exceedance of water quality criteria for both SW and GW
- discharge of arsenic to the Kewaunee River is minimized or eliminated.
- overall quality of the marsh will be improved to support ecological function and recreational use in accordance with Wis. Admin Code chs. NR 103 and 104.
- Numerically, remedial action needs to be implemented to ultimately meet the applicable criteria, thresholds, and guidelines as follows:

Surface water (SW)
For protection of human health from cancer risk, arsenic concentration in surface water needs to meet water quality criteria of 40 ug/l and 13.3 ug/l within the marsh and near the shore of the Kewaunee River or in the area below ordinary-high-water-mark (potentially at 580.2 ft mean sea level), respectively. As references, for protection of vegetation and wildlife, arsenic concentration in surface water may not exceed 3-28 ug/l and 15-32 ug/l, respectively. In addition, loading of arsenic to the Kewaunee River from the site via surface discharge should be minimized or eliminated in order to reduce impact to Lake Michigan which is a drinking water source.

Groundwater (GW)
Arsenic in groundwater should be reduced to meet the public health enforcement standard (ES) of 10 ug/l. Because of the marsh condition, the groundwater samples collected may represent the surface and pore water; therefore, the surface water criteria as stated above may be referenced, particularly at the interface between groundwater and surface water at the transition zone between the marsh and Kewaunee River. In addition, discharge of arsenic to the Kewaunee River from the site via groundwater transport should be minimized in order to reduce impact to Lake Michigan.

Soil and Sediment (SS)
Although the statewide soil background arsenic level is 8 mg/kg, concentration of arsenic not to exceed 20 mg/kg in SS is an appropriate objective for remediation at the site in order to achieve the background level in the future. As documented by STS (2004), arsenic concentration of 20 mg/kg was derived from human cancer risk-based site specific residual contaminant level (RCL) assuming adolescent trespassers exposes to arsenic via ingestion of arsenic contaminated soil (Table 1). Because of the complicated hydrologic condition at the site, portion of marsh material is also considered as sediment. Arsenic thresholds for protection of fresh water benthic community in sediment ranges from 10 to 33 mg/kg with a median level of 21 mg/kg (Table 1). In terms of marsh vegetation and wildlife, there are no existing regulatory criteria. A numerical value of 50 mg/kg is suggested as a reference for this site. This reference value was derived from water phase thresholds recommended by the US Fish and Wildlife Services (USFWS) and US EPA and State of Michigan as discussed in Appendix A.

Considering arsenic currently present in SS and associated aqueous phase is the primary source causing elevated arsenic concentrations detected in SW and GW and discharge to the Kewaunee River, remedial action performance standard established for SS governs the remedial action objectives. Comparing the threshold limits for SS with respect to different biological endpoints, it is determined that the site specific RCL (C_{As} = 20 mg/kg) is the baseline performance standard which is more stringent than the thresholds for protection of vegetation and wildlife and the same as the median level guideline for sediment. This baseline performance standard applies to all arsenic contaminated solid and associated aqueous phase without differentiation of vertical location from ground surface. Any deviation of remedial action levels from the baseline performance standard needs to be supported by additional evaluation on the nature and extent of contamination at the site as discussed below.

Nature and extent of contamination

Comparison of arsenic concentrations to applicable criteria and thresholds

To develop performance standards, site specific characterization of arsenic contamination needs to be fully understood. A review of arsenic data collected from 1994 to 2018 was conducted. As the record shows that substantial amount of information has been collected for different purposes. Historically, some spatial analyses using GIS tool were conducted (STS, 2006 and RMT 2010); however, not all arsenic data are in georeferenced format. As part of the current review, efforts were made to compile all the arsenic data for three environmental media with georeferencing for each sample so that the data can be imported for spatial analyses using tools such as GIS. Summary of data compilation is discussed in Appendix A.

After all the data were compiled, arsenic concentrations were compared to applicable criteria and thresholds without differentiation in spatial distribution and potential uncertainties associated with the data. Fig. 2 through 4 show the comparison of arsenic concentrations to criteria and thresholds for SW, GW, and SS on a temporal scale.

A total of 160 SW sample results were compiled for arsenic concentration. No samples were collected from 1998 to 2000, from 2006 to 2009, and in 2015. On a temporal scale, arsenic concentration in SW showed an apparent decrease trend in samples from 1994 to 1997 but have not changed significantly since 2001 (Fig. 2). This temporal trend may be affected by where the samples were collected for what purpose. For instance, samples collected in 2018 were all located within the capped area. Nevertheless, all SW samples exceeded human cancer risk-based criterion of 0.2 ug/l for Lake Michigan water and majority of the samples contained arsenic greater than the human cancer risk-based criteria of 40 ug/l and 13.3 ug/l for the Kewaunee Marsh and Kewaunee River, respectively. Samples collected from the cap surface in 2018 exceeded acute toxicity criteria of 340 ug/l which is applicable to all three surface water systems of the marsh, river, and Lake Michigan.

Substantial number of GW samples have been collected since 1995 with a total of 573 samples analyzed. No samples were collected from 1998 to 1999, from 2006 to 2009, and from 2015 to 2016. Arsenic in most of the samples exceeded GW enforcement criterion of 10 ug/l (Fig. 3). Opposite to the trend obverted in SW, between 1996 and 2002 arsenic concentrations were comparable, but after 2004, higher concentrations were detected. Even higher frequency of exceedance of the surface-water-quality-criteria based discharge limits of 925 and 680 ug/l were observed. The increase of the frequency in detection of higher concentrations may be partially attributed to variation of spatial location of the monitoring wells as shown in Fig. A-9 (Appendix A) as well as fluctuation of groundwater table (Fig. A-10) and potentially the transport patterns. In addition, the GW samples may represent SS pore water, particularly samples collected from shallow wells.

As shown in Fig. 4, the latest SS samples were collected in 2011 with data gaps from 1998 to 2000, from 2007 to 2008, and after 2010. Among 502 samples analyzed, approximately 60% of SS samples were detected with arsenic concentrations exceeding the site-specific RCL of 20 mg/kg for soil and PEC of 33 mg/kg for sediment, respectively. About 70% of samples exceeded TEC of 10 mg/kg for sediment. To some extent hazardous waste may be potentially present at the site based on comparison of the concentrations in SS with associated TCLP or SPCP test results in the past. However, the in-situ remediation pilot project may have reduced arsenic concentrations in leachates of SS in the treated area. If verified, those materials may be declassified as non-hazardous for disposal.

Horizontal extent of contamination

Concentration is a qualitative measure of the degree or severity of contamination present at a site. Comparing concentrations to criteria and thresholds provides an understanding of the nature of contamination on a screening level. Development of performance standards for site cleanup needs to integrate the nature of contamination with the horizontal and vertical extent of contamination. Understanding the extent of contamination not only help define the current and future sources of contamination but also implicitly evaluate exposure risks. At the KWASS site, the larger an area with higher concentration is, the higher risk the area will pose to human health and the environment. The more mass of arsenic present in a specific area, the longer time the system will take to recover to environmentally sound condition. The closer an area with higher concentration to the Kewaunee River is, the more mass of arsenic discharge to the river. Results from evaluation of spatial extent of contamination can support determination of performance standards, evaluation of remedial actions, and selection of remedial techniques.

Ideally the data used to evaluate the extent of contamination would be collected within the similar time period because concentration of arsenic in each medium post spill changes with time. The change is governed by the fate and transport of arsenic in the marsh. The existing data were collected for different purposes from different locations within a long time between 1994 and 2018. To be conservative, it is determined to use all available arsenic data as if they were collected recently to examine the extent of contamination so that the maximum extent maybe identified.

Fig. 5 shows the outlines of horizontal boundaries where arsenic exceeded 40 ug/l in SW, 10 ug/l in GW, and 20 mg/kg in SS, respectively. These outlines are drawn based on the outmost location of samples with arsenic concentration detected higher than the corresponding criteria and threshold without differentiation of vertical location of the samples for SS. The numerical limits chosen to be compared with are the SW human cancer risk-based criterion for the marsh, enforcement criterion for GW, and site-specific RCL for SS. Area bounded by arsenic detected at greater or equal to the value is considered as baseline boundary of contamination for each medium. Criteria and threshold lower than these values are not selected for delineating the baseline extent because there were limited samples showing exceedance as such:

- for SW: comparing to 13.3 ug/l, only one sample (C_{As}=26 ug/l) showed exceedance on west side of the baseline boundary and a few samples were detected on north which were considered as local background area. One sample from the background area had pore water detected at 6.6 mg/l. Verification of SW quality at the background location may be needed in the follow up work.
- for GW: only three samples were collected outside of the baseline boundary. These samples are located on south side of the fence and arsenic concentrations were detected less than 10 ug/l.
- for SS: only three samples had arsenic concentration exceeding 8 mg/kg outside of the baseline boundary. Of these three samples only one sample exceeded 10 mg/kg (TEC for sediment). In addition, average concentration of all samples collected outside the extent was about 5 mg/kg.

Therefore, it is reasonable to consider the boundaries displayed in Fig. 5 as baseline extent for evaluation of horizontal extent of contamination. A noticeable fact is that the baseline boundaries extended beyond the fenced-in area, particularly for the SS on the north and northeast. On direct east of the fence, the baseline concentration boundary extends out from the fence for all three media, similarly, some areas in the south side as shown in Fig. 5. The largest gap between the fence and baseline boundaries was observed for the SS boundary on the northeast side.

The discrepancy of the fence perimeter and baseline boundary in some areas leads to a question of whether to include these areas for remediation. It is determined that with frequent detection of higher arsenic concentration in three media and its proximity to the Kewaunee River, the east side of the fence will be included for evaluation of remedial actions. On the south side, the difference was mainly attributed to the exceedance of arsenic criteria in SW and GW. Because concentrations of arsenic in SW and GW are governed by fate and transport of arsenic in SS, these areas are less likely subject to active remediation. However, area close to the original spill site may need additional SS samples collected. This conclusion is supported by the data as described in Appendix A. Relatively larger extent towards the north side was caused by detection of higher arsenic concentration present in SS and GW. Final decision of whether to include these areas for active remediation will be made during remedial option evaluation phase.

In addition to the baseline boundaries, horizontal extent was also examined for each medium with different arsenic levels. Fig. 6 shows the horizontal extent of arsenic concentration (C_{As}) in SW as such $C_{As} \geq 13$ ug/l, ≥ 40 ug/l, ≥ 152 ug/l, ≥ 340 ug/l, and $\geq 1{,}000$ ug/l, respectively. For this evaluation, $C_{As} \geq 13$ ug/l was included to show relative change of surface area comparing to that of $C_{As} \geq 40$ ug/l. The surface area under $C_{As} \geq 13$ ug/l does not differ significantly from that bounded by $C_{As} \geq 40$ ug/l, only with an increase of 6%. Similarly, surface area does not change much between $C_{As} \geq 152$ ug/l and ≥ 340 ug/l. However, the area decreases significantly where $C_{As} \geq 1{,}000$ ug/l (1 mg/l) comparing to the rest. Relative to the area bounded by $C_{As} \geq 13$ ug/l, about 56% of the area has arsenic exceeding 1,000 ug/l detected as indicated in the table (Fig. 6).

Similarly, GW data were compared to different concentration levels to delineate the boundaries of exceedances. Fig. 7 displays approximate horizontal extent with arsenic concentration (C_{As}) in groundwater exceeding applicable criteria and threshold of C_{As} ≥10 ug/l, ≥40 ug/l, ≥152 ug/l, ≥340 ug/l, and ≥1000 ug/l, respectively. The area highlighted for C_{As} ≥5,000 ug/l is just for information purpose and the boundaries cannot be defined due to limited number of wells, particularly for the area on the east side close to the river. Relative to the area bounded by exceedance of 10 ug/l, approximately 89% of the area have arsenic detected exceeding 40 ug/l, 48-62% exceeding 152-340 ug/l, and 37% exceeding 1,000 ug/l, respectively, as summarized in the table inserted in Fig. 7. With the same concentration of 1,000 ug/l, contamination seems less spread in GW (5 acres) than in SS (10 acres). Vertical location of the screening may affect the distribution patterns of arsenic in GW. The top of the screening in the wells located in east side with arsenic concentration detected greater than 5,000 ug/l ranged from 1.5 to 2.5 ft below ground surface level (bsl) comparing to 4.5 to 10 ft bsl located near the original spill area. Most of the samples from the east end of the cap were collected from wells screened about 3-5 ft bsl.

Fig. 8 shows approximate horizontal extent with arsenic concentration (C_{As}) in SS of C_{As} ≥20 mg/kg, ≥50 mg/kg, ≥100 mg/kg, ≥500 mg/kg, and ≥1000 mg/kg with the deeper layers projected to as in surface. Obviously, the horizontal extent with exceedance of 20 mg/kg is the largest among boundaries evaluated. Again, thresholds less than 20 mg/kg was not used for comparison because only in limited samples arsenic exceeded 8 mg/kg outside of the baseline boundary. With the maximum concentration examined, the area bounded by 1,000 mg/kg has the same size as the capped area (about 4 acres) but the location shifted towards further south of the cap with an overlap of about 2.5 acres. Overall, relative to the area bounded by exceedance of 20 mg/kg, approximately 69% of the area have samples detected exceeding 50 mg/kg, 56% exceeding 100 mg/kg, 30% exceeding 500 mg/kg, and 21% exceeding 1,000 mg/kg, respectively, as summarized in the table inserted in Fig. 8.

Although the three media were treated as disconnected when horizontal extent of arsenic contamination was evaluated, development of performance standards needs to combine the state of contamination in all media as whole. There are common areas where arsenic concentrations exceeded thresholds in all media. As an example, Fig. 9 shows horizontal extent for three media under different boundaries was examined for selected limits. An important factor Fig. 9 demonstrates is that if SS is remediated to the extent of C_{As}≥100 mg/kg boundary, substantial area with arsenic concentration exceeding 1,000 ug/l in SW and 152 ug/l in GW will be addressed. If the performance standard is lowered to 50 mg/kg of arsenic in SS, additional areas with arsenic concentrations fall between 40 ug/l and 152 ug/l in SW and between 10 and 152 ug/l in GW will be addressed. Results from evaluation of combined concentration boundaries for the three media support the decision that SS is the primary medium for establishing RAPS. It also implies that arsenic in SS is the current and future continuous source causing high concentrations of arsenic in both water phases. Only when arsenic in SS is addressed, the quality of SW and GW will improve and gradually the site can recover to meet the ultimate environmental cleanup goals. Stated differently, remediation of SW and GW alone will not solve arsenic contamination problem at the site. With this understanding, arsenic present in SW and GW was not used for further development of RAPS based on horizontal and vertical extent of arsenic concentration and mass at the site.

Area-weighted concentration and distribution of mass

Quantity of contaminant present in environment is another important measure of level of contamination. For this site, understanding the distribution of mass in horizontal extent helps further define the center of contamination and areas of arsenic mass under various concentration boundaries. As a screening method, distribution of area-weighted concentration and mass was estimated by multiplying average concentration within a boundary with the surface area and then a relative mass is calculated comparing to a baseline condition. This estimation only applies to SS. Arsenic concentrations of C_{As} = 20, 50, 100, 500, and 1000 mg/kg were used as evaluation thresholds and the corresponding area-weighted concentrations bounded by the exceedance of these thresholds are defined with scenarios of M**20, M50, M100, M500, and M1000,** respectively. Area-weighted concentration in the area bounded by $C_{As} \geq 20$ mg/kg is treated as the baseline for comparison. Therefore, the ultimate results are mass distribution under different scenarios relative to **M20** assuming that vertical extent of arsenic contamination and bulk density across the entire site are the same.

Results of the analyses are displayed in Fig. 10 and the associated tables. The line figure shows the distribution of cumulative area-weighted concentrations relative to **M20** which is the same as cumulative mass distribution assuming same vertical extent and bulk density for the entire site. Cumulatively, relative to **M20**, approximately 76%, 70%, 39%, and 30% of total mass were estimated to be present in areas under **M50, M100, M500,** and **M1000**, respectively. The results indicate that if performance standard is set at 50 mg/kg, more than 76% of mass present under baseline boundary (**M20**) will be addressed.

The bar chart in Fig. 10 displays the increment of relative mass to **M20** starting from the area bounded by $C_{As} \geq 1000$ mg/kg. For instance, the total mass in the area bounded by $C_{As} \geq 1000$ mg/kg (Scenario **M1000**) is about 30% of the total mass under **M20**. Between **M1000** and **M50** ($1000 > C \geq 50$) arsenic mass was estimated to increase by 10% relative to **M20**. However, the average concentration may not be reflective of the true concentrations of arsenic in SS between these two boundaries because it is controlled by the higher concentrations in **M1000.** With high uncertainties, particularly the calculated average concentrations between scenarios, the results may provide the information relative to **M20** that:

- significant amount of arsenic mass (30%) is present in the center bounded by concentration of 1,000 mg/kg (**M1000**) with a lesser area of approximately 21%.
- significant amount of mass may present in the area between scenarios **M500** and **M100 (31%)**. Increase of mass between two boundaries seemed primarily due to increase of surface area (26%).
- increase of mass between **M100** and **M50** is insignificant (5%) although the area was increase by 13%.
- with the similar reason, due to increase of area, a big increase of arsenic mass (24%) between scenario **M50** and **M20** is observed. Area between these two scenarios increases from 13 to 19 acres (about 31%).

Volume-weighted concentration and distribution of mass

With respect to human health concerns via direct contact, the site specific arsenic RCL of 20 mg/kg is applicable to the top 4 ft of soil in accordance with NR700 rules series. However, this site is located within a marsh and adjacent to the Kewaunee River, arsenic present in SS deeper than 4 ft of SS is of a great concern as well because arsenic in any depth serves as a long-term source directly or indirectly causing impact to the marsh ecological community and discharging to the Kewaunee River. For remedial action evaluation and implementation, therefore, it is important to understand the vertical extent of contamination and associated mass amount.

In the analyses of area-weighted concentration and distribution of mass in different boundaries, the vertical extent was not spatially differentiated while the existing data have clearly indicated that vertical contamination may vary from 6 inches to 23 ft at the site and the concentration of arsenic also varies significantly. In general, higher concentration of arsenic has been detected mostly in the upper 10 ft of SS (Fig. 11). Further deep, arsenic exceeded 20 mg/kg were detected only in three samples in the interval of 18-20 ft and one sample in the interval of 20-23 ft. Spatially, these deeper samples are located exclusively near the original spill area and potentially in ballast materials. It is inevitable that there is a need to further define the mass distribution in 3-D perspective. Tools are available for 3-D analyses; however, for the preliminary analyses they are not explored. Instead, the follow-up analyses were conducted for individual layers of SS that was segmented with different thickness intervals according to the segmentation schemes applied to core samples in previous site characterization. Because vertical depth had no datum referenced for cores in the reports, the vertical extent is referenced relative depth from ground surface.

In addition, based on the results from the evaluation of area-weighted concentration and relative mass distribution, the vertical extent of contamination was conducted only for three arsenic concentrations of 20 mg/kg, 50 mg/kg, and 100 mg/kg. Following the similar process, the mass present in the prism bounded by arsenic concentration of $C_{As} \geq 20$ mg/kg is considered as baseline scenario (**C20**) and the other two are then defined as scenarios **C50** and **C100**, respectively. Also, an attempt was made to estimate total mass potentially present in the prism under scenario **C20** based on the data collected since 1994, which is assumed to be the most probable mass present at the site.

Key parameters for evaluation of volume weighted arsenic concentration, relative mass distribution, and the total mass under **C20** include surface area, thickness, and average concentration of arsenic bounded by the prisms defined by $C_{As} \geq 20$, ≥ 50, and ≥ 100 mg/kg, respectively. The evaluation followed the steps as described below:

1) Divide the SS under the area defined by **C20** into eight layers from the surface to 23 ft, mostly in 2-ft intervals with two exceptions. One exception is the designation of surface layer. Results from grab samples collected are considered to represent the top 1ft SS while the top 2 ft (0-2ft) SS from core samples is another representation of surface layer. These two segmentation schemes resulted in evaluation of minimum and maximum lateral extent of contamination for surface layer as well as the associated mass estimate. The other exception is the deeper SS. Corse segmentation scheme was applied for SS deeper than 12 ft when samples were collected. Due to limited number of core samples

available, a 6 ft thick segment was defined for SS between 12 and 18 ft and the last layer was defined as depth (D) greater than 18 ft (D>18) but with limited average thickness of 3 ft for the interval of 18- 23 ft. As a result, a total of eight layers and subsequently eight prisms were evaluated for volume-weighted concentration and mass.

2) Define the horizontal extent for each layer under scenarios **C20**, **C50**, and **C100**.
3) Calculate surface area for each layer as defined in Step 2).
4) Calculate volume for each layer as defined in Step 2) and the thickness. Compare the volume of SS under **C50**, and **C100** relative to **C20**
5) Calculate relative volume weighted concentration and distribution of relative mass. This step is more complicated and can be further described as follows:
    a. Select all samples under the outline determined from Step 2) for calculation of average arsenic concentration for each layer under scenarios **C20, C50**, and **C100**. The average concentration (C_{ave}) for baseline scenario **C20** was used for calculating total arsenic mass in each layer with assumptions that data collected between 1994 and 2010 are representative for average concentration present in 2010.
    b. Estimate mass of arsenic for each layer under **C20** assuming a constant bulk density of 0.5 g/cm3 and sum up the mass in each layer total mass estimate.
    c. Start with scenario **C100,** volume weighted concentration or mass ($M_{\mathbf{C100}}$) was calculated for each layer by multiplying the volume (V) with average concentration (C_{ave}) without considering bulk density because ultimately it will be canceled out when relative mass distribution was estimated for each layer if the assumption of same bulk density is valid.
    d. Calculate the increment of volume (ΔV) in the transition zone between boundaries of scenarios **C100** to **C50** and **C50** to **C20** by multiplying the increase of area (ΔA) with thickness of (D) for each layer.
    e. Identify samples located in the transition zone between **C100 - C50** and **C50 - C20** for each layer. Calculate average concentrations of arsenic (C_{dta}) based on the samples located within the transition zone for each layer.
    f. Calculate increment of volume weighted concentration or mass for scenarios **C50** and **C20** ($\Delta M_{\mathbf{C50}}$ and $\Delta M_{\mathbf{C20}}$) by multiplying ΔV with C_{dta} for each layer. This approach was used to reduce uncertainties of volume weighted concentration or mass associated with significant change of average concentration of arsenic in samples within the transition zones between scenario boundaries. The average concentration as used for area weighted concentration estimation (C_{ave}) does not capture the concentration gradient between scenario boundaries for each layer but C_{dta} does.
    g. Estimate total volume weighted concentration or mass ($\sum V_iC_i$) for each layer by adding $\Delta M_{\mathbf{C50}}$ and $\Delta M_{\mathbf{C20}}$ to $M_{\mathbf{C100}}$, which is equivalent to the total volume weighted concentration or mass under **C20**. Summation of $M_{\mathbf{C100}}$ and $\Delta M_{\mathbf{C50}}$ is the total volume weighted concentration or mass for scenario **C50.** Then the relative distribution of mass under each scenario can be evaluated by comparing the volume weighted concentration or mass for each layer under scenarios **C100** and **C50** to that under baseline **C20**.

h. Consider uncertainties associated with known variation, such as sampling methods and spatial distribution of the samples in estimation. One fact is that arsenic data for surface SS contained both grab and core sample results. The grab samples cover larger horizontal extent than the core samples do. Another fact is that deeper than 2ft, sometimes the horizontal extent of boundary was increased significantly due to only one or two samples. Therefore, a range of minimum to maximum of volume-weighted concentration or mass was calculated for affected layers:
    i. For the top 2 ft of SS, minimum values were calculated based on average concentration and surface area from the core samples. The maximum value was the minimum plus the increment bounded by the larger surface extent derived from grab samples and with assumption of 1-ft thick of SS.
    ii. For some of the deeper layers, without additional sampling and further statistical analyses, when only one or two samples made the lateral extent extensively larger, the values derived from the larger area are considered as maximum relative to the minimum values excluding these points. This treatment applied to thickness from 4 to 10 ft of SS.

The evaluations results are presented in Tables 2 and 3. Table 2 summaries surface area, average concentration, and volume of arsenic contaminated SS for each layer under scenarios of **C20, C50** and **C100.** Also summarized in Table 2 is the percent of contaminated volume under scenarios **C50** and **C100** relative to that under **C20. T**he average arsenic concentrations in layers of 0-2, 4-6, 8-10, and 12-18 ft are higher than that in the other layers as shown in Table 2.

Impacted surface area decreases with the depth with a skewed upside-down cone shape for all scenarios. Fig. 12 is an example of the horizontal extent in each layer for scenario **C50**. As shown in the figure the area of contaminated SS is the largest in surface (0-2 ft) and smallest in depth greater than 18ft. Overall, horizontal extent between 0 to 6 ft from surface were substantially larger than deeper layers. Although the contaminated area decreases as it gets deeper, the average concentrations were similar except in layers of 2-4 ft and deeper than 18ft (Table 2). The lower concentration in 2-4 ft may be biased by the location of samples because after the cap was placed in 1996, most of the samples were collected from outside of the cap.

Total volume under **C20** ranges from 65,000 to 87,000 cyd (Table 2). If performance standard changes from 20 mg/kg **(C20)** to 50 mg/kg **(C50)** or 100 mg/kg (**C100**), the total volume is reduced to 48,000 -63,000 cyd or 44,000 - 50,000 cyd, respectively, which are about 57% to 74% of that under **C20**.

Fig. 13 shows the vertical distribution of relative mass of arsenic estimated for each layer and total mass under baseline scenario **C20.** The top 2 ft SS alone contains about 59% of the total arsenic mass. Cumulatively, based on the estimation, approximately 94% of mass is present in the top 6 ft of the SS, 98% in the top 8 ft, and 99% in the top 10 ft. This vertical profile of mass distribution coincides with the distribution pattern of arsenic concentrations detected in groundwater as shown in Fig. A-9 of Attachment A.

As summarized in the table associated with Fig. 13, approximately 23,000 – 28,000 kg (23-28 tons) of arsenic may be present in the volume of 65,000 to 87,000 cyd of SS based on all samples collected from 1994-2010 under **C20**. This mass amount is compared well with 21,000-27,000kg (21-27 tons) remained by 2010 based on the estimate of total amount spilled minus total amount of arsenic discharged to the river in the same time period assuming maximum discharge amount of 11,250 kg (11 tons) as discussed in Appendix A. It is reasonable to use the maximum value for the estimation because there are more discharge locations than the two sloughs. The total arsenic spilled was estimated to be approximately 38,000kg (38 ton). Without remediation, on annual basis, maybe 9 -161 kg of arsenic could continue to discharge to the Kewaunee River via two sloughs alone. There is possibility of more arsenic being discharged when considering the shoreline of the marsh.

Table 3 is a summary of volume weighted concentration or mass in different SS layers and relative distribution of mass under **C50** and **C100** to that under **C20.** Significant observations include:

- under scenario **C100** and relative to the total mass of arsenic under **C20** – within the boundary, the prisms contain approximately 90%-99% of total mass in layers of 0-6 and 12-18 ft and 20-73% in the rest of layers, respectively. Only one sample was detected greater than 100 mg/kg in SS deeper than 18 ft. Overall, if the site is cleaned up to 100 mg/kg horizontally and vertically, approximately 85%-89% of the total mass relative to that under **C20** will be addressed.
- under scenario **C50** and relative to the total mass of arsenic under **C20** – within the boundary, the amount of mass was the same as that under **C20** in layers 8-10 and greater than 18 ft because of the same lateral extent. All other prisms contain over 90% of total mass except for layers 6-8 ft and 10-12 ft in which it ranged from 29% to 82%. Overall, if the site is cleaned up to 50 mg/kg horizontally and vertically, approximately 89%-94% of the total mass under **C20** will be addressed.

Spatially, the relative mass distribution for each layer under three scenarios are shown in Fig. 14-25. In each 2-ft interval within the top 6 ft, proportionally, almost or over 90% of total mass under **C20** was estimated to be present in **C50** and **C100** while the relative area ranged from 48% to 93%.

Conclusions and recommendation

Exceedance of arsenic criteria and standards are significant in SS, GW, and SS at the site. Arsenic present in the marsh SS and associated aqueous phase is a long-term source that will continue to cause adverse impact to SW and GW and pose risks to human health and ecosystem. By 1994, approximately over 23,000 to 28,000 kg (23-28 tons) of arsenic may be present in the marsh compared to an estimate of 38,000kg (38 tons) spilled on to the site assumed in 1940. Historically, maybe 14,000 kg of arsenic over the time period of 1940 (assuming the spill year) to 2010 have discharged to the Kewaunee River. On annual basis, maybe 18 -194 kg of arsenic discharged and could continue to discharge to the Kewaunee River via two sloughs alone, not to count advective and diffusive transport at the interface of the marsh and river.

Results of distribution of area and volume weighted concentration and hence mass at the site indirectly link to the probability of exposure risk associated with arsenic contamination at the site. The larger the spatial extent with higher concentration, the higher risks the area may pose to the environment and human health. In addition, the more mass in a given area the more important as a source to contribute arsenic to cause long-term environmental impact. The results lead to determine that arsenic concentration in a range of 20 and 50 mg/kg in SS is the potential RAPS for the site. Combination of different performance standards applying to specific units may be appropriate for remedial actions evaluation and selection of a remedial option. For examples, the action level of either 20 mg/kg or 50 mg/kg is both acceptable for layers of 4-6, 6-8, deeper than 12 ft, and potentially the top 2 ft because similar extent of contamination will be addressed. But for the rest of the layers, the standard may need to be set at 20 mg/kg; however, the target levels may be modified if additional samples are collected. This proposed range of performance standards is not only protective to human health but also for protection of vegetation and wildlife.

Further evaluation is needed to optimize a combination of different cleanup technologies in conjunction with different remedial performance standards and cost-effectiveness. Optimization of remedial options with consideration of feasibility is one of the tasks during remedial option evaluation by the consultants. However, it is believed that with 20 mg/kg of arsenic in SS considered as the baseline action level for remediation, arsenic contamination at the site and thus the adverse impact to the environment will be greatly improved. Subsequently, with time after remediation, the quality of water will recover to meet the criteria set forth in chs. NR105 and NR140. At the same time, loading of arsenic to the Kewaunee River and Lake Michigan will be significantly reduced or eliminated.

References:

WDNR, 2000. Baseline Ecological Risk Assessment for the Arsenic Contaminated Wetland associated with the CD Besadny fish and Wildlife Area and the Kewaunee River, prepared by WDNR Bureau of Watershed Management Water Quality Standards Section, April 2000.

Victor, 2018. Site Investigation Summary and Data Package. Kewaunee Marsh Arsenic Spill Site, Kewaunee, WI.

STS, 1996. Construction Documentation Report Interim Action, Kewaw1ee Marsh Arsenic Site Kewaunee, Wisconsin.

STS, 2004. Site Assessment and Remedial Action Alternatives Report

RMT, 2007. WDNR-Kewaunee Marsh Treatability Project Final Report

RMT, 2010. Hot Spot Investigation Documentation and Remedial Options Analysis Report

TRC, 2012. Arsenic Source Area In-situ Remediation documentation Report and Baseline Performance Monitoring Report

U.S. Fish and Wildlife Service, 1988. Arsenic Hazards to Fish, Wildlife, and Invertebrates: A Synoptic Review by Ronald Eisler Patuxent Wildlife Research Center, Biological Report 85(1.12) Contaminant Hazard Reviews January 1988 Report No. 12

Shields. S, Memo, 2018, 2019. Applicable Water Quality Criteria for the Kewaunee Marsh Arsenic Spill Site

Table 1. Summary of applicable standards and thresholds for development of remedial action performance standards*

Environmental Medium (unit)	**Conc**	**Comments**	**References**
Soil (mg/kg)			
Direct Contact	20	Human cancer risk -based site specific residual contaminant level (RCL) assuming expoure via ingestion of soil by adolescent trespasser (calculated result was 20.6 mg/kg but 20 mg/kg was recommended)	20040317_37_39SIR_RAOR, Appendix I
Surface water (based on pore water extraction) and groundwater protection at 50 ug/l	400	Incorrect usage of data for plotting and should not be considered for future use	Table 4 , STS, 20040317_37_39_SIR_RAOR
Hazardous material characterization for disposal (TCP>5 mg/l)	**1,000**	Discussed to use this level for delineation of the extent of hot spot but was not used for acutal in-situ treatment	RMT Hot Spot Investigation and Remedial Options analyses (2009-2010). Resource Conservation and Recovery Act (RCRA) Subtitle C - waste characteristics regulations
In-situ hot spot treatment (>5mg/l in GW)	**2,000**	Predcited that in 4-5 years the soil will not be characterized as hazardous material for disposal. Used as residual concentration for in-situ treatment	TRC 2012-03-21-151 remedial option report
Sediment (mg/kg)			
Probable effect concentration (PEC	*33*	These are guidelines and were considered in the past but not used as performance standards. However, in a 2004 report by STS, 21.4 mg/kg was referenced as potential action level.	Sediment consensus based guidelines. Report STS Table 4 (2004). TEC- below which adverse effects are not expected to occur. PEC; above which adverse effects are expected to frequently occur
Threshold effect concentration(TEC)	*10*		
Median level between PEC& TEC(MEC)	21		
Groundwater (ug/l)			
Acute toxicity in surface water (339.8 ug/l)	**925**	Calculated from surface water criteria assuming groundwater discharges to surface water.	July 16, 1998 DNR comments on STS Final Report. DNR report 20030320_350_251_PA_SSI
Chronic toxicity in surface water (148 ug/l)	**680**		
Public health GW quality criterion (enforcement)	10	Has not been used as performance standard	NR140
Public health GW quality criterion (preventative)	1	Has not been used as performance standard	NR140
In-situ treatment goal	**148**	It was derived from surface water criteria	DNR Remedial Action Options Memo(Aug 2010). RMT
Surface Water (ug/l)*			
wildelife	15 to 32	Reference values recommended by the US EPA and the State of Michigan	July 25, 1995 Memo Regarding Water Quality Criteria. Maybe equivalent to 25-85 mg/kg in soil (FWS 1988)
Acute toxicity based	339.8	Same for the marsh, river, and Lake Michigan	RMT Hot Spot Investigation and Remedial Options analysis (2009-2010). DNR memos (1998 - 2019)
Chronic toxicity based for the marsh and river	152.2	Limited aquatic life and warm water sport fishery, respectively	
Chronic toxicity based for Lake Michigan	148	Cold water public water supply	
Human Cancer risk based for the marsh	40	Not used in the past. The DNR SurfaceWwater Qquality program recommend implimentation of human cancer risk based criteria for the site	
Human Cancer risk based for the river	13.3		
Human Cancer risk based for Lake Michigan	0.2		

*numerical values highlighted in red were used in the past for assessment and interim actions

Table 2. Estimates of surface area, average concentration, and volume of contaminated SS under different thresholds[1]

Range	**Interval**	**D_seg**	**C20**			**C50**			**C100**			[a]V_{C50}/V_{C20}	[a]V_{C100}/V_{C20}
			V	C_{ave}	**A**	**V**	C_{ave}	**A**	**V**	C_{ave}	**A**		
	ft	**ft**	**cyd**	**mg/kg**	**ac**	**cyd**	**mg/kg**	**ac**	**cyd**	**mg/kg**	**ac**	**%**	**%**
Min	**[b]0-2**	**2**	36,139	1,157	11.2	26,459	1,341	8	23,619	1,359	7	73	65
	2-4	**2**	19,293	697	6.0	13,860	767	4	13,860	767	4	72	72
	4-6	**2**	6,039	1,479	1.9	5,163	1,680	2	4,614	1,813	1	85	76
	6-8	**2**	1,626	909	0.5	1,129	1,111	0.4	848	1,141	0.3	69	52
	8-10	**2**	709	1,578	0.2	709	1,578	0.2	445	1,759	0.1	100	63
	10-12	**2**	152	995	0.05	97	1,101	0.03	78	1,101	0.02	64	51
	12-18	**6**	563	1,211	0.06	304	1,395	0.03	300	1,395	0.03	54	53
	>18	**3**	29	141	0.01	29	141	0.01	15	141	~	100	51
Subtotal			**64,549**			**47,749**			**43,778**			**74**	**68**
Max	**[c]0-2**	**1**	48,723	1,386	19	34,687	1,976	13	28,685	2,303	10	71	59
	2-4	**2**	19,293	697	6.0	13,860	767	4	13,860	856	4	72	72
	4-6	**2**	12,101	1,414	3.8	11,293	1,421	4	5,848	1,733	2	93	48
	6-8	**2**	5,316	909	1.6	1,130	1,111	0.4	848	1,141	0.3	21	16
	8-10	**2**	1,118	1,578	0.35	1,118	1,578	0.3	445	1,759	0.1	100	40
	10-12	**2**	152	995	0.05	101	1,101	0.03	78	1,101	0.02	67	51
	12-18	**6**	563	1,211	0.06	304	1,395	0.03	304	1,395	0.03	54	54
	>18	**3**	29	141	0.01	29	141	0.01	15	141	0.00	100	51
Subtotal			**87,293**			**62,522**			**50,081**			**72**	**57**

[1] The purpose of the volume estimation is to define mass distribution for development of performance standards. Each value may carry high uncertainties but with relative proportion as the endpoint, the variation may be reduced but estimation of the values is considered in conceptual level. **C20**, **C50**, and **C100** are the scenarios if SS is remediated to arsenic concentration of 20 mg/kg, 50 mg/kg, and 100 mg/kg. Only one sample exceeded 100mg/kg for segment deeper than 18 ft and the area was assumed to be half of that under **C20**. cyd – cubic yard; C_{ave} – average arsenic concentration within the surface area for each layer; ac – acres.

[a] Relative volume in percent: volumes under **C50 (V_{C50})** and **C100 (V_{C100})** relative to **C20 (V_{C20})**, respectively.

[b] For layer 0-2 ft, core samples were used for delineation of horizontal extent and calculation of average concentration. The results are considered as minimum.

[c] For layer 0-2 ft, grab samples were used to define the additional horizontal extent and associated concentrations were used for calculation of average concentration and mass in addition to the minimum values. The mass is the sum of minimum and the additional mass assuming 1 ft thickness.

Table 3 Estimation of relative mass distribution in each layer for scenarios of **C20, C50**, and **C100**[a] and total mass under **C20**

Range	Inter	D	Total V	Total $\sum V_iC_i$	C50 - C20				C100- C50				C100				Mass percent		Total mass (C20)
					ΔV	ΔM_{C20}	C_{dta}	ΔA	ΔV	ΔM_{C50}	C_{dta}	ΔA	V	M_{C100}	C_{ave}	A	$M_{C50}/\sum V_iC_i$	$M_{C100}/\sum V_iC_i$	
	ft	ft	cyd	ppm . Cyd	cyd	ppm . Cyd	ppm	ac	cyd	ppm . Cyd	ppm	ac	cyd	ppm . Cyd	ppm	ac	%	%	kg
Min	**0-2**	**2**	36,139	35,575,807	9,680	2,168,320	224	3.0	2,839	1,308,994	461	0.9	23,619	32,098,493	1,359	7.3	94	90	13,519
	2-4	**2**	19,293	11,624,641	5,433	994,240	183	1.7	-	-	767	-	13,860	10,630,402	767	4.3	91	91	4,417
	4-6	**2**	6,039	9,207,546	876	51,686	59	0.3	549	790,437	1,441	0.2	4,614	8,365,424	1,813	1.4	99	91	3,499
	6-8	**2**	1,626	1,973,016	497	594,300	1,196	0.2	282	411,979	1,462	0.09	848	966,737	1,141	0.3	70	49	750
	8-10	**2**	709	932,727	-	-	569	-	264	150,419	569	0.08	445	782,308	1,759	0.1	100	84	354
	10-12	**2**	152	116,891	55	23,038	420	0.02	19	8,326	436	0.01	78	85,526	1,101	0.02	80	73	44
	12-18	**6**	563	429,414	259	5,437	21	0.03	-	-	1,395	-	300	418,480	1,395	0.03	99	97	163
	>18	**3**	29	4,055	-	-	141	-	15	2,043	141	0.003	15	2,012	141	~	100	50	2
Subtotal			**64,549**	**59,864,097**	**16,800**	**3,837,021**			**3,968**	**2,672,198**			**43,778**	**53,349,381**					**22,748**
Max	**0-2***	**2**	48,723	42,733,167	14,036	3,066,624	64	5.7	6,002	2,089,202	130	2.8	28,685	37,577,341	191	10	93	88	16,239
	2-4	**2**	19,293	12,858,156	5,433	994,240	183	1.7	-	-	767	-	13,860	11,863,917	856	4.3	92	92	4,886
	4-6	**2**	12,101	10,892,765	808	186,548	231	0.3	4,517	474,320	105	1.7	5,848	10,134,449	1,733	2.1	97	93	4,139
	6-8	**2**	5,316	4,841,225	4,185	3,461,368	827	1.3	283	413,120	1,462	0.1	848	966,737	1,141	0.3	29	20	1,840
	8-10	**2**	1,118	1,159,264	-	-	560	-	673	376,956	560	0.2	445	782,308	1,759	0.1	100	67	441
	10-12	**2**	152	116,963	50	21,131	420	0.02	24	10,306	436	0.01	78	85,526	1,101	0.02	82	73	44
	12-18	**6**	563	429,414	259	5,437	21	0.03	-	-	1,395	-	304	423,977	1,395	0.03	99	99	163
	>18	**3**	29	8,047	-	-	141	-	-	4,023	141	-	29	4,023	141	0.01	100	50	3
Subtotal			**87,293**	**73,039,000**	**24,771**	**7,735,347**			**11,498**	**3,367,928**			**50,095**	**61,838,278**					**27,755**

[a] Inter - interval of SS examined; D- thickness of the interval; Total V = total volume; Total $\sum V_iC_i$ = sum of volume weighted concentration or mass ($\sum V_iC_i = M_{C100} + \Delta M_{C20} + \Delta M_{C50}$); and ΔV and ΔA = increment of volume and surface area between scenarios **C100** – **C50** and **C50** – **C20**; C_{dta} = average concentrations based on the samples located within the transition zones of **C100** – **C50** and **C50** – **C20**. ΔM_{C50} and ΔM_{C20} = increment of volume weighted arsenic concentration or mass between boundaries of **C100** – **C50** and **C50** – **C20**. M_{C100} = volume weighted arsenic concentration or mass under scenario C100.

* For interval 0-2, the total volume is the sum of the minimal value based on the core samples and the additional volume bounded by the grab samples with 1 ft of SS. All estimated values are considered in conceptual level

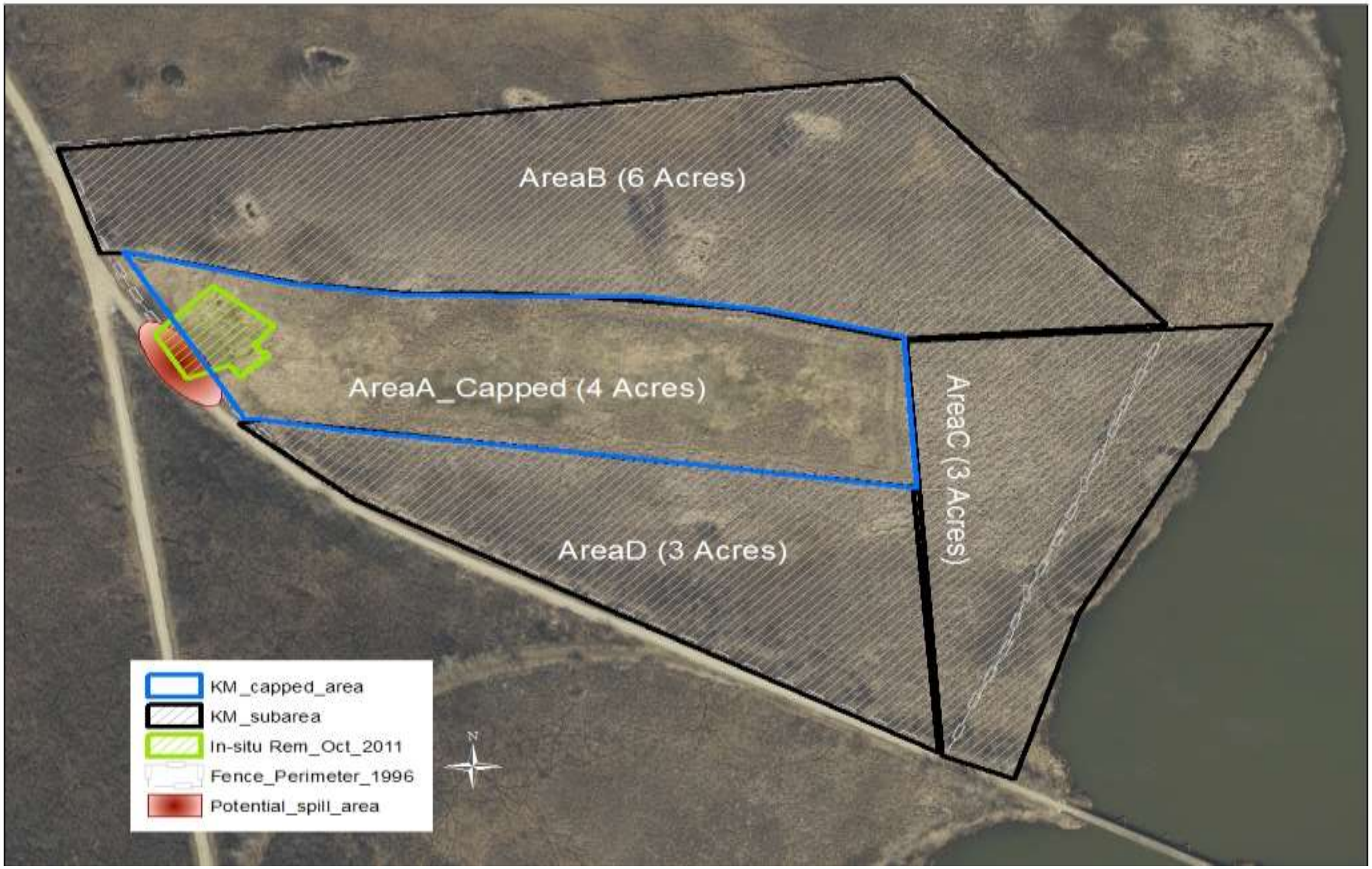


Fig. 1 Surface extent of interim actions took place in 1996 and 2011(KM_capped_area and Fenc_perimeter_1996: extent of 1996 action with placement of woodchips and installation of a chain-link fence; In-situ Rem_Oct_2011: extent of pilot in-situ treatment in 2011. Potential_spill_area: the potential spill area not in scale just for reference purpose. KM_subarea: boundaries of subarea from Area A to D bounded by the fence with an extension towards the eastside close to the river)

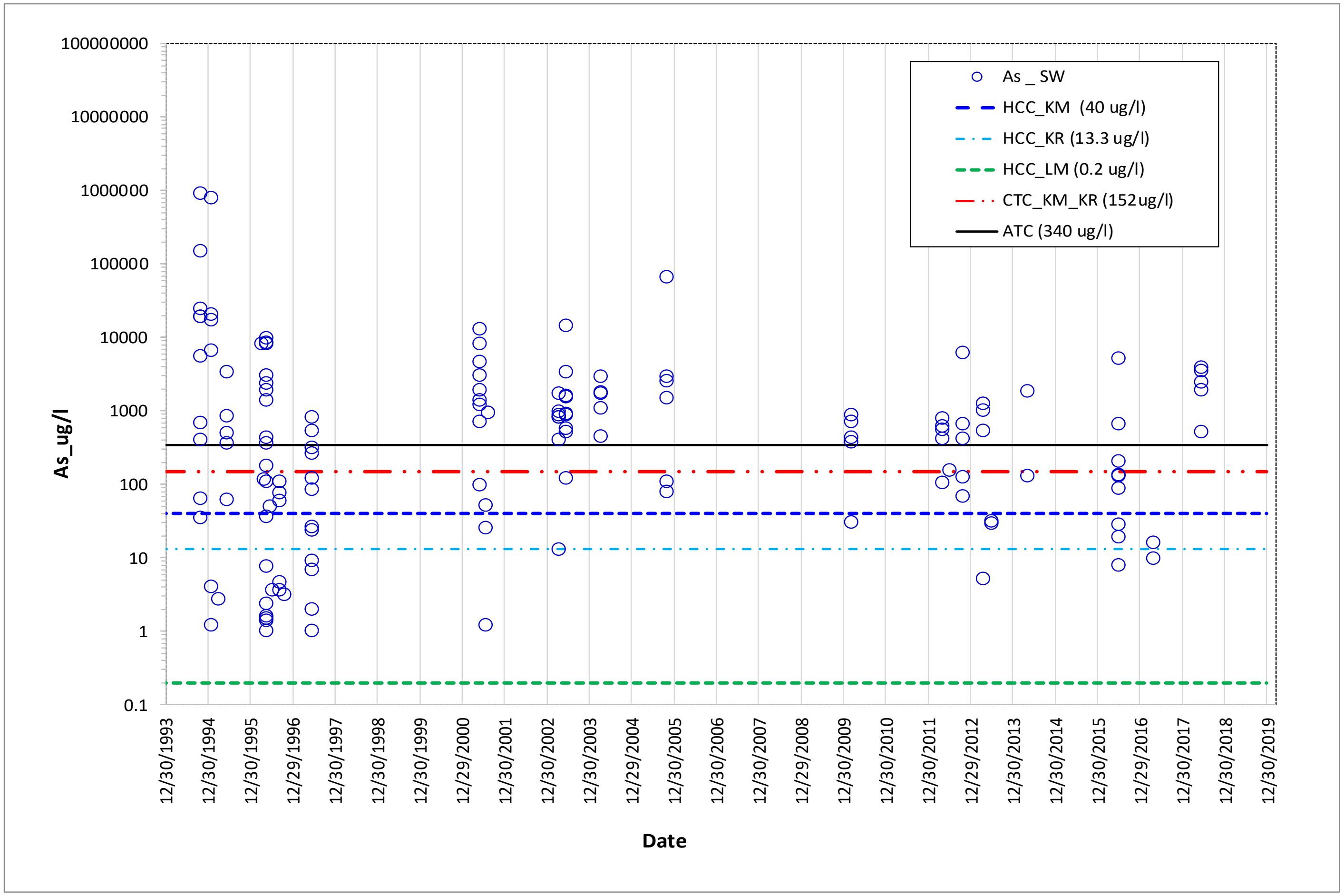


Fig. 2 Comparison of arsenic concentration in SW samples to applicable criteria for 1994 - 2018 (As_SW: arsenic concentration in surface water; HCC_KM: human health cancer risk - based criterion for surface water in the Kewaunee Marsh; HCC_KR: human cancer risk - based criterion for the Kewaunee River, HCC_LM: human cancer risk - based criterion for Lake Michigan. CTC_KM_KR: chronic toxicity - based criterion for surface water in the Kewaunee Marsh and River, ATC: acute toxicity - based criterion for all three water bodies, the Kewaunee Marsh, Kewaunee River and Lake Michigan)

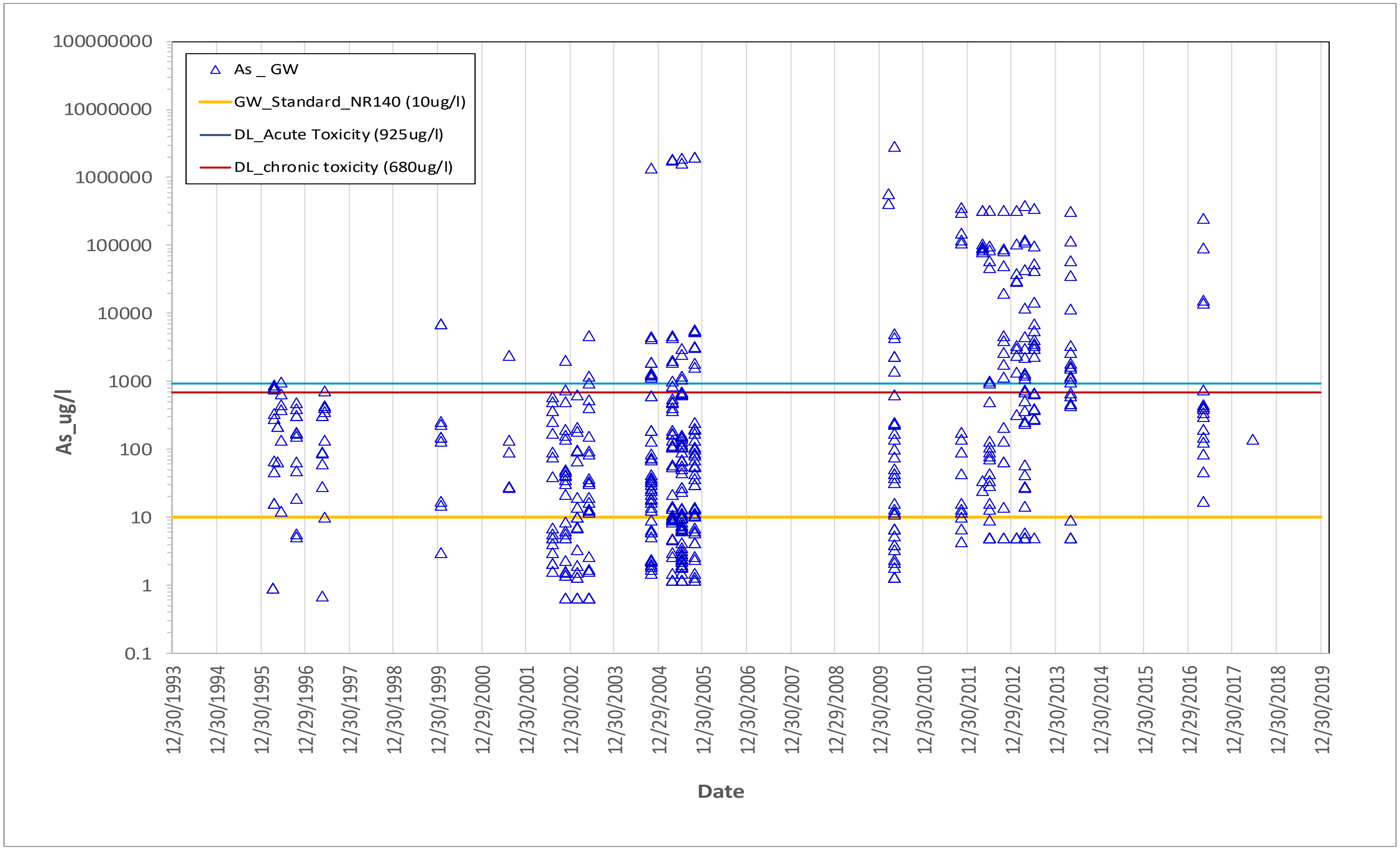


Fig. 3 Comparison of arsenic concentration in GW to applicable criteria for1996 - 2018 (NR140: enforcement groundwater criterion of 10 ug/l, DL_acute toxicity: previously established discharge limit based on acute toxicity criterion of 340 ug/l in SW, DL_chronic toxicity: previously established discharge limit based on chronic toxicity criterion of 152 ug/l in SW)

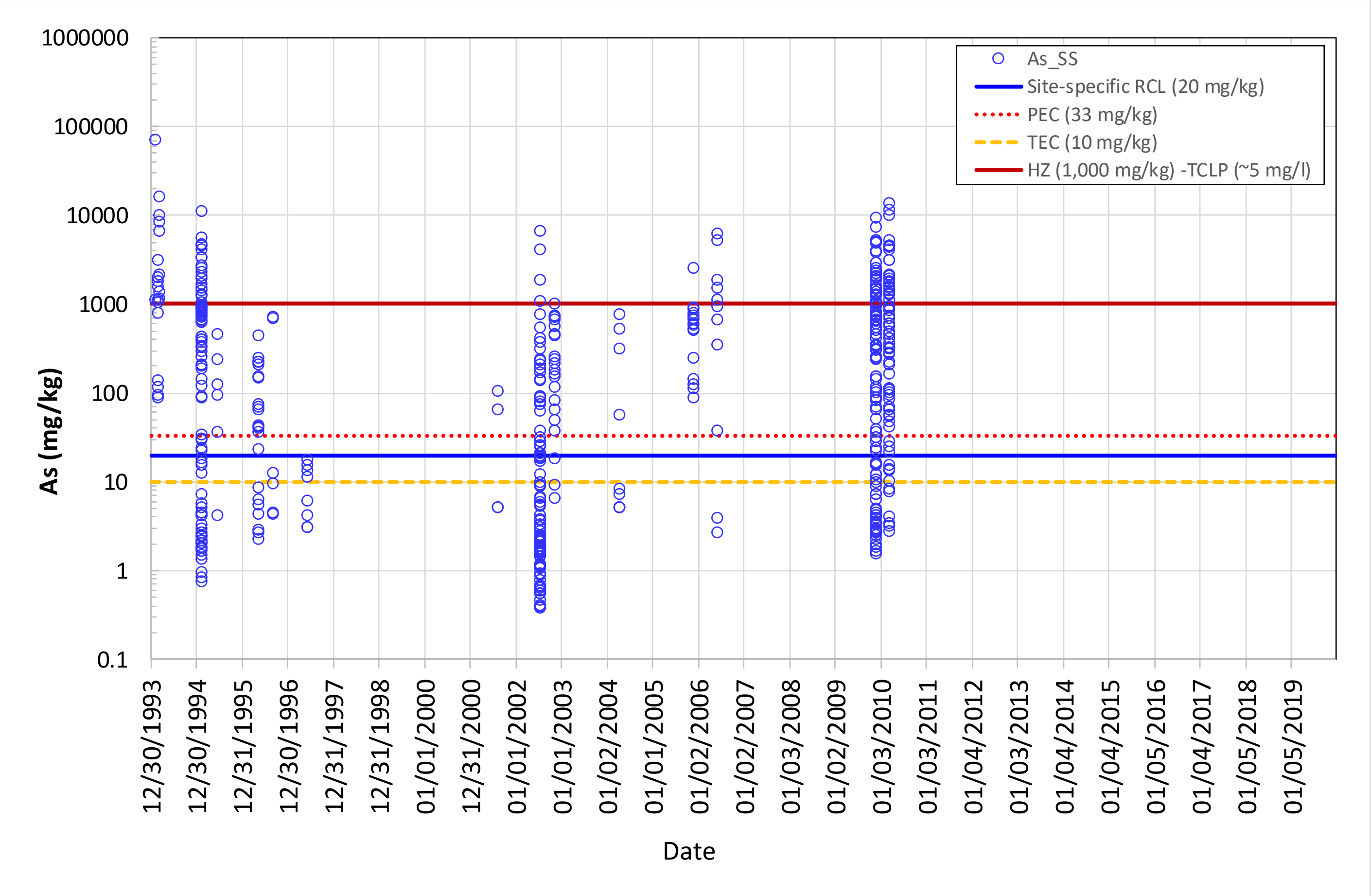
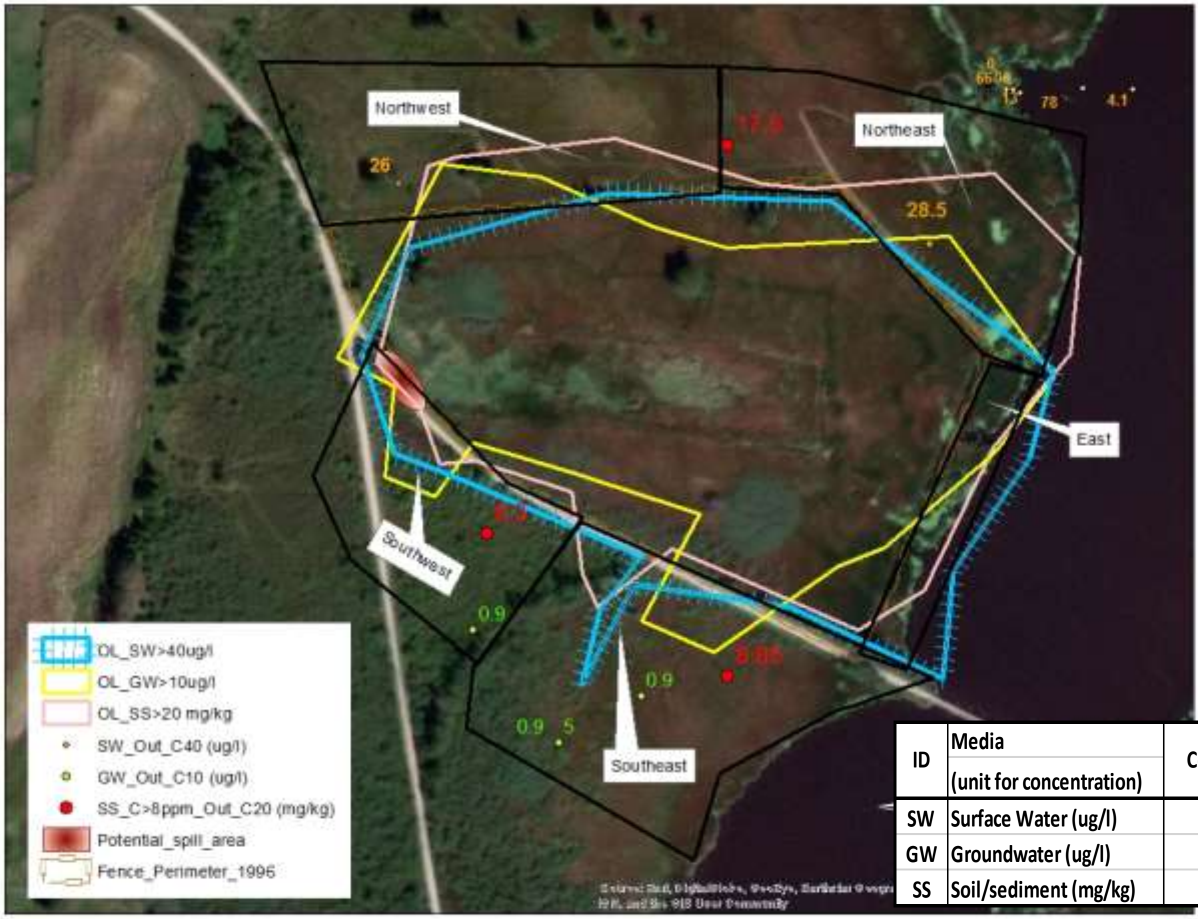
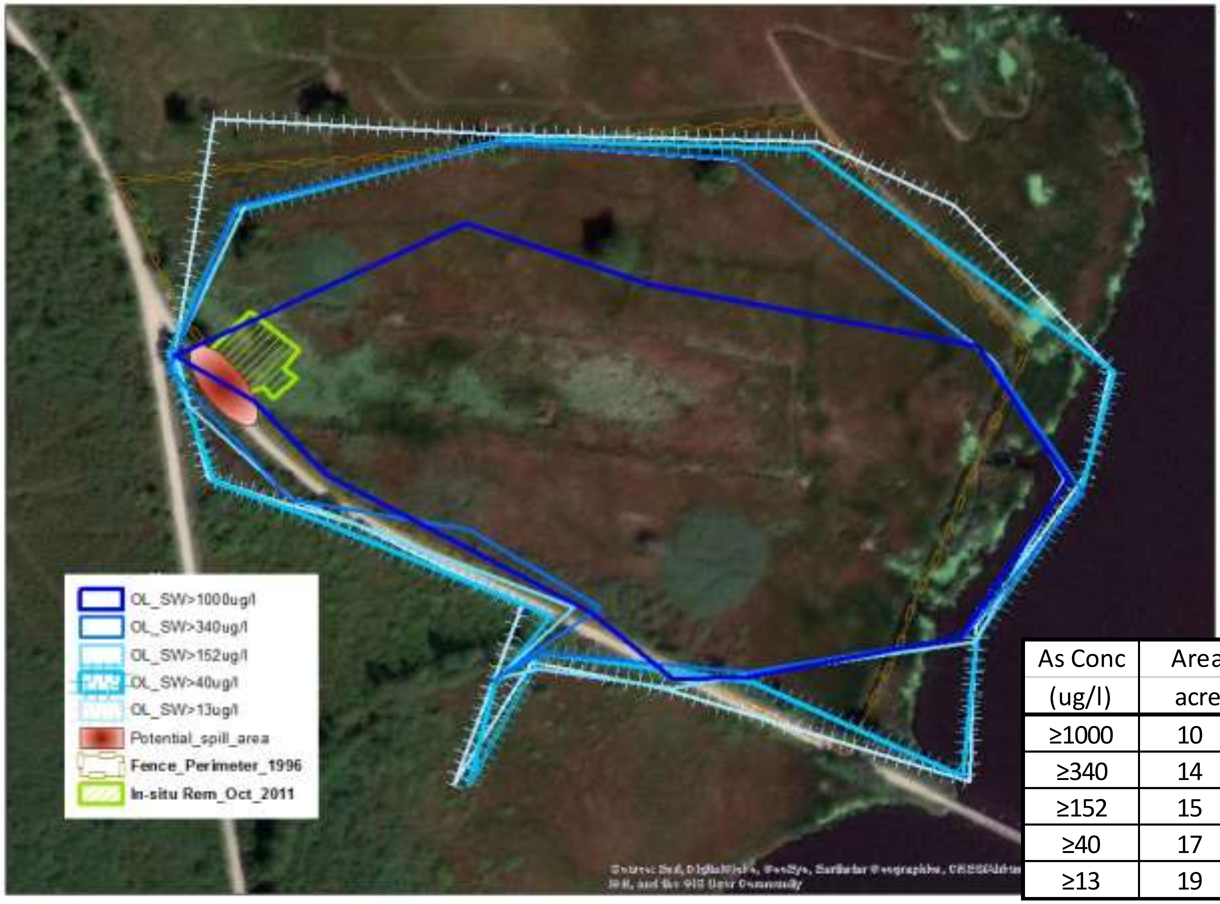


Fig. 4 Comparison of arsenic concentration in SS to applicable thresholds for 1994 - 2010 (Site-specific RCL: modified soil residual contaminant level specific to the site; PEC: probable effect concentration in sediment; TEC: threshold effect concentration in sediment; HZ: hazardous material for disposal)



ID	Media (unit for concentration)	Conc	Area acre	Area % relative to A_{SS}
SW	Surface Water (ug/l)	40	17	89
GW	Groundwater (ug/l)	10	15	79
SS	Soil/sediment (mg/kg)	20	19	100

Fig. 5 Delineation of horizontal extent with arsenic concentration exceeding corresponding SW, GW, and SS criteria and threshold based on data collected since 1994 (criteria and threshold are listed in Table 1. These outlines are developed considering remediation goals for SW and GW and baseline scenario for the SS. OL_SW≥40ug/l: outline bounded by samples with concentration ≥ 40ug/l in SW. OL_GW≥10ug/l: outline bounded by samples with concentration ≥10ug/l in GW. OL_SS≥20mg/kg: outline bounded by samples with concentration ≥20mg/kg in SS. SS Samples with exceedance of the baseline thresholds but located outside of the boundaries are also displayed with concentrations. Numerical values labeled in orange are for SW, green for GW samples, and red for SS samples.)

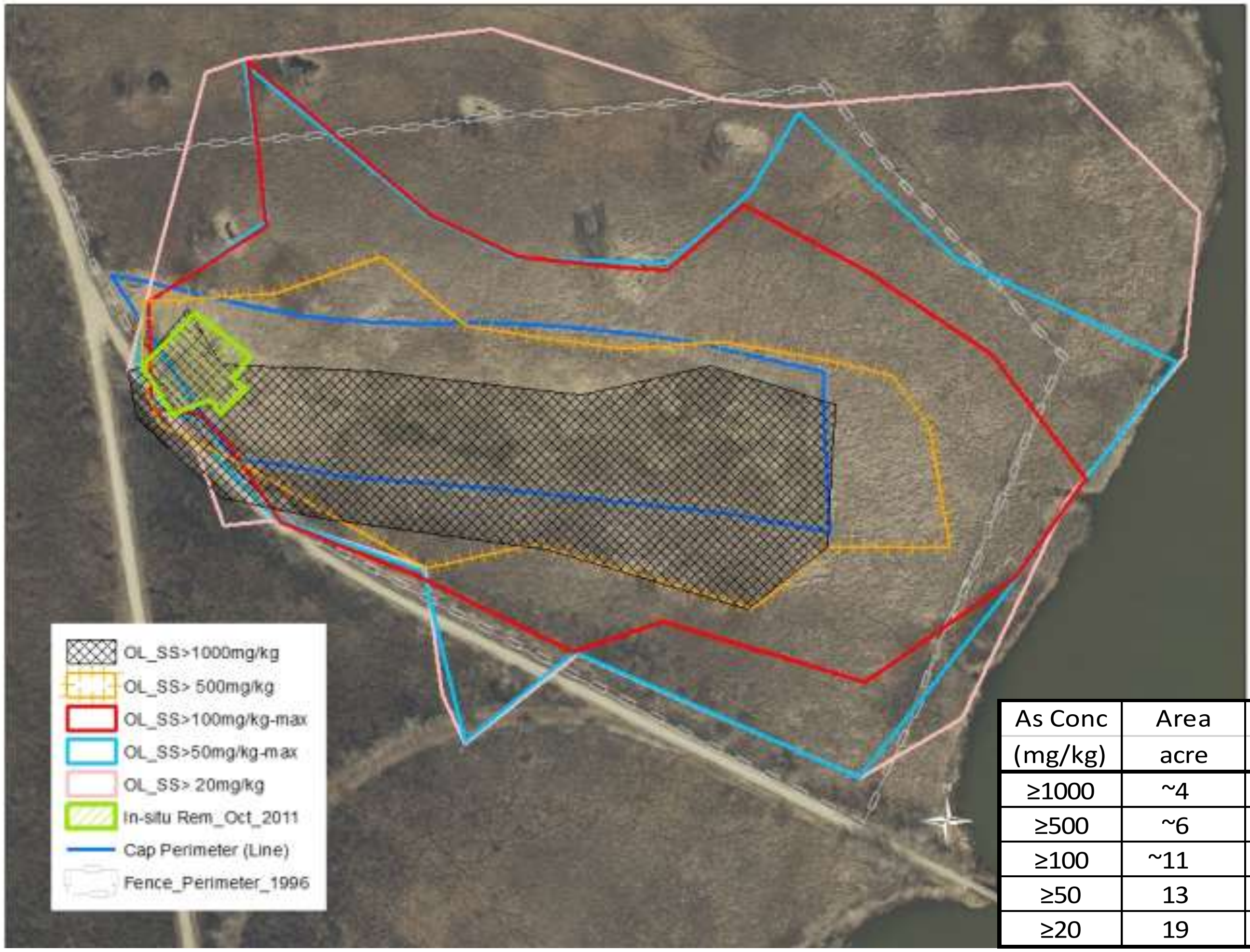


As Conc (ug/l)	Area acre	Ratio* %
≥1000	10	56
≥340	14	76
≥152	15	81
≥40	17	92
≥13	19	100

Fig. 6 Delineation of horizontal extent with arsenic concentrations exceeding surface water criteria and threshold (criteria and threshold are listed in Table 1. OL_SW>1000ug/l, >340ug/l, >152 ug/l, >40 ug/l, and >13 ug/l: outlines bounded by arsenic concentrations ≥ 1000ug/l, ≥ 340ug/l, ≥ 152ug/l, ≥ 40ug/l, and ≥ 13ug/l, respectively; *area relative to that bounded by C_{As}≥13 ug/l)

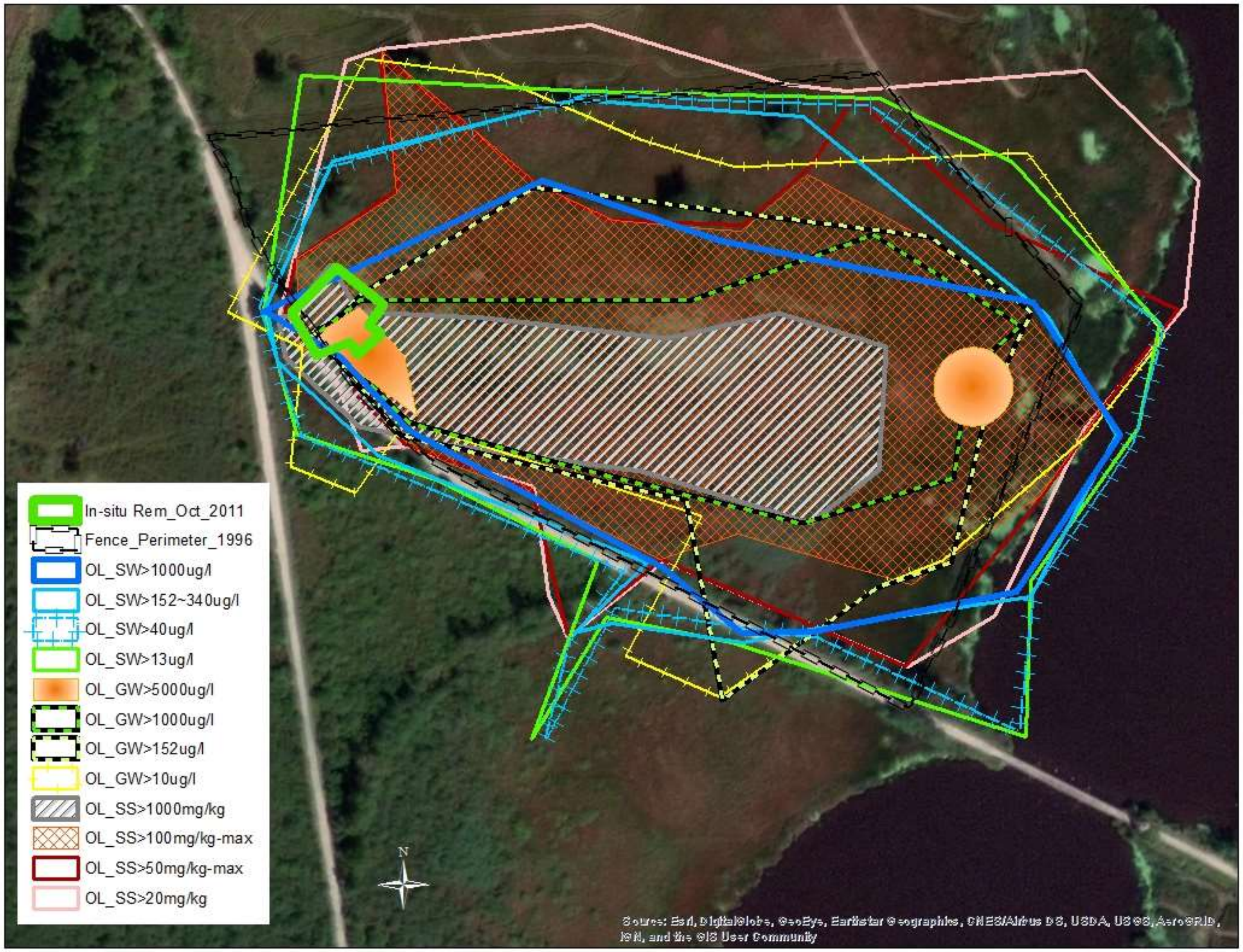
As Conc (ug/l)	Area acre	Ratio* %
≥1000	5	37
≥340	7	49
≥152	9	61
≥40	13	89
≥13	14	99
≥10	15	100

Fig. 7 Delineation of horizontal extent with arsenic concentrations exceeding groundwater criteria and thresholds (criteria and thresholds are listed in Table 1. OL_GW>1000ug/l, >340ug/l, >152 ug/l, >40 ug/l, >13 ug/l, and >10 ug/l: outlines bounded by arsenic concentrations ≥ 1000ug/l, ≥ 340ug/l, ≥ 152ug/l, ≥ 40ug/l, ≥ 13ug/l, and 10 ug/l, respectively; Numerical values (in blue) represent the top of screening of wells below ground surface at three locations; *area relative to that bounded by C_{As}≥10 ug/l.



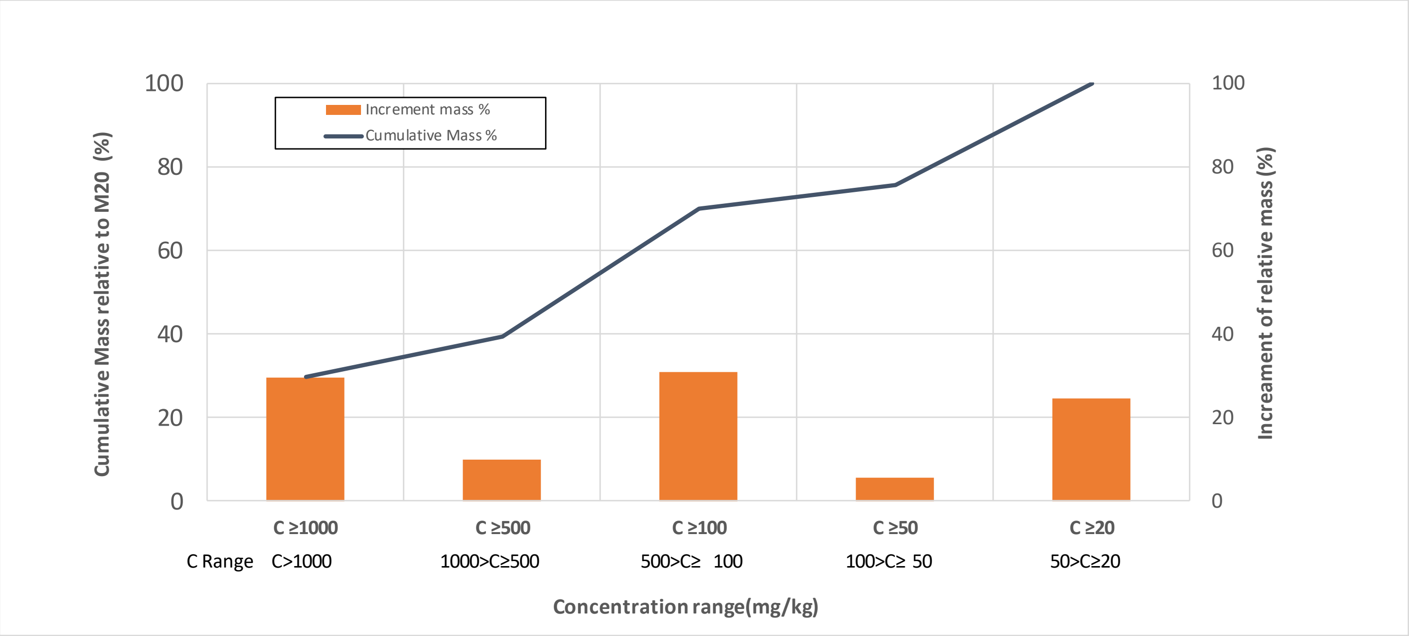
As Conc (mg/kg)	Area acre	Ratio* %
≥1000	~4	20
≥500	~6	31
≥100	~11	56
≥50	13	68
≥20	19	100

Fig. 8 Delineation of horizontal extent with arsenic concentrations exceeding soil and sediment thresholds (thresholds are listed in Table 1. OL_SS>1000mg/kg, >500mg/kg, >100 mg/kg, >50 mg/kg, and > 20 mg/kg: outlines bounded by arsenic concentrations ≥ 1000mg/kg, ≥ 1000mg/kg, ≥ 500mg/kg, ≥ 100mg/kg, and 20 mg/kg, respectively; *area relative to that bounded by C_{As}≥20 mg/kg.



Source: Esri, DigitalGlobe, GeoEye, Earthstar Geographics, CNES/Airbus DS, USDA, USGS, AeroGRID, IGN, and the GIS User Community

Fig. 9 Integration of delineated horizontal extent for three media: SW, GW, and SS (outlines for GW> 5,000 ug/l are shown as highlights not in scale)



Data for Fig. 10

Definition (Arsenic conc C_i)	Area (A)	C_{ave} under C_i	**M** (A*C_{ave})	Cumulative Mass relative to **M20**	Cumulative A under C_i
(mg/kg)	ac	(mg/kg)	(mg/kg)*ac	%	%
M1000(C_i ≥1000)	4	1432	5585	30	21
M500(C_i ≥500)	6	1306	7444	39	30
M100(C_i ≥100)	11	1249	13239	70	56
M50(C_i ≥50)	13	1089	14266	76	69
M20(C_i ≥20)	19	994	18886	100	100

C_i Range	Incremen of relative mass under Ci Range to **M20**	Incremen of A under C_i Range
(mg/kg)	%	%
C ≥1000	30	21
1000> C ≥500	10	9
500> C ≥100	31	26
100> C ≥50	5	13
50> C ≥20	24	31

Fig. 10 Distribution of area weighted arsenic concentration and mass in SS (increment mass for the concentration range was calculated relative to M**20**)

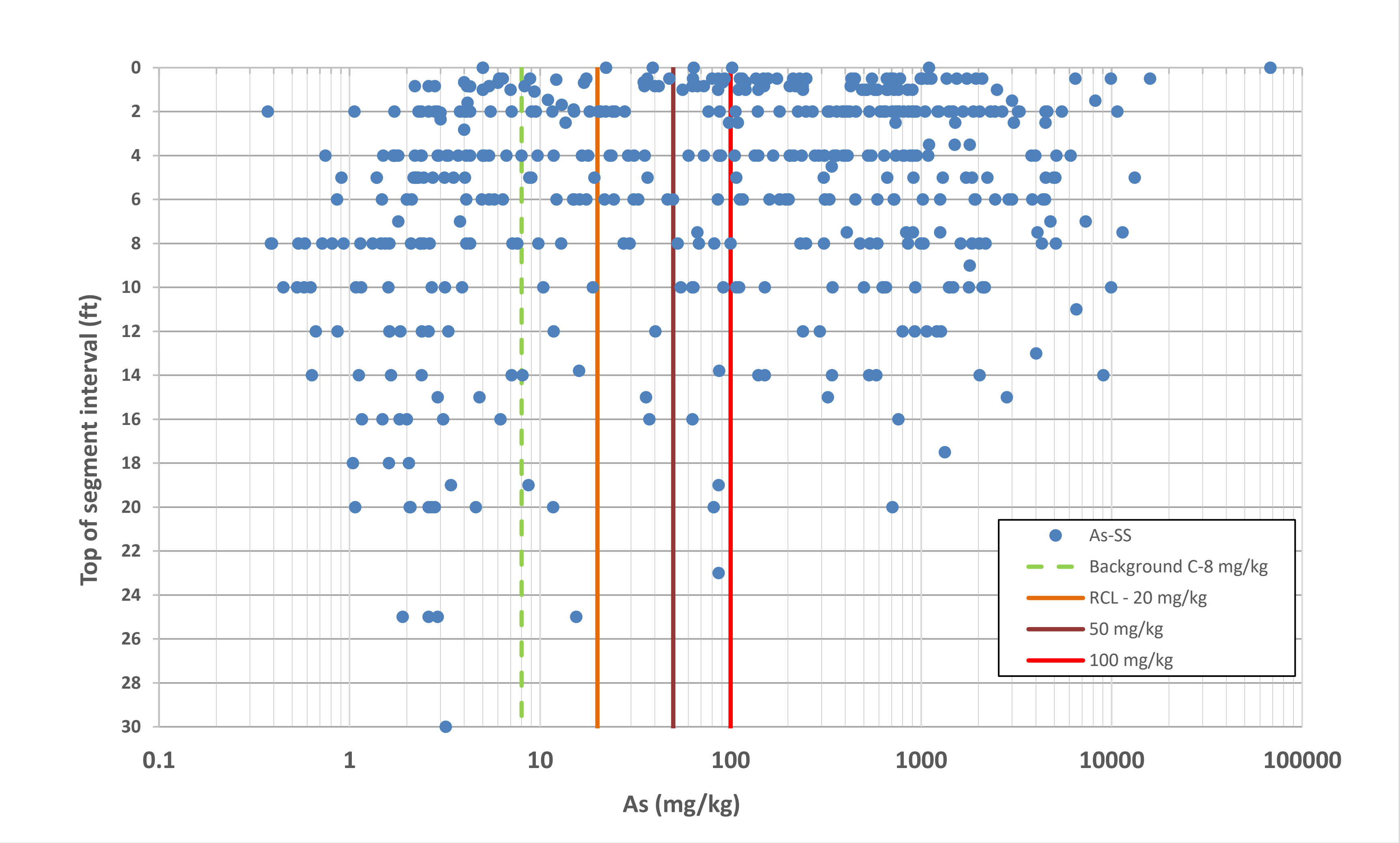


Fig. 11 Vertical distribution of arsenic concentrations in SS based on the data collected from 1994 to 2010 (As-SS: arsenic concentration in SS (mg/kg); Background C-8 mg/kg: statewide background concentration; RCL: site-specific residual contaminant level in soil)

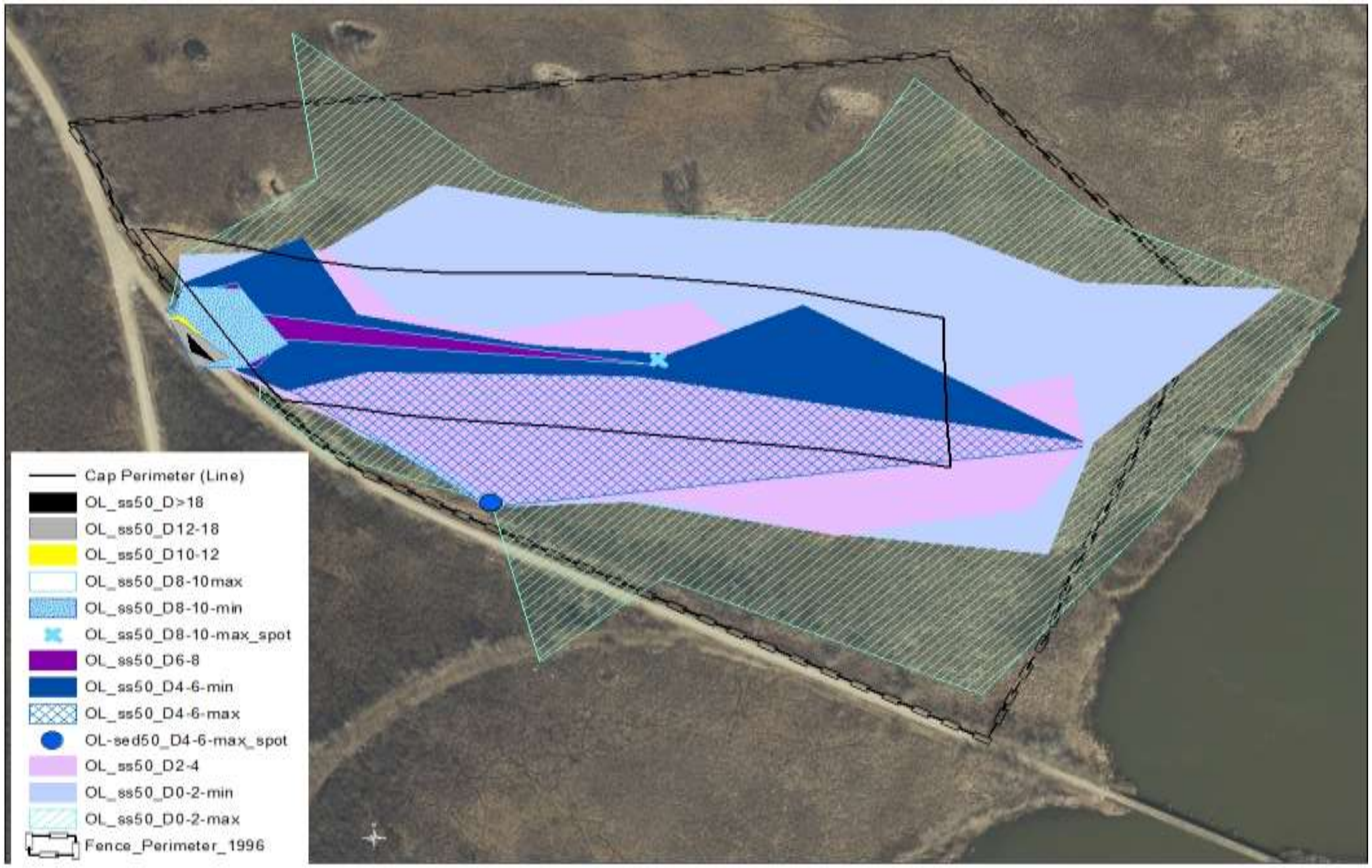
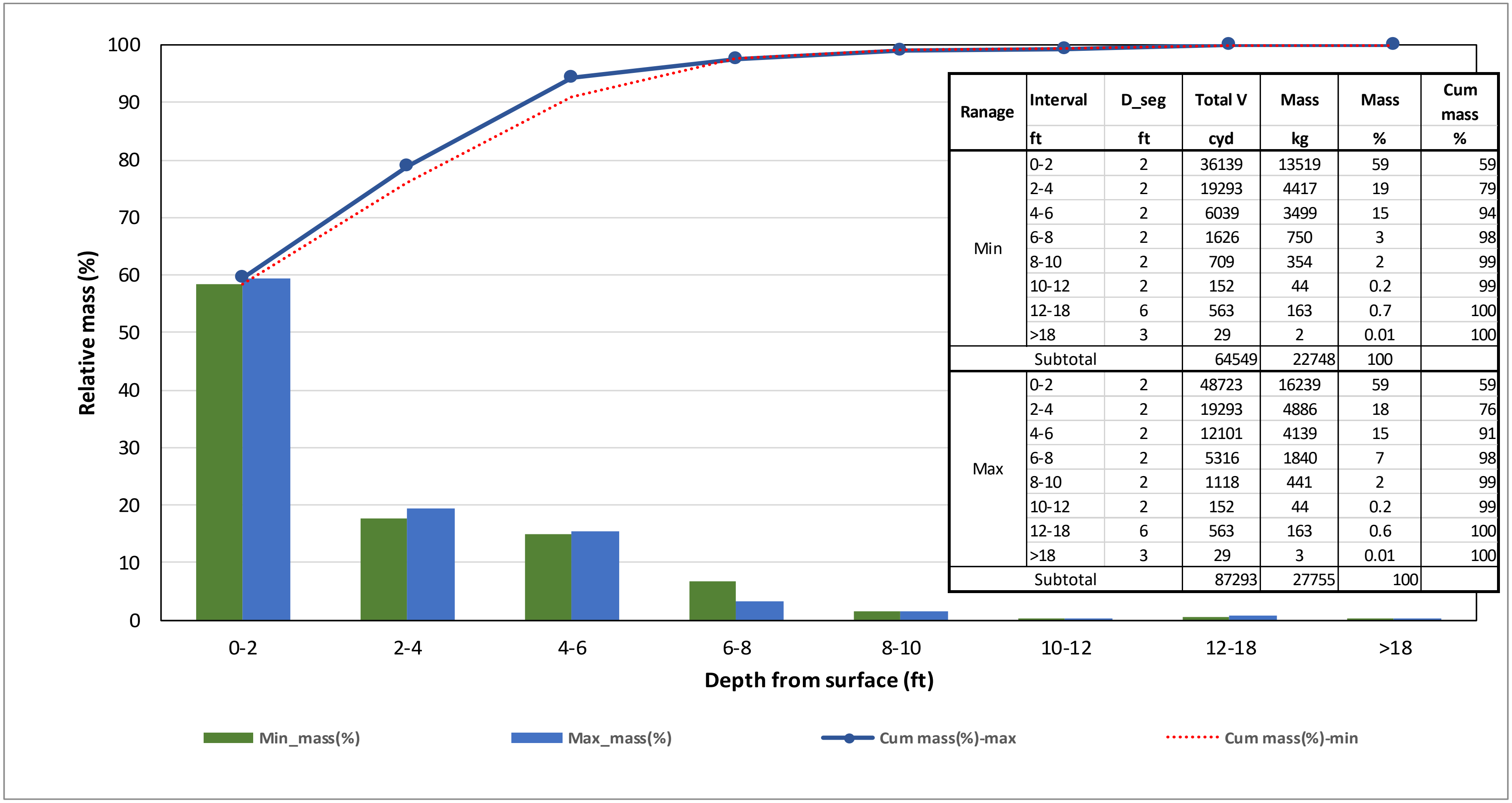


Fig. 12 Horizontal extent in each SS layer for Scenario **C50** (This is an example. Evaluation was conducted for scenarios of **C20** and **C100** as well. Legend example: OL_sed50_D>18 - outline (OL) for arsenic concentration exceeding 50 mg/kg (sed50) at depth (D) > 18 ft. For some layers the minimum and maximum extent are displayed with the influential samples, for instance OL_ss50_D8-10-max_spot is displayed)



Ranage	Interval ft	D_seg ft	Total V cyd	Mass kg	Mass %	Cum mass %
Min	0-2	2	36139	13519	59	59
	2-4	2	19293	4417	19	79
	4-6	2	6039	3499	15	94
	6-8	2	1626	750	3	98
	8-10	2	709	354	2	99
	10-12	2	152	44	0.2	99
	12-18	6	563	163	0.7	100
	>18	3	29	2	0.01	100
	Subtotal		64549	22748	100	
Max	0-2	2	48723	16239	59	59
	2-4	2	19293	4886	18	76
	4-6	2	12101	4139	15	91
	6-8	2	5316	1840	7	98
	8-10	2	1118	441	2	99
	10-12	2	152	44	0.2	99
	12-18	6	563	163	0.6	100
	>18	3	29	3	0.01	100
	Subtotal		87293	27755	100	

Fig. 13 Estimates of arsenic mass in different depth under baseline scenario **C20** (The mass was estimated by assuming the same bulk density in horizontal and vertical directions at 0.5 g/cm^3 and arithmetic average concentration of all samples within the boundary without differentiation in vertical variation and between boundaries. D_seg: thickness of the segment interval or layer; Total V: total volume in cubic yard (cyd), Cum mass: percent cumulative mass from the surface to the depth greater than 18 ft. The last segment is assumed to be 3ft thick in average; Min and Max: minimum and maximum values; Mass%: relative mass in percent corresponding to subtotal of mass in minimum and maximum values.)

Fig. 14 Comparison of minimum extent and arsenic mass in percent for SS segment interval of 0-2 ft under scenarios **C50** and **C100** to maximums under **C20** (Legend example: OLR_sed100_D0-2min: outline of arsenic concentration ≥100 mg/kg in SS for depth 0-2 ft based on core samples as minimum extent; C50 – 94% and C100-90%: mass under **C50** and **C100** relative to that under **C20**; C20 -100%(~14,000kg): total mass under **C20** in layer 0-2ft**;** OL_SW>40 ug/l: a reference for comparison to the extent of concentration at 40 ug/l in SW)

Fig. 15 Comparison of maximum extent and arsenic mass in percent for SS segment interval of 0-2 ft under scenarios **C50** and **C100** relative to the maximums under **C20** (Legend example:OLR_sed100_D0-2max - outline of arsenic concentration ≥100 mg/kg in SS for depth 0-2 ft based on combination of grab and core samples; C50 – 93% and C100-88%: mass under **C50** and **C100** relative to that under **C20**; C20 -100%(~16,000kg): total mass under **C20** in layer 0-2ft**;** OL_SW>40 ug/l: a reference for comparison to the extent of concentration at 40 ug/l in SW)

Fig. 16 Comparison of extent and arsenic mass in percent for SS segment interval of 2-4 ft under scenarios **C50** and **C100** relative to **C20** (Legend example:OLR_sed100_D2-4 - outline of arsenic concentration ≥100 mg/kg in SS for depth 2-4 ft based core samples; The horizontal extent for **C100** is the same as that for **C50** and so is the relative mass of 91%.); C20 -100%(~4,500kg): total mass under **C20** in layer 2-4ft**;** OL_SW>40 ug/l: a reference for comparison to the extent of concentration at 40 ug/l in SW).

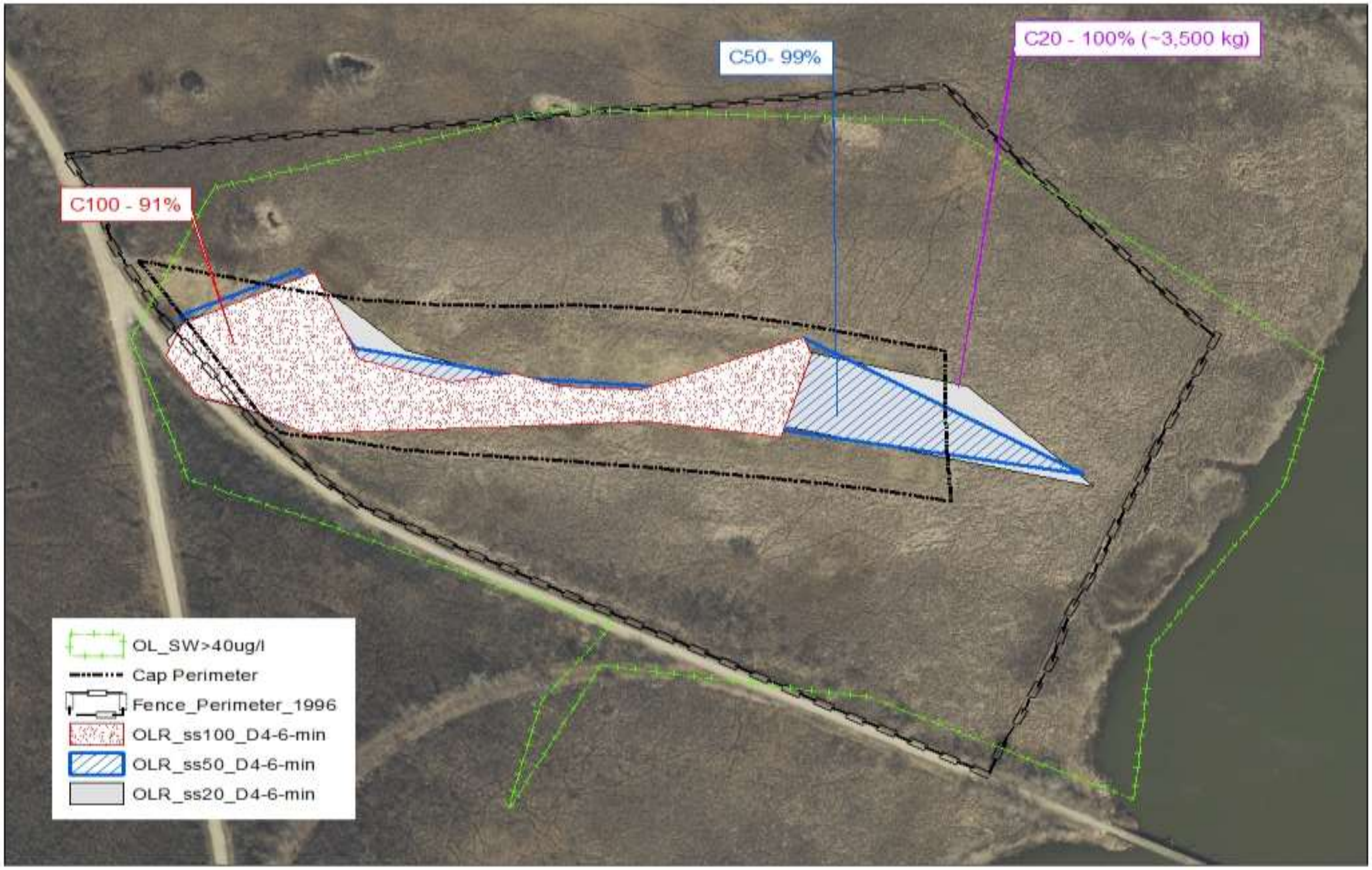


Fig. 17 Comparison of minimum extent and arsenic mass in percent for SS segment interval of 4-6 ft under scenarios **C50** and **C100** relative to **C20** (the legend and labels are the same for Fig. 16 except for the segment interval. Perimeters for cap and fence area shown.)

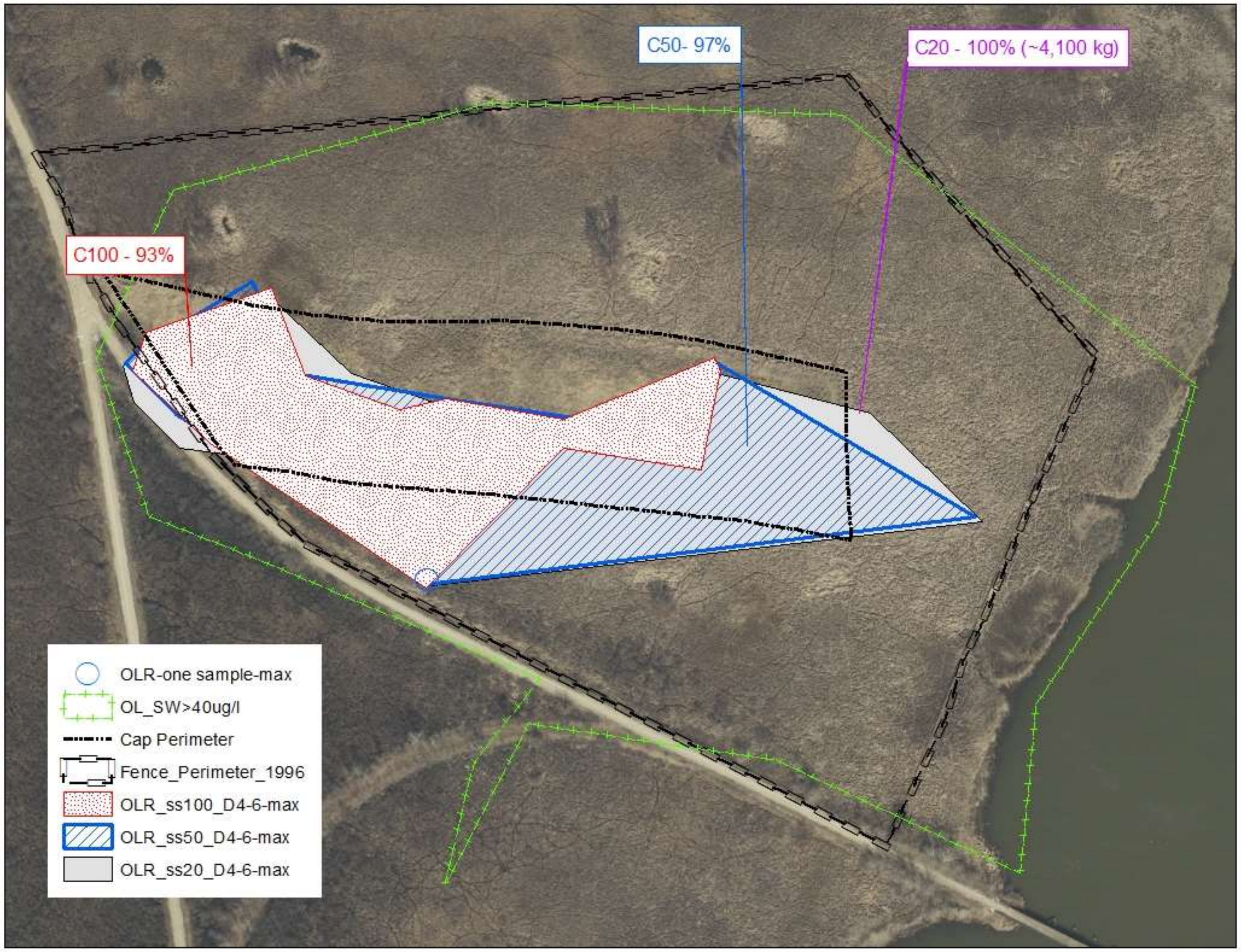


Fig. 18 Comparison of maximum extent and arsenic mass in percent for SS segment interval of 4-6 ft under scenarios **C50** and **C100** relative to the maximums under **C20** (the legend and labels are similar to that for Fig. 17 except this figure is for maximum extent.)

Fig. 19 Comparison of extent and arsenic mass in percent for SS segment interval of 6-8 ft under scenarios **C50** and **C100** relative to the minimums under **C20 (**the legend and labels are similar to Fig. 16 except for the segment interval and minimal value for **C20**.)

Fig. 20 Comparison of extent and arsenic mass in percent for SS segment interval of 6-8 ft under scenarios **C50** and **C100** relative to the maximums under **C20** (the legend and labels are the same for Fig. 19 except for the segment interval and maximum extent for interval 6-8ft.)

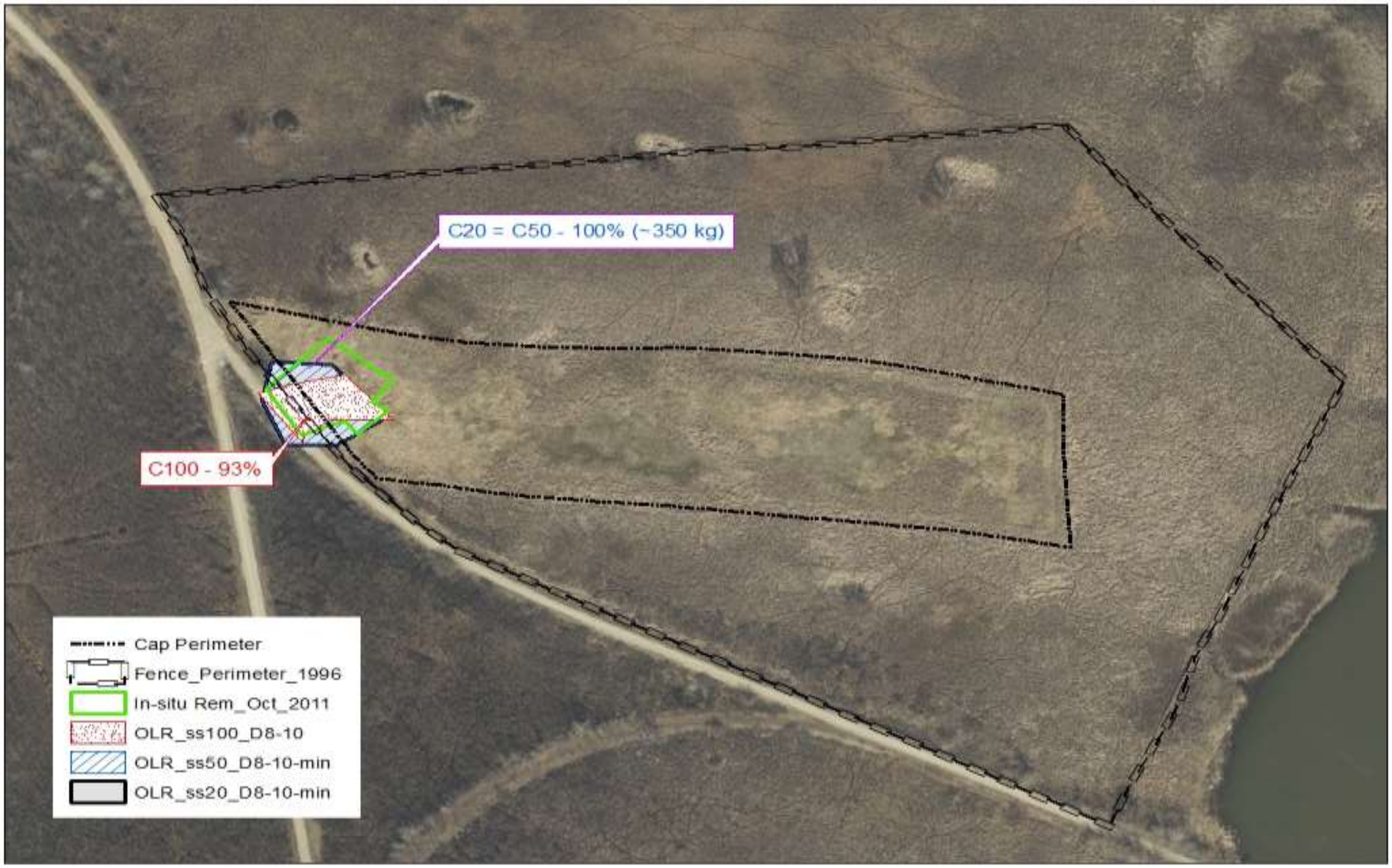


Fig. 21 Comparison of extent and arsenic mass in percent for SS segment interval of 8-10 ft under scenarios **C50** and **C100** relative to the minimums under **C20** (the legend and labels are the same for Fig. 19 except for the segment interval with minimal extent. Approximate boundary of in-situ remediation is displayed.)

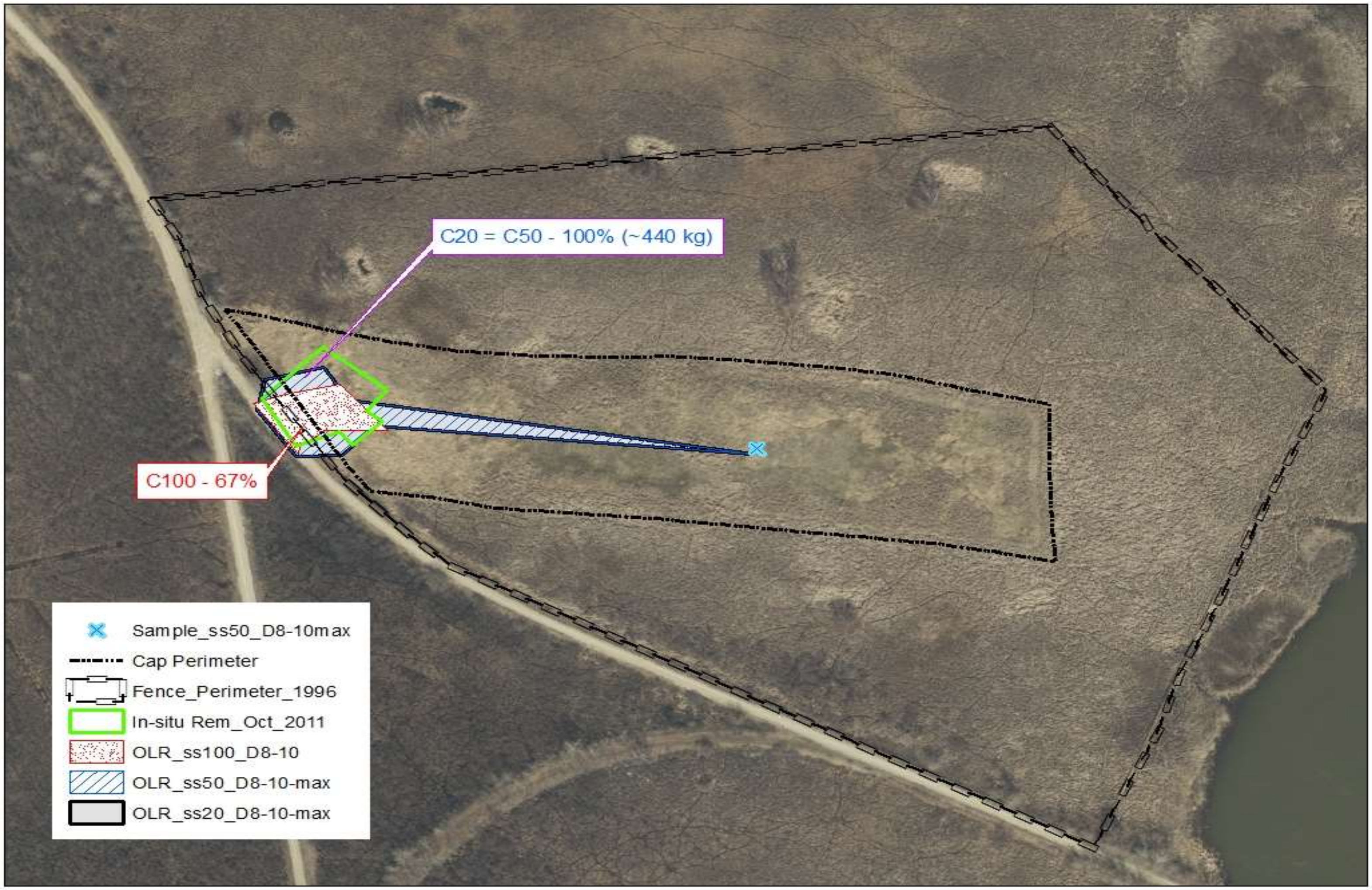


Fig. 22 Comparison of extent and arsenic mass in percent for SS segment interval of 8-10 ft under scenarios **C50** and **C100** relative to the maximums under **C20** (the extent and mass under **C50** is the same as under **C20**. The sample location that affected the delineation of the maximum extent is shown.)

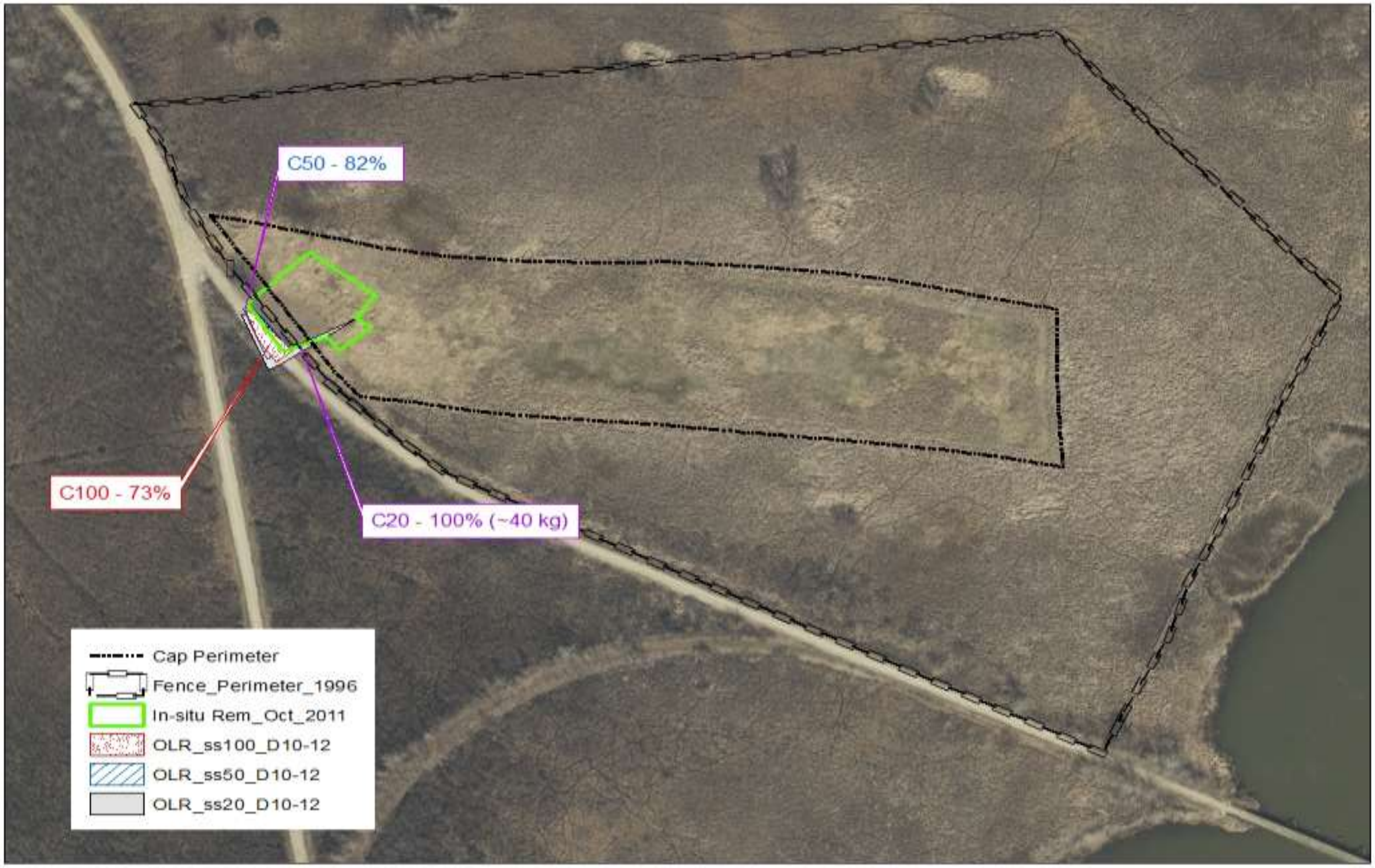


Fig. 23 Comparison of extent and arsenic mass in percent for SS segment interval of 10-12 ft under scenarios **C50** and **C100** relative to the maximums under **C20**

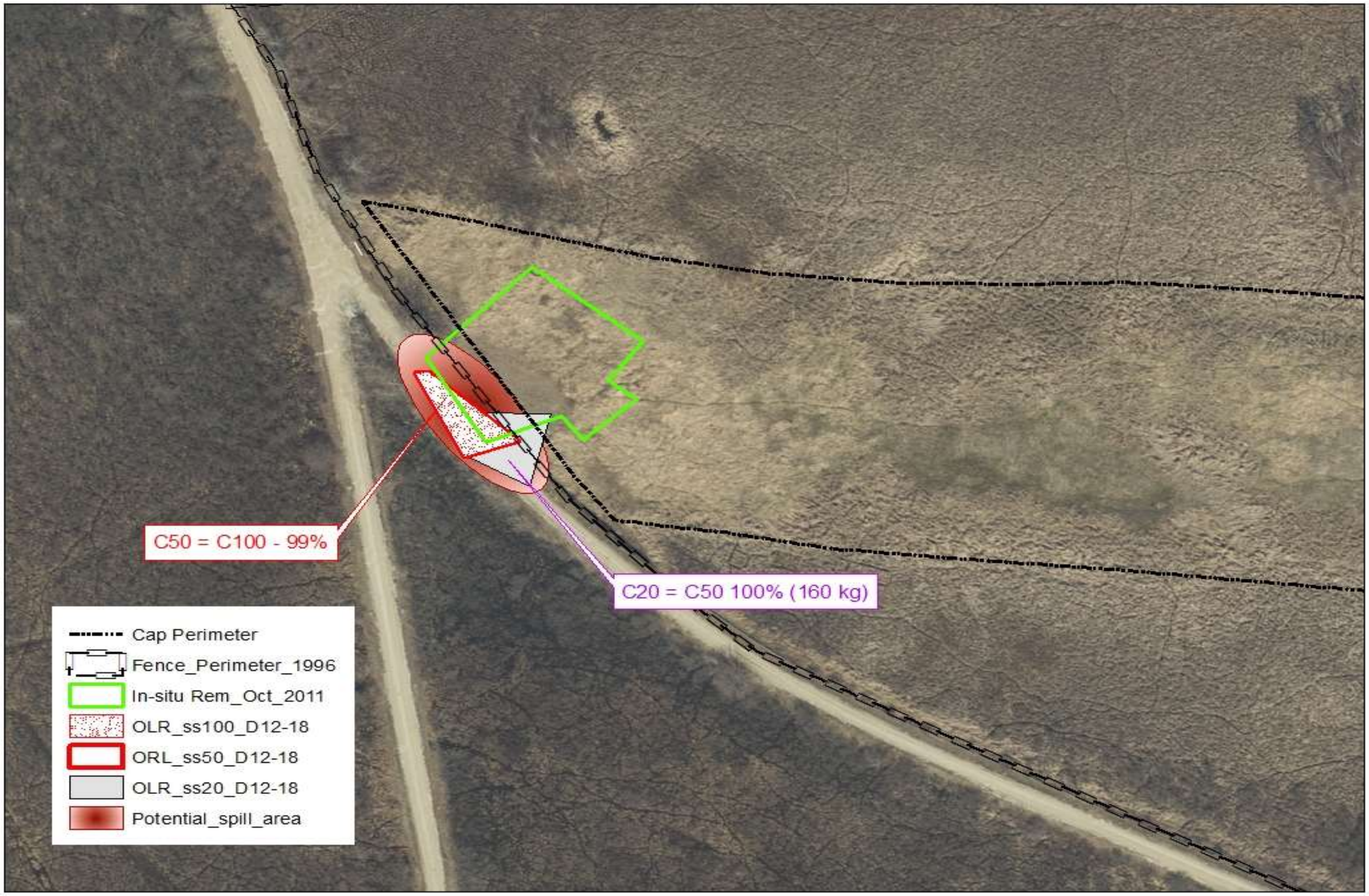


Fig. 24 Comparison of extent and arsenic mass in percent for SS segment interval of 12-18 ft under scenarios **C50** and **C100** relative to the maximums under **C20** (potential spill location is shown)

Fig. 25 Comparison of extent and arsenic mass in percent for SS deeper than 18 ft under scenarios **C50** and **C100** to the maximums under **C20** (surface areas are the same for .**C20** and **C50**. Only one sample exceeded 100 mg/kg)

Appendix A - Supplemental evaluation of arsenic data collected from the site

General Site Information

Kewaunee Marsh Arsenic Contaminated Site (KMASS) is located inside of a large meander bend of the Kewaunee River northwest of Kewaunee, Wisconsin (WI), just north of the Ahnapee Rail Trail, and is part of the 2,632 -acre state owned CD Besadny Fish and Wildlife Area. An approximately 15 acres of marsh area was fenced-in in 1996 as part of the interim action. The original source of the arsenic is attributed to a historic spill of herbicide or pesticide from a railcar derailment potentially in 1940s. Contamination was not discovered until 1993 when distressed vegetation was observed.

Subsequent investigation by then the owner of then active railroad line Fox Valley and Western Railroad, Ltd (FVWR) and Wisconsin Department of Natural Resources (DNR) revealed high arsenic concentrations in surface water (SW), groundwater (GW), soil and sediment (SS). The arsenic contamination spread from the former railroad bed out over the marsh, particularly in southeast direction. Historically, maximum arsenic concentrations of 920 mg/l, 2,840 mg/l, and 68,000 mg/kg, were detected in SW, GW, and SS, respectively. The early investigation lead to an interim action in 1996 of placing a woodchip cap and fenced in approximately 15-acres that are inaccessible to public. The chain-link fence is about 2,430 ft long. Maintenance of the cap and chain-link fence was carried forward as a continuing obligation since then and groundwater monitoring has been implemented.

As part of management plan, site investigation, remedial option evaluation, feasibility studies, and remedial bench and field tests have been conducted by FVWR and the DNR since 1995. Remedial alternatives were evaluated and reported by STS (2004) and RMT (2007). Alternatives included no action, in-situ treatment to removal of the entire 15-arce soil and sediment. In-situ treatment was conducted at the 0.2-acre area (TRC, 2010). During site assessment, remedial alternative evaluation, and remediation work, the usage of the former railroad line has changed. The State of Wisconsin purchased the portion of line adjacent to the wetland and subsequently converted to it rail trail. The contaminated site became a State Lead Site and managed by the state with partial funding by a settlement agreement with the railroad in 2008.

In 2011, a pilot in-situ remediation project was conducted in an area of approximately 9,000 ft^2, about 70 ft along the railroad bed and 100 ft away from the ballast into the marsh to mitigate the on-going release of dissolved-phase arsenic from source area into the marsh. Thickness of soil and sediment treated varied and extended down to 19 ft from the ground surface. A total of approximately 3,000 cyd of soil and sediment with arsenic concentrations greater than 2,000 mg/kg as detected in 2009 and 2010 were chemically treated with 5% hydrogen peroxide (~2,600gal), granular ferric sulfate (138,700 lbs), crushed limestone (118,250 lbs). Upon completion of chemical treatment 222,000 lbs (approximately 2,400 cyd) of bentonite were mixed into the materials to reduce permeability so that groundwater flow can be restricted and therefore the long-term performance of the treatment can be improved as stated in the report (TRC, 2011).

After the remediation, groundwater has been monitored within and immediately downgradient of the treated area. Between November 2011 and May 2017, concentration of arsenic in groundwater samples decreased compared to the previous data but were still in higher level of 12 to 304 mg/l within the treated area and 14 to 380 mg/l immediately downgradient of the area, respectively. The high level of arsenic in the groundwater is not expected as treatability study demonstrated. The results indicate that large-scale application of in-situ stabilization technique would likely result in large areas having levels of arsenic remaining well above the remedial action objective of 0.148 ug/l. Long term stability of bounded arsenic in the treated area is hard to predict due to complex temporal changes of physical, chemical, and biological conditions in the marsh. Arsenic may become soluble and be transported elsewhere years after treatment. In addition, implementation of the technology does no necessary eliminate risks to human health and ecosystem via direct contact because arsenic is left in place.

Recently, a new patch of distressed vegetation has appeared in the most east end of the capped area, potentially a sign of arsenic transported from upstream or from the deeper strata of soil and sediment to the cap surface. This hypothesis is supported by arsenic detected in the cap materials and surface water. The cap materials should be free of detection of arsenic when they were placed in 1996. In 2010, an average of 112 mg/kg arsenic with a range of 15 to 734 mg/kg were detected in the surface layer (0-2.5 ft), presumably the woodchip materials. In 2018, arsenic was detected in five surface water samples collected from the east end of the cap, ranging from 0.5 to 3.9 mg/l with an average of 2.5 mg/l.

The elevated concentrations of arsenic in samples of surface water in the capped area, groundwater from in-situ remediated area, and cap materials lead the Department to believe that active remedial action may be required to control the arsenic contamination. Woodchip capping and in-situ treatment only may not address environmental concentration of arsenic at the site.

Hydrogeologic Setting

Surficial soil beneath the marsh consist of organic black peat ranging in thickness from 4 to 8 ft. Organic content within the peat is approximately 80%. Beneath the peat is a dark grey to greyish brown organic silt material containing between 8% and 20% organics. The organic silt ranges from 15 to 26 feet thick. Ground moraine clay underlies the peat deposits and ranges in thickness from 50 to 100 feet. Bedrock consists of undifferentiated dolomite and has not been encountered in any of the wells drilled on site.

The water table occurs at a depth of about 0 to 2 feet below ground surface and is primarily in contact with the peat layer. The groundwater elevation is directly controlled by the depth of the water in the Kewaunee River and Lake Michigan.

Site Conditions and Access

Access to the site is via the Ahnapee Trail. The trail can be accessed through a driveway located on private property just off County Rd E. There is a locked gate at the end of the driveway to restrict entry to the trail. The Department can coordinate with the property owner for access to the property. Winter access to the marsh via the trail needs to be coordinated with the local club that grooms the trail for snowmobile use.

Three gates provide access to the fenced-in site from the trail. One of these is a double gate for vehicular entry. There is a steep slope from the gates into the property limiting site access. There are no on-site facilities or managers.

Site features include dense wetland vegetation (cattails, reed canary grass, and Phragmites), standing water (3"- >12") during portions of the year, and poor visibility in the summer months due to vegetative growth. Most site work is performed during the non-summer seasons. The DNR has been mowing paths to groundwater sampling locations during in later winter and early spring seasons.

Vegetation (Woodchip) Cap

Approximately 4 acres of the most contaminated soil and sediment were capped in 1996 to address exposure by direct contact. The cap consists of 155,000 square ft of permeable geotextile covered by between 2 and 2.5 ft of woodchips. In two areas within the cap, totaling approximately 0.35 acres, 5-inch-thick sheets of polystyrene were placed directly overtop the soil and sediment and beneath the geotextile. To anchor the geotextile and limit runoff from the cap, using additional fill material, earth berm was constructed in the easternmost limit of the cap and on both side from the easternmost limit extending approximately 170 ft westward. The cap was seeded with a variety of grasses upon completion. In 2003, a survey of the thickness of the cap was conducted. The results of this survey indicated that up to 2 ft of subsidence (both vegetation and woodchips) had occurred in several places on the top of the cap since 1996.

The cap was inspected in the summer of 2016 in accordance with the cap maintenance plan. During the summer, the elevation of the Kewaunee River was 1 to 1.5 ft higher than when the cap was installed in 1996. The cap was observed to be vegetated by mainly reed canary grass in the center of the cap and by cattails and Phragmites along the edges of the cap. Much of the eastern portion of the cap was occupied by standing water. A large area of what appeared to be stressed and dead reed canary was observed near the eastern end of the cap, in areas of standing water. Aerial photos of the capped area were taken and show the area of stressed vegetation (Figure 4. Aerial Photo taken by DNR on 7-13, 2016). It is not known if the vegetative cover cap is breaking down and exposing the arsenic contaminated sediment/soil

Existing Monitoring Well Network

The monitoring well network at the site consists of 15 shallow, 10 intermediate, and 4 deep wells. There are also 31 unprotected monitoring wells; fifteen outside the fence and 16 inside the fence. All wells except two (2) (missing wells) can be located by GPS.

<u>Evaluation of arsenic thresholds in SS for protection of vegetation and wildlife</u>

There are no enforceable arsenic SS criteria for protection of vegetation and wildlife. The US Fish and Wildlife Services (USFWS) reported that if arsenic in SW is greater than 3-28 ug/l it can cause damage to crop and vegetation [USFWS, 1988]. It is acknowledged here that the lower limit is less than SW human cancer risk-based criteria for the Kewaunee Marsh and River but higher than the criterion for protection of Lake Michigan water. The upper limit is between the criteria applicable to the river and marsh of 13-40 ug/l with respect to human cancer risk concerns. The USWS report further stated that the threshold concentration for water was equivalent to 25-85 mg/kg of arsenic in soil without further elaboration of how the conversion was made. Without putting effort to find support information, an attempt was made to use site specific data to develop a correlation between concentrations of arsenic in SW and SS so that prediction of arsenic threshold in SS for protection vegetation and wildlife can be made based on the SW criteria and thresholds. Paired SW and SS samples have been collected from co-locations or in close vicinity at the same time between 1996 and 2004 with a larger sample size from 1996.

Fig. A-1shows the available datasets and a linear regression of arsenic concentrations in SS and SW based on the 1996 data (n=10). Concentrations detected in both media are correlated well with a correlation coefficient of 0.86 (R≈0.9). This trend is confirmed by the data collected later in 2001 and 2004 with one exception when C_{ss} is equal to 164 mg/kg (2004 data set). However, this linear regression model may not be applicable when C_{ss} is <45 mg/kg, potentially due to the effect from complex geochemical and thermodynamic conditions and potentially the microbial community may alter the linear function. The regression model was then used to predict site specific equivalent thresholds of arsenic in SS for a low limit of 45 mg/kg based on the recommended concentration of 3-28 ug/l reported by the USFWS f. As a result, the site specific equivalent arsenic concentration in SS ranges 46-50 mg/kg. Given the small ranges, rounding the lower limit up to the nearest 10 makes the reference value as 50 mg/kg for protection of vegetation.

As for protection of wildlife, the US EPA and State of Michigan recommended the concentration of arsenic be less than 15-32 ug/l in surface water (Table 1 of the memo). Using the same linear regression model, the site specific equivalent arsenic concentration in SS for protection of wildlife is estimated to be 47-50 mg/kg. Rounding the lower limit up to the nearest 10 makes the reference value also equal to 50 mg/kg. Therefore, arsenic concentration of less than 50 mg/kg in SS is considered as reference threshold for protection of both vegetation and wildlife.

Supplemental Data Evaluation

Arsenic in SS

Since the discovery of high concentrations of arsenic in SS at the Kewaunee Marsh in 1994, site investigation, remedial option evaluation, and limited remedial actions have been conducted by then active railroad line Fox Valley and Western Railroad, Ltd (FVWR) and Wisconsin Department of Natural Resources (DNR). Surface water (SW), groundwater (GW), and SS samples have been collected and analyzed for arsenic and limited geochemical parameters. Bulk sediment toxicity tests were also conducted for limited samples.

From 1994 to 2018, SS samples with either a surface grab or cores were collected for different purposes. Fig. A-2 shows the location of all samples collected for the time period. Because each assessment project had different objectives, spatial distribution of these sample differs as shown in Fig. A-3 and A-4. In 1994 and 1995, samples spread to a wide area and the results lead to an interim action by placing vegetation cap on a 4-acre area and chain-link fence over 15-acre area. Additional samples from1996 and 2002 were limited to outside of the capped area. Between 2004 and 2006 some samples were collected inside the cap for comparison of concentration trend pre- and post-cover placement. Samples collected in 2009 and 2010 mainly were used for purpose of in-situ remediation design. The in-situ remediation work was conducted in 2011 for an approximately 0.2 acres close to the spill site and vertically extended to 15 ft.

As a summary, a total of 502 SS samples have been analyzed for arsenic with a maximum concentration of 68,000 mg/kg detected in a grab sample collected in1994. About 30% of samples collected had arsenic less than 8 mg/kg, the statewide soil background level. The grab samples (about 16% of the total samples), represent the top 0.5 to 1 foot of materials and they covered a larger area than core samples for the surface sediment as defined between 0-2 ft thick. The maximum concentration detected in core samples was 10,700 mg/kg in surface segment of the cores (0-2 ft). Core samples were often segmented into 2-ft intervals with some exceptions starting from 12 ft and deeper. The maximum core thickness was recorded at 25 ft that was located near the original spill site.

Temporal trend of arsenic concentration in SS was evaluated for the capped area by RMT in 2010. The evaluation concluded that arsenic concentration decreased in the equivalent sediment segment, i.e., the surface SS sample in 1994 and the upper 2 feet under the cap material or 2-4ft of materials from surface in cores in 2006. However, the attenuation rate calculated could carry high uncertainties because the evaluation did not consider some critical physical, chemical, and biological conditions, such as but not limited to incomparable relative geolocation with respect to surface water transport pathway and water content in samples.

Relative geolocation of SS samples used for trend analyses is a significant variable to consider. If samples collected in later years are located upstream of the ones collected in previous years, the declining in concentration may be attributed to artifact that arsenic in upstream location may have transported downstream. As shown in Fig. A-5, although the impacted area is relatively flat, the topography shows that starting from the former rail track on west side surface elevation drops from 587.5 to 580.3 ft towards east in the capped area. Therefore, the dominant pathway of arsenic transport in SW is eastwards. Paired samples chosen for trend analyses should be collected from the same location. If not possible then the later-year-samples should be located downstream of the early-year-samples. Unfortunately, according to the information obtained, all groups except one used for analyses had later-year-samples located upstream. The only group, samples B-34 (1994), TS-21 (2006), and M-10F (2010) followed the transport pathway. The decreasing rate (Fig. A-5) estimated for this group was lower than the other cases as reported (RMT 2010). Further evaluation shows that sample B-15 collected in 1994 was closer to M-10F than B-34 and TS-21. If samples B-15 and M-10F are paired for comparison, even slower apparent decreasing rate is observed as shown in Fig. A-5. The decreasing trend was in parallel to that based on another pair of samples B-27 (1994) and TS-24 (2006).

Concentration of contaminants in SS samples is composed of dissolved and particulate phases. Water content in SS samples can influence the total concentration, particularly for the arsenic because it is highly water soluble at the site. The dissolved phase may contribute high proportion of total arsenic in SS if water content is high. Fig. A-6 shows a positive correlation trend between water content and arsenic concentration in these selected SS samples. Therefore, potential variation of water content in samples selected for trend analyses may affect the estimation of decreasing rate. Unfortunately, no water content was reported for samples collected in 1994 and 1995. For the sample pairs with water content available, such as samples TS-21 (2006) and M-10F (2010), the water content varied. It was higher in TS-21 (75.6% in the interval of 2-4 ft) than in M-10F (59.3% in the interval of 0-4 ft). Potentially, arsenic concentration would be higher than 357 mg/kg in M-10F if it was adjusted by water content; therefore, the apparent decreasing rate would lower in comparison to what was reported. In addition, because it has been under the cap over a decade at least, it is believed that the physical structure of 2006-2010 SS may be incomparable to those present in surface in 1994 and 1995. Nevertheless, high uncertainties exist in the estimated decreasing rate as reported by RMT (2010).

The more alarming observation regarding change of arsenic distribution at the site is the detection of arsenic in surface or cap materials in recent years. It is safe to assume that when it was placed in 1996, the cover materials did not contain detectable level of arsenic. In recent years, arsenic was detected up to 2,500 mg/kg with an average concentration of 790 mg/kg (n=6) in 2005. Between 2009- 2010, it was detected up to 4,500 mg/kg with an average concentration and 1050 mg/kg. Fig. A-7 shows the temporal changes of arsenic concentration in surface materials. RMT [2010] suggested a few potential causes to the increase of arsenic concentration, including contaminated groundwater rising into the vadose zone, groundwater fluctuations, settlement of the cap, or migration due to conversion of arsenic to arsine gas. One significant potential mechanism that was not mentioned is the surface water transport. Because the surface elevation is about 4-5 ft higher at the spill site compared to the east end of the cap. Arsenic present in the top 5 ft at the source area can transport downstream to the surface area eastward, particularly when it is fully saturated. Although in 2011 approximately 9,000 ft^2 area or 3,000 cyd of SS was treated, similar amount of arsenic mass may remain at the site and can be mobilized when conditions permit. Arsenic in particulate and dissolved phases in the area may continue to transport down gradient towards south and southeast directions via surface and groundwater transport pathway.

Downstream transport of arsenic in SW is also evident with higher concentrations observed in surface SS as shown in Fig. A-8 with comparison to that in the deeper SS. These samples were collected downstream and southeast of the cap near the river. The top 2 ft SS contains the highest concentrations over the years. This observation suggests that surface water transport may be the dominating transport pathway from upstream to downstream.

Even if natural attenuation is occurring at the site, it does not mean the natural process has addressed the contamination. Decrease of concentration in SS only means arsenic has been discharging to the river, volatilizing to the air, and uptake by plants and wildlife. If substantial amount of arsine gas is formed at the site, it can be an exposure concern to human health. Therefore, caution should be taken when evaluating the apparent attenuation of arsenic in SS at the site.

Without further investigation of the mechanisms, high arsenic detected in the cap materials demonstrates that the cap has failed to serve the original purpose. Due to complex physical, chemical, and biological processes governing the fate and transport of arsenic in the marsh, even if the cap is repaired to the original design, arsenic will continue to spread in the marsh and have potential of discharging to the river if active remediation such as removal is not implemented.

Arsenic in surface water (SW)

A total of 15 SW sampling events were carried out from 1994 through 2018 for different purposes and resulting in 160 analyses for arsenic. Although lumped into surface water, the samples were collected from different types of “surface water”, consisting of standing surface water, sediment pore water, and pond water depending on the sampling purpose and presence of the type of water. Also, location of these SW samples varied because some areas had standing water present at one sampling event but dry at next time. Only two sets of SW samples were collected from the capped area with one set in 1994-1995 as pre-capping and one set in 2018 as post-capping conditions.

Often pore water contains higher arsenic concentration than the other types of surface water samples. Some of the samples were filtered for analyses of dissolved fraction of arsenic. Among all samples analyzed, a maximum total arsenic concentration of 920 mg/l was detected near the original spill area as shown in Fig. A-9. Arsenic up to 3.89 mg/l was detected in SW samples collected from the capped area in 2018 (post-capping) compared to 920 mg/l in 1994-1995 (pre-capping) as shown in Fig. 9, although the comparison may be skewed by the location of samples.

Arsenic in groundwater

Over 500 groundwater samples have been collected since 1996. For convenience, even if the samples may represent pore water, they are defined as groundwater in this discussion. Most of the samples with arsenic concentration detected greater than 1 mg/l (1,000ug/l) were collected from the wells with the top of screening located about 5 ft below surface level (bsl) as shown in Fig. A-10. The maximum concentration of 2,840 mg/l was detected in 2010 near the original spill site with the top of screening located at about 5 ft bsl (Fig. A-10). Also illustrated by Fig. 10, most of the samples with arsenic concentration exceeding 5 mg/l are from the wells with the top of screening located at 5 or 10 ft bsl. Horizontally, majority of samples with arsenic detected ≥5 mg/l is from the wells located at the original spill area but two wells further down east outside of the cap. Average concentration of arsenic in the samples with exceedance of 5 mg/l on the east side of the cap was 5.3 mg/l with a maximum of 7 mg/l detected in 2000.

The most recent samples from wells located outside of capped area with arsenic exceeding 5 mg/l were collected in 2013. One well is located at the eastside of the capped area and the other is direct south and close to the original spill area (Fig. A-10).

Arsenic concentrations as high as 312 mg/l and 249 mg/l were detected in a well downgradient of treated area in May 2014 and in May 2017, respectively. This well was screened at about 7 ft bls. The results exceeded the in-situ remediation objective of 148 ug/l and the hazardous waste characterization of 5 mg/l although no TCLP or SPLP was performed.

Arsenic concentration in GW can be affected by many factors such as the groundwater table, pH, and other geochemical and environmental conditions. Concentration detected in different time is a result of composite result of fate and transport governed by hydrologic, hydraulic, and geochemical conditions. GW table records during sampling between 2002 and 2017 indicated high variation with a maximum change of approximately 4 ft at well location MW02-7d. Fig. A-11a-c show examples of change of GW surface elevation or water table for selected wells. Deeper well at location MW02-3 had higher water table than the shallow and intermediate wells (Fig. A-11a). The water table in shallow well MW11-3 has been significantly lower than that in the intermediate well at the same location (MW11-3i in Fig. 11b). It is not sure if it was due to the in-situ treatment. Elevation of GW table at well location of MW02-6 were above ground surface level sometimes (Fig. A-11c) which were also observed at other 5 well (MW02-2, MW02-4, MW02-5, MW02-6, and MW02-7) closer to the river, which may be an indication that an open GW table may exists in the area.

The water table elevation was similar to the surface water and lake levels between 2002-2003 and 2017-2018 (at the well locations examined except for at MW11-1 for one sampling event in 2016 maybe due to higher ground elevation). Potentially the concentration of arsenic in GW from these wells are a result of mixing between groundwater and surface water. Concentrations of arsenic in GW detected in these two time periods seemed to be either lower than the rest or decreased from prior sampling event (Fig. A-12a), potentially diluted by the surface water. Temporal variation of arsenic concentrations in samples from these wells were selected for evaluation because they represent the spatial trend of contamination from the original spill area to downstream and the current condition within and immediate downstream of the in-situ treated area. Well MW04-10 is located the uppermost from the river near the original spill area and the concentrations are used as references for comparison for other wells. All GW samples from this well were collected before in-situ treatment (before Oct. 2011). It was abandoned during remediation and no more samples were collected after Oct. 2011. Instead new wells were installed.

Wells MW11-1 and MW11-3 were installed post-in-situ remediation and within and immediate downstream the in-situ treated area. They are downstream of MW04-10 but nearby. Although well screening depth was similar at these two locations, the samples collected might reflect different transport pathway or SS conditions because the surface elevation dropped by approximately 3 ft from MW11-1 to MW11-3. Right after remediation, arsenic concentrations were comparable to each other in samples from both shallow or intermediate wells although MW11-1 is located within the treated area and MW11-3 is downstream. Then the concentration from the shallow well at MW11-1 decreased sharply followed by almost same level after 2013 with some small fluctuation. Contrary to the shallow well, the concentration did not change much in samples from the intermediate well MW11-1i. Not only was little change of concentration observed from this well but also the concentration was higher than that from the shallow well. The concentration variation observed from samples between shallow and intermediate wells may indicate that the remediation did not address the deeper SS or the condition of SS did not stabilize arsenic in depth. Opposite to the cluster of wells at MW11-1, arsenic concentrations in shallow well MW11-3 stayed higher than that from the intermediate well, MW11-3i, and it was even higher than that from MW11-1. Temporally, arsenic concentration decreased at MW11-3 slightly but significantly at MW11-3i which was almost the same as that detected at MW11-1 which may indicate that groundwater 4.5 ft bsl at MW11-1 may influence 10 ft bsl at MW-11i due to 3 ft drop of the surface ground level.

Samples collected from location M02-3 represent half way from the original spill area to the stream bank within in the cap but towards north edge. Most of the data were collected prior to the in-situation remediation for the intermediate and deeper wells. Only one sample was collected from the intermediate well post in-situ remediation as shown in Fig. 12. Apparently at this location arsenic concentrations stayed higher in the shallow GW (top of screening is at 2.6 ft bsl) than that in deeper GW. If the in-situ remediation had some positive affect at the location, it might only be temporary in 2012. Arsenic concentration increased sharply in samples in 2013 and then decreased. Most recent samples collected in 2017 and 2018, had arsenic level at an average of 110 ug/l, similar to the level detected in samples collected before 2006. The variation may be caused by variety of factors, including arsenic profile in SS. Concentration ranged from 24-134 mg/kg in the top 4 ft of SS and 1.5 mg/kg in the interval of 6-8 ft (sample location SB02-23) near well M02-3 and M02-3i, respectively.

Wells located further downstream and slightly towards south are labeled as MW02-6 and -6i. This cluster wells are located outside of the cap. The arsenic concentration from intermediate well was comparable to that from MW2-3i for the data available. However, in general the shallow GW at this location contained higher concentration than that from well MW02-3 but with relative lower concentration in the 2013 samples. Also comparing the results between shallow and intermediate GW at MW02-6, significant difference with a maximum of two orders of magnitude was observed. The difference may be as a result of arsenic transport patterns and different arsenic concentrations in SS. The top of screening of the shallow well is located about 2.5 below the ground surface while it was 7.5 below the ground surface in the intermediate well. The corresponding arsenic concentration in SS was 139 and 72 mg/kg for the top 4 ft and 0.4 mg/kg at the interval of 6-8 ft (sample location SB02-14), respectively. Two orders of magnitude difference in GW sample are reflected in the SS samples at this location. If to some extent arsenic concentration in the shallow GW is a measure of pore water, maybe it can be compared with that in SW collected nearby. Two SW samples ST04 (collected in 1996) and SW-10 (ponded water collected in 2012) collected near wells MW2-6 had arsenic concentration of 2.4 mg/l and 6.1 mg/l, respectively (Fig. A-12). One sample SW18-2 (collected in 2018) is located near well MW02-3 and a total concentration of 3.9 mg/l was detected in the surface water sample. Much higher concentration observed in the SW than in GW or pore water samples indicated that surface water transport pathway may be more significant than the subsurface or groundwater transport and interaction of arsenic in SS and SW is of more concern.

Distribution of arsenic outside of the fence

Because of the interim action conducted for SS at the site in 1996, the data collected inside and outside of the fence needs to be evaluated separately for delineation of areas for remedial action. East side of the fence has arsenic detected in three media with high frequencies of exceeding corresponding standards and thresholds and the area is close to the river; therefore, it’s subject to remediation and no further evaluation is needed. The direct west side of the fence was not subject to additional evaluation because most of the data in direct west side were collected from the rail track where original spill occurred and will be included for remedial option evaluation. What left are the north and south sides of the fence.

Statistical results of the data collected from both the north and south sides of the fence are shown in Fig. A-13 with spatial distribution of the data shown in Fig. A-14. For SW, because there were no samples exceeding 40 ug/l detected outside of the fence on the north side, only the data from the south side were evaluated. As a result, a total of 16 SW samples were analyzed for arsenic from the south side and cumulatively about 31% of samples had arsenic concentration less than 40 ug/l. Only 1 sample exceeded 1,000 ug/l which is close to the spill site.

All GW samples collected outside of the fence was evaluated together without spatial differentiation due to a limited number of wells installed. A total of 89 GW samples were analyzed for arsenic over the years. Cumulatively about 74% of the samples had arsenic less than 10 ug/l of arsenic. Only three samples exceeded 150 ug/l with a maximum of 415 ug/l detected in 1997 from the north side of the fence.

SS samples were evaluated separately for north and south sides of the fence. As Fig A-13 shows, in general on the south side arsenic in approximately 89% of SS samples did not exceed 20 mg/kg with a maximum concentration of 91 mg/kg. Approximately 71% if samples from north side did not exceed 20 mg/kg with a maximum concentration of 213 mg/kg. Six out of total 21 samples had arsenic exceeded 20 mg/kg and 1 sample exceeded 100 mg/kg.

Based on the statistical results of the data distribution for areas outside of the fence, it is concluded that remedial action will primarily limit to the fenced-in area and the direct east close to the river. Maybe additional sampling for SS from the north side close to sample SS02-03 need to be conducted in order to exclude the area for remediation in remedial design phase.

Estimation of arsenic discharging to the Kewaunee River

There are two predominant surface water drainage channels, namely North and South Sloughs, discharging surface water to the Kewaunee River when the lower portion of the marsh is not flooded according to documentation available. Potentially many smaller size drainage channels are present but cannot be easily identified. According to STS (2006), flow monitoring at the weirs installed at the main sloughs in 2005 suggests that there is a consistent discharge of surface water from the marsh to the river over the years. The amount of arsenic discharged to the River may be in an order of 1-5 pounds per year from each slough. However, STS did not provide details of how the loading was estimated. Therefore, a review of data and estimate of mass of arsenic potentially discharging to the river through the two sloughs were conducted as part of the development of remedial action performance standards.

Flow data were collected from weirs on each of the slough between March 2005 and November 2005. The results were documented in the Supplemental Environmental Monitoring Report by STS [2006]. As reported, the flow rate ranged from 0 to 5 gal/min for the monitoring period. At the same time STS predicted that peak flows might range from 22-55 gal/min during spring thaw based on observed level of ice in the transducer well and water level upstream of the V-notch in the weirs. When the flow was monitored, surface water samples were also collected from downstream of weirs at two locations, SW-1 and SW-2 (Fig. A-15) for analyses of arsenic. Additional SW data close to the area are available from other sampling events as summarized in Table 15 of the report prepared by the Department (Victor, 2018). Arsenic loading from the sloughs to the river was then estimated based on the flow data and arsenic concentrations detected. Because of uncertainties, the goal of the estimation is to provide a range of minimum to maximum loading of arsenic mass to the river from two sloughs. The controlling variables are the quantity of water discharging from the marsh to the river and arsenic concentration in the discharge stream.

Without a dynamic transport model, the mass loading can be estimated based on various combinations of observed base flow and peak flow with variation of arsenic concentrations. For the purpose of this memo the following conditions were considered:

Slough	Base Flow (gal/min)		Peak Flow (gal/min)		As Concentration (ug/l)		
	Average (Q_{ave})	Maximum (Q_{max})	Q_p 30 days/yr	Q_p 75 days/yr	Cs_{min}	Cs_{max}	Cf_{max} (fence)
South	1.4	5	22	22	968	1,520	3,100
North	1.5	4.5	55	55	813	2,960	4,600

These values were based on the monitoring records. The minimum loading from each slough was bounded by the average base flow (Q_{ave}) for a duration of 150 days and a peak flow for a duration of 30 days per year in combination with the minimum arsenic concentration (Cs_{min}). The maximum loading was estimated based on the maximum observed base flow (Q_{max}) for 150 days and peak flow for 75 days per year combined with the maximum concentration (Cs_{max}). Concentration of arsenic could also be higher at locations where it is not in constant exchange with the river water. Therefore, another scenario was examined by using the maximum concentration (Cf_{max}) observed at the fence area, which is located upstream of the other samples used for estimation (Cs_{min} and Cs_{max}).The reason of providing an estimate of arsenic discharge from the last scenario is that the arsenic concentration detected close to the fence area may represent the true condition of surface water from the site before being diluted by the river water. In addition, the peak flow may occur not only during spring thaw but also under storm events.

The following steps were carried out to define the annual loading of arsenic from the marsh to the river:

1. Estimate discharge of water
    a) Estimate annual discharge under base flow condition at each slough (Q_{base})
        - applying the 2005 flow rates collected by STS (2006) as base flow via the south and north sloughs, respectively (Q_{bi}) with the minimum (average of the monitoring data) and the observed maximum value
        - assuming that the sloughs discharge under the base flow for 24 hours per day over 150 days per year (T_{base}) at Q_{bi} (unit conversion)

  - calculating the annual discharge of water under base flow condition at each slough $Q_{base} = Q_{bi} x T_{base}$

  b) estimating annual discharge under peak flow at each slough mouth (Q_p)
    - assuming peak flow rates of 22 and 55 gal/min (Q_{pi}) for the south and north sloughs, respectively
    - assuming the sloughs discharge under the peak flow condition for 30 days and 75 days per year (T_p) (unit conversion)
    - calculating the annual discharge under peak flow condition at each slough $Q_p = Q_{pi}$ x T_p

  c) estimating total annual discharge by adding peak discharge to the base flow discharge (Q_{yr_min} and Q_{yr_max})

2. Estimate mass loading
  a) multiplying various concentrations of arsenic with estimated minimum and maximum annual discharges of water at the slough mouth and near the fence for estimation of annual mass loading to the river

Table A-1 summarizes the predictive results. Potentially, 9 kg to 162 kg of arsenic may discharge from the marsh to the river annually through the two sloughs. The estimation does not include advective discharge or diffusive transport from other channels and along over 800 ft shoreline. If the entire interface between the marsh and river is considered the total mass loading may increase.

Based on the estimated annual loading rate, the total arsenic discharging from the site to the Kewaunee River since spill was predicted to range from a minimum of approximately 600 kg to 11,400 kg between 1940 and 2010. Accumulatively, significant amount of arsenic may have discharged to the Kewaunee River and further to the Lake Michigan. It is worrisome that the higher frequency of intensive precipitation observed in more recent years may cause increase of discharge of arsenic to the river.

Estimation of arsenic mass spilled

An attempt was made to estimate potential total mass of arsenic spilled in order to verify arsenic mass estimated based on the concentrations detected in SS. According to records, a typical railcar may have a capacity of 70 tons. For simplicity, it was assumed that when derailed the car was loaded to its capacity. Although arsenic speciation studies (STS, 2006 and RMT, 2010) indicated that inorganic arsenic might be the form of the product spilled, but it may not rule out then popular product of sodium cacodylic acid (molecular weight of 160) or cacodylic acid (molecular weight of 138) given the presence of white powder observed at the site as reported. For calculation, these two compounds were assumed for proportion of arsenic in weight as summarized in Table A-2. As a result, potentially a total of 32,000 to 38,000 kg (32-38 tons) arsenic might have spilled at the site historically.

A simple mass balance calculation was then conducted to verify the estimation of arsenic may still present at the site between 1994 and 2010, the latest sampling year. It is assumed that discharge from the North and South Sloughs to the river is the only pathway for arsenic leaving the site while the amount of loss via volatilization and uptake by vegetation and wildlife is negligible. Applying the maximum annual mass loading of 162 kg/yr, it is estimated that about 8,800 kg (8.8 tons) of arsenic would have left the site between 1940 and 1994 while it was about 11,400 kg (11.4 tons) between 1994 and 2010. By subtracting the arsenic discharged to the river to the total amount potentially spilled, approximately 23-29 tons of arsenic might remain at the site in 1994 or 20-27 tons in 2010. The estimates of mass from this method can be compared to the mass amount calculated based on the concentration of arsenic in soil and sediment at the extent of greater or equal to 20 mg/kg. The comparison will help further confirm the quantity of arsenic spilled.

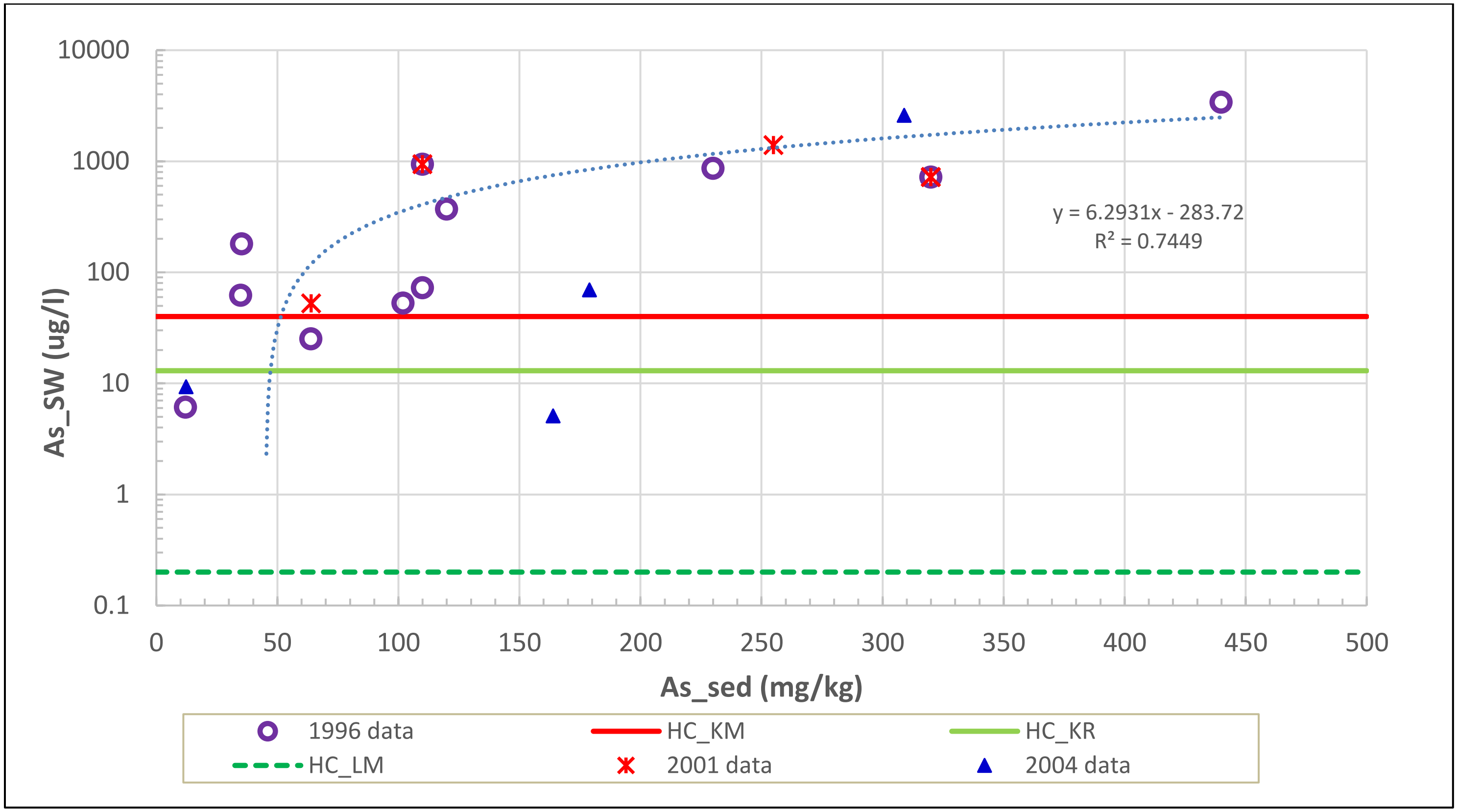


Fig. A-1 Correlation of arsenic concentration in SS and SW based on data collected in 1996 and verification using data collected in 2011 and 2004 (HC_KM: human cancer risk based criterion for the marsh at 40 ug/l; HC_KR: human cancer risk based criterion for the river 13 ug/l; and HC_LM: human cancer risk based criterion for Lake Michigan at 0.2 ug/l)

Fig. A-2 Distribution of SS samples collected for arsenic analyses from 1994 to 2010

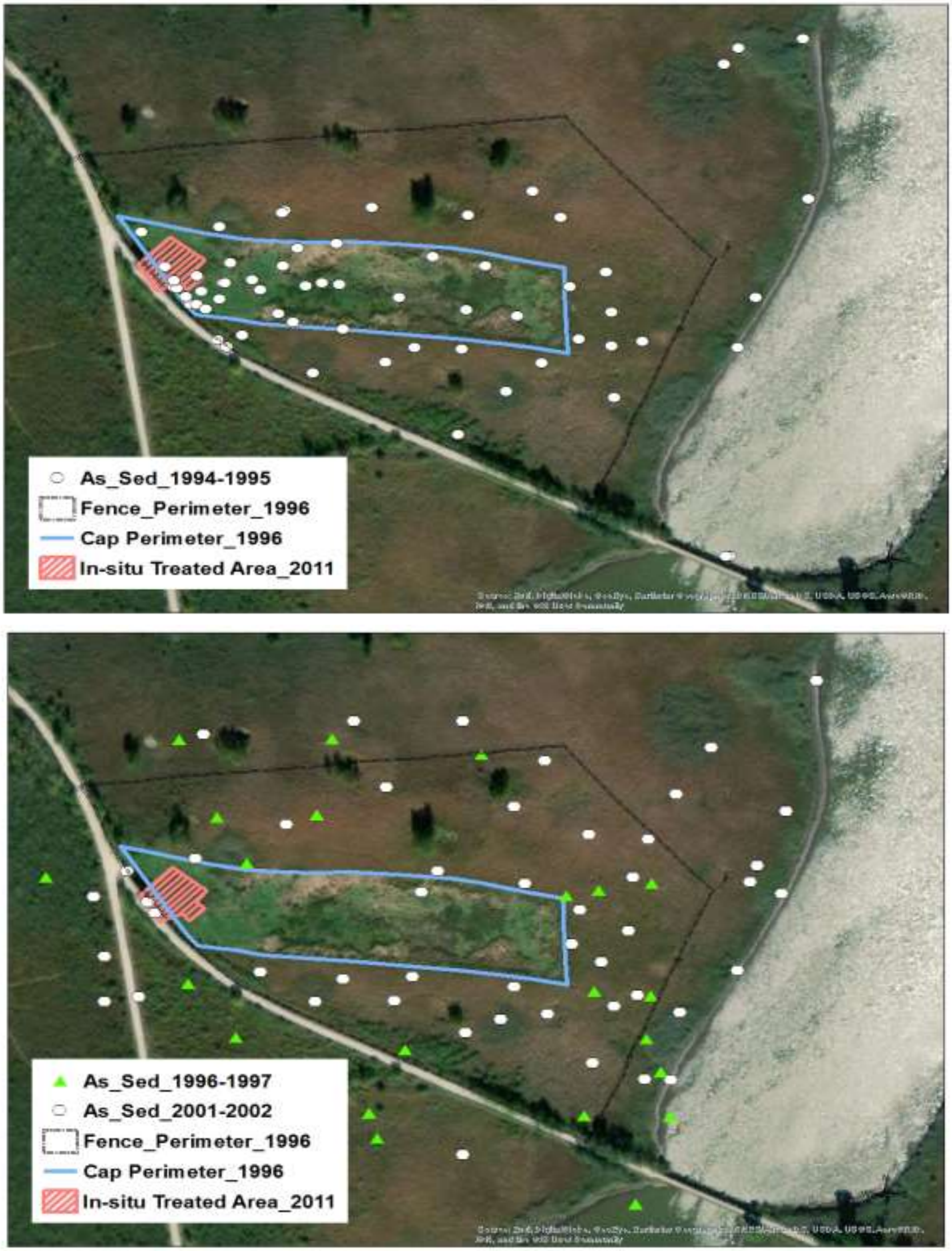


Fig. A-3 Distribution of SS samples collected for arsenic analyses between 1996 and 2002

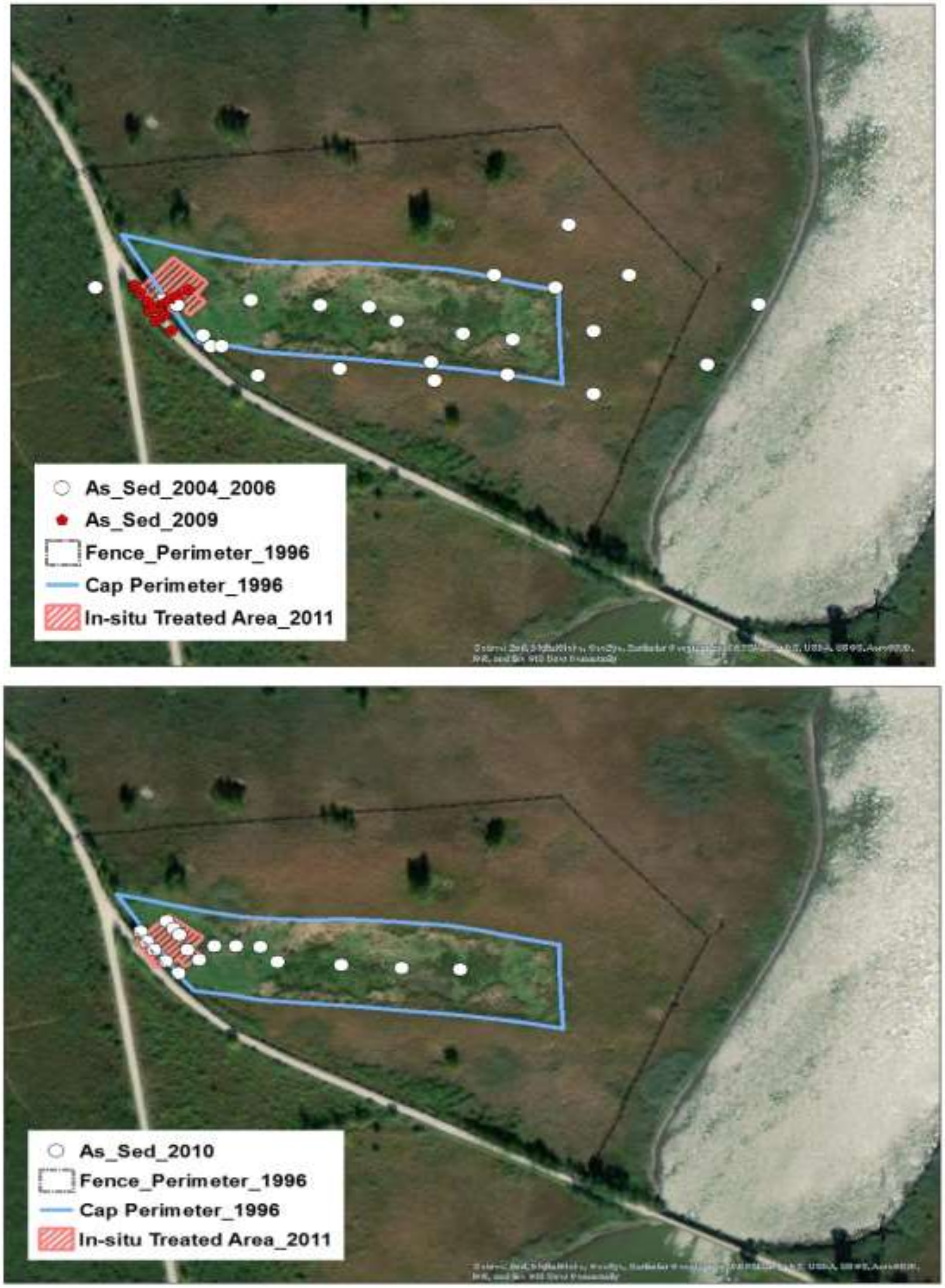


Fig. A-4 Distribution of SS samples collected for arsenic analyses in 2010

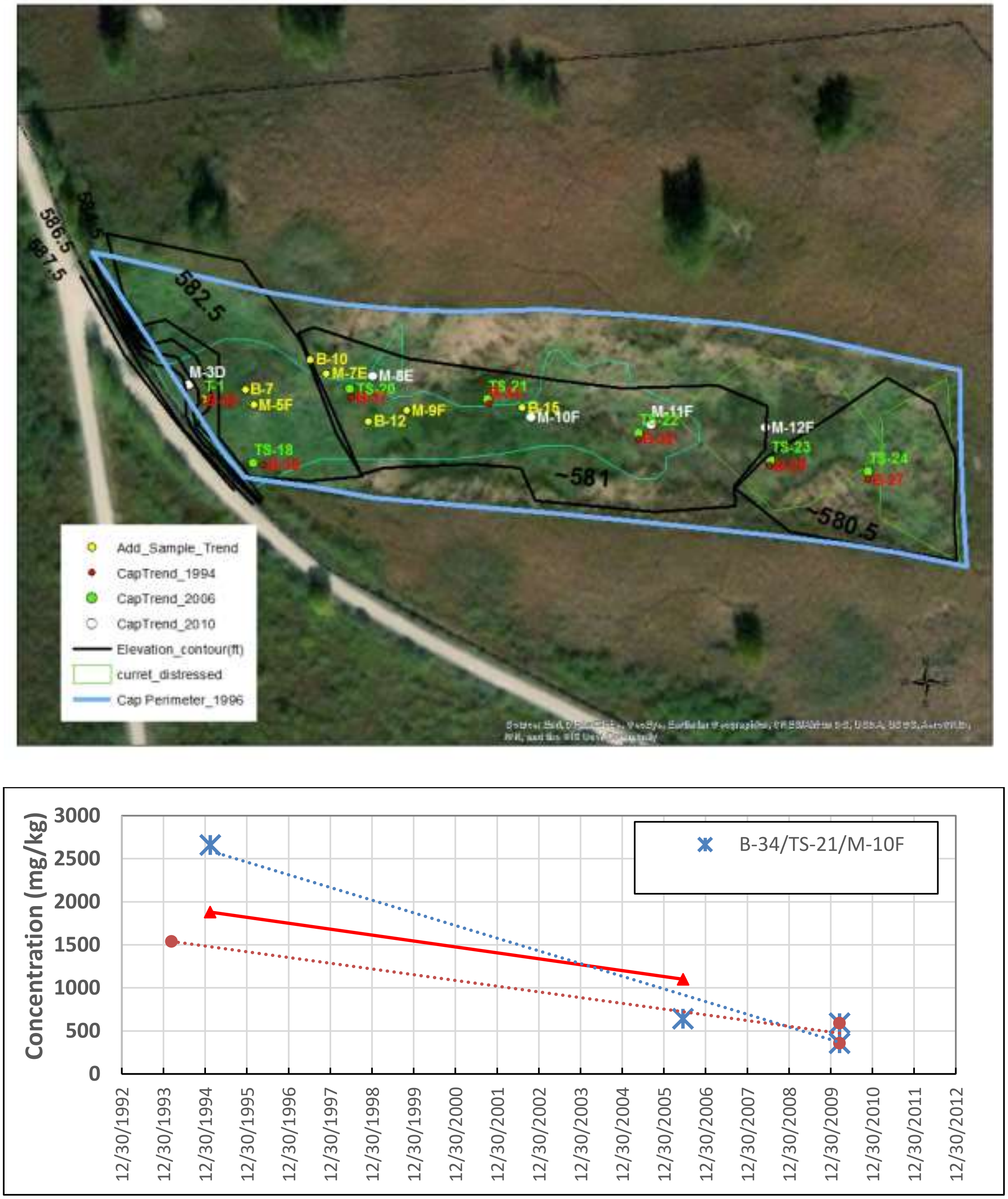


Fig. A-5 Location of SS samples collected for assessment of arsenic attenuation
(Add_Sample_Trend: additional samples evaluated for this memo; CapTRen_1994, _2006, and _2010: samples collected from the capped area in 1994, 2006, and 2010; distressed: vegetation in the areas are currently distressed.)he lines for linear interpretation are just for information purpose, particularly for the pair of samples B-27/TS-24 because only two samples were available for analyses)

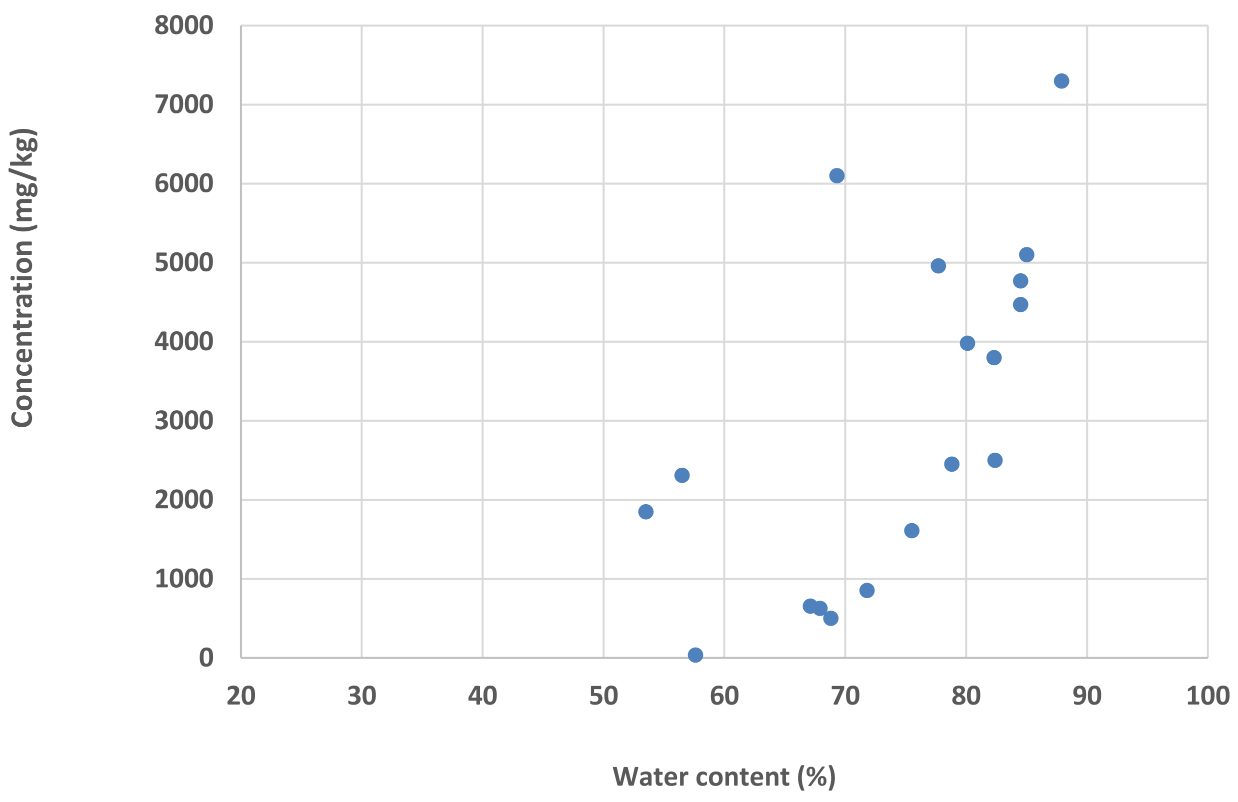


Fig. A-6 Trend of relationship between water content and arsenic concentration in selected SS samples

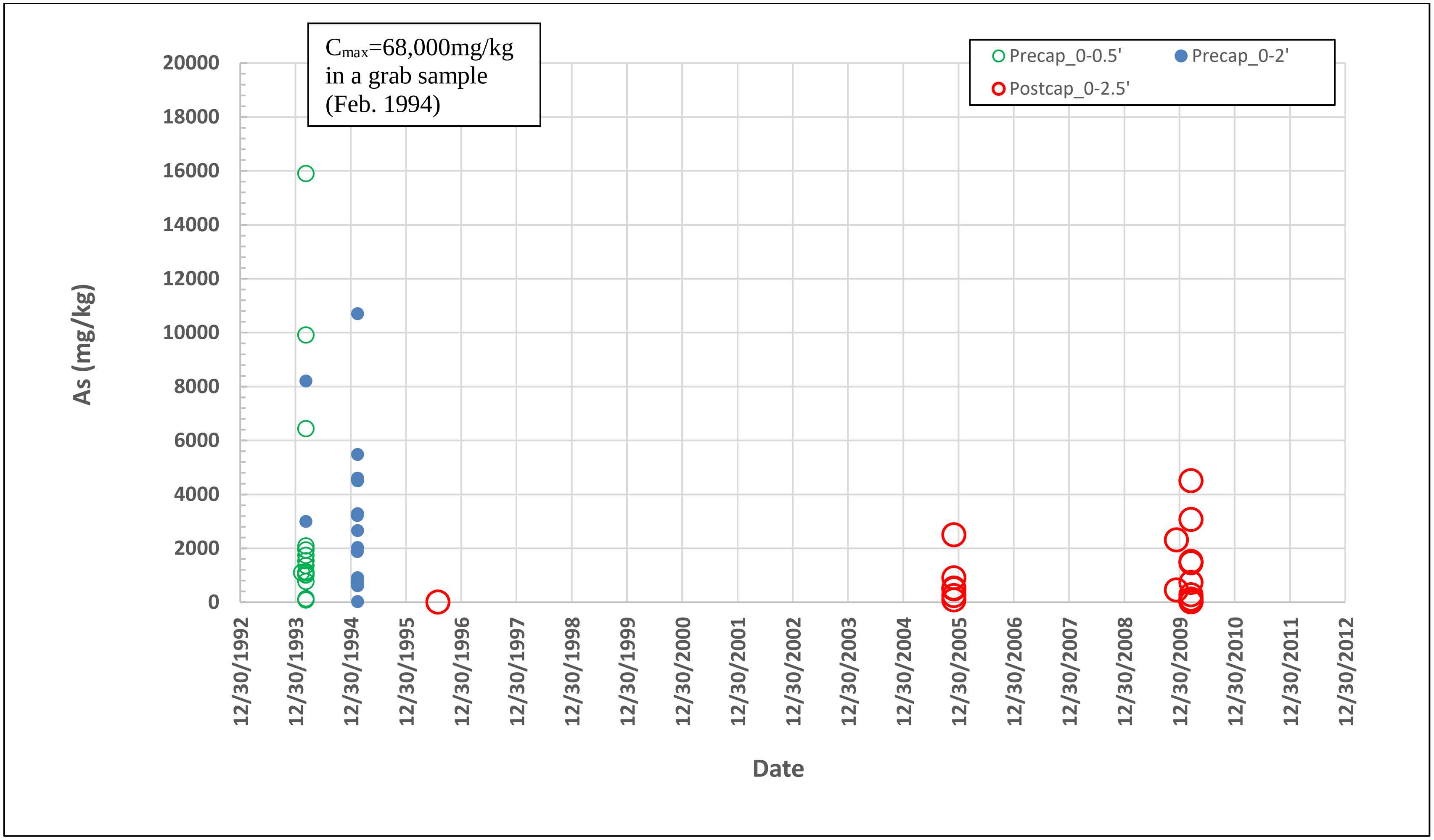


Fig. A-7 Arsenic concentration in surficial SS pre- and post-capping (samples collected from railroad bed in 2009 are not included)

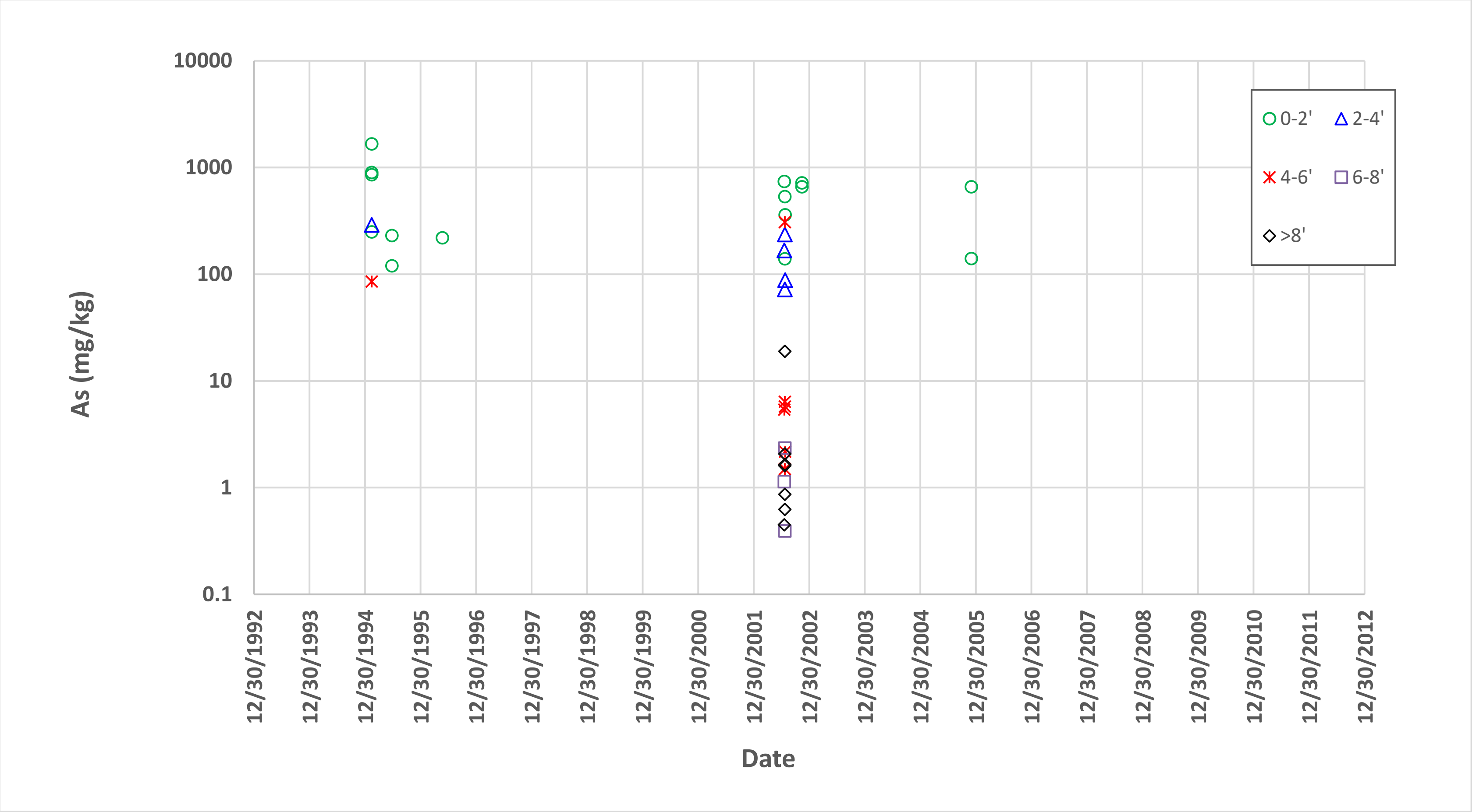


Fig. A-8 Arsenic concentration in surficial SS from southeast of the cap and adjacent to the Kewaunee River (represents the condition in the dominant surface water transport pathway from the marsh to the river)

Fig. A-9 Spatial distribution of SW samples (1996-2018) with concentration labeled (mg/l) for samples collected from the capped area 1994-1995 and in 2018 (numerical numbers in yellow were for samples collected in 1994-1995 and in orange were samples collected in 2018)

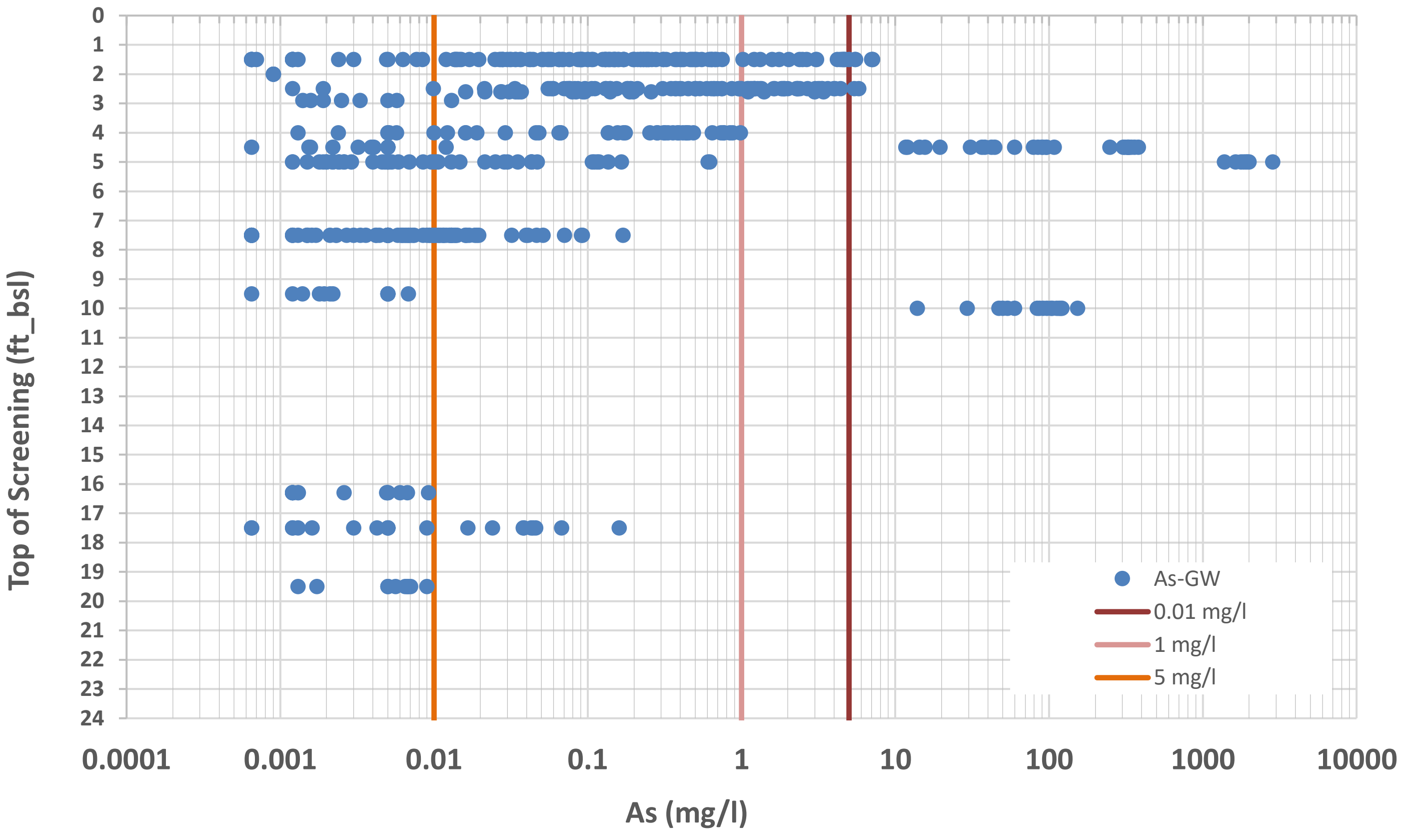
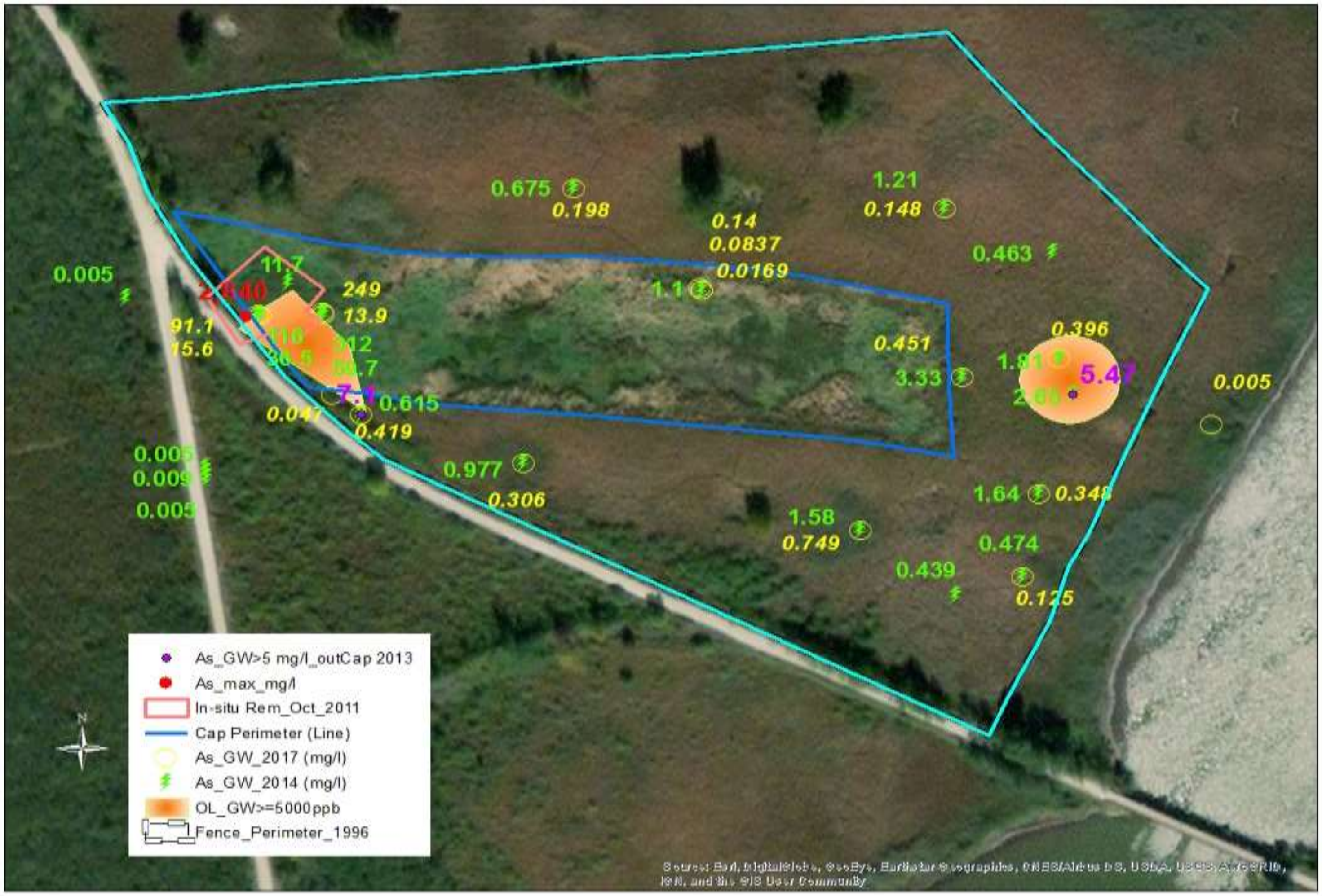


Fig. A-10 Vertical profiles of arsenic in GW samples collected from all the wells from 1996 to 2018 based on the elevation of top of screening



Source: Esri, DigitalGlobe, GeoEye, Earthstar Geographics, CNES/Airbus DS, USDA, USGS, AeroGRID, IGN, and the GIS User Community

Fig. A-10 Spatial distribution of GW sampling wells with arsenic concentrations labeled for selected samples (As_GW_2014 and As_GW_2017: samples collected in 2014 and 2017 after in-situ remediation and the concentration are labeled in green and yellow, respectively. As_GW>5 mg/l_outCap 2013: concentration detected >5 mg/l and located outside of capped area are labeled in purple. As_max_mg/l: maximum arsenic concentration labeled in red.)

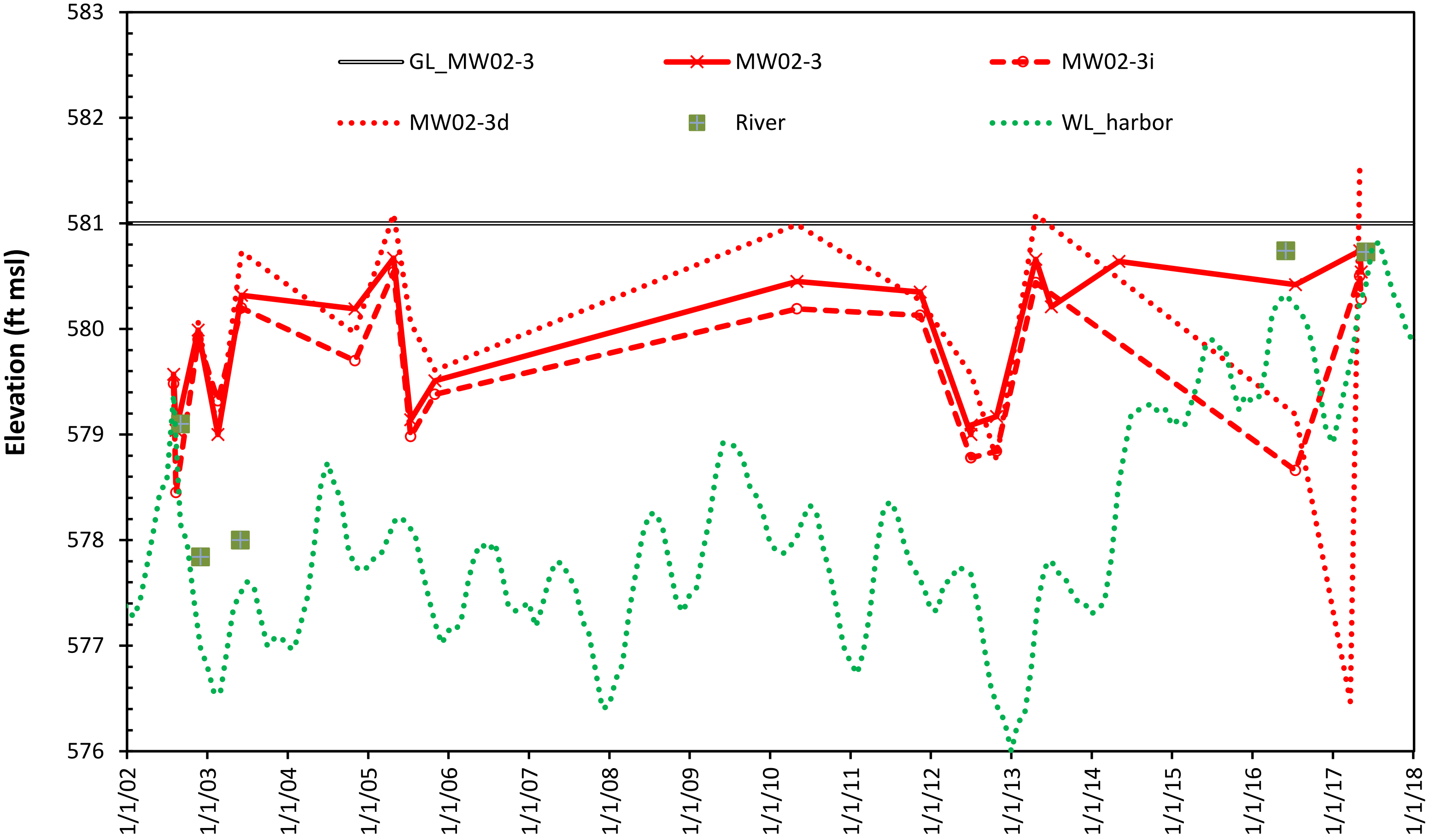


Fig. A- 11a Temporal variation of groundwater table observed at selected wells (note: GL_: ground level; MW02-3: shallow well; MW-02-3i: intermediate well; MW-02-3d: deep well; River: surface water elevation in the Kewaunee River; WL_harbor: surface water elevation in the Kewaunee Harbor at NOAA station. Records for collected in 2017 may not be at equilibrium state. Some of the extreme lower values are not plotted. Lines are plotted just for display only not for prediction of the elevation. Lines between points are plotted just for display purpose, not for prediction of the elevation.)

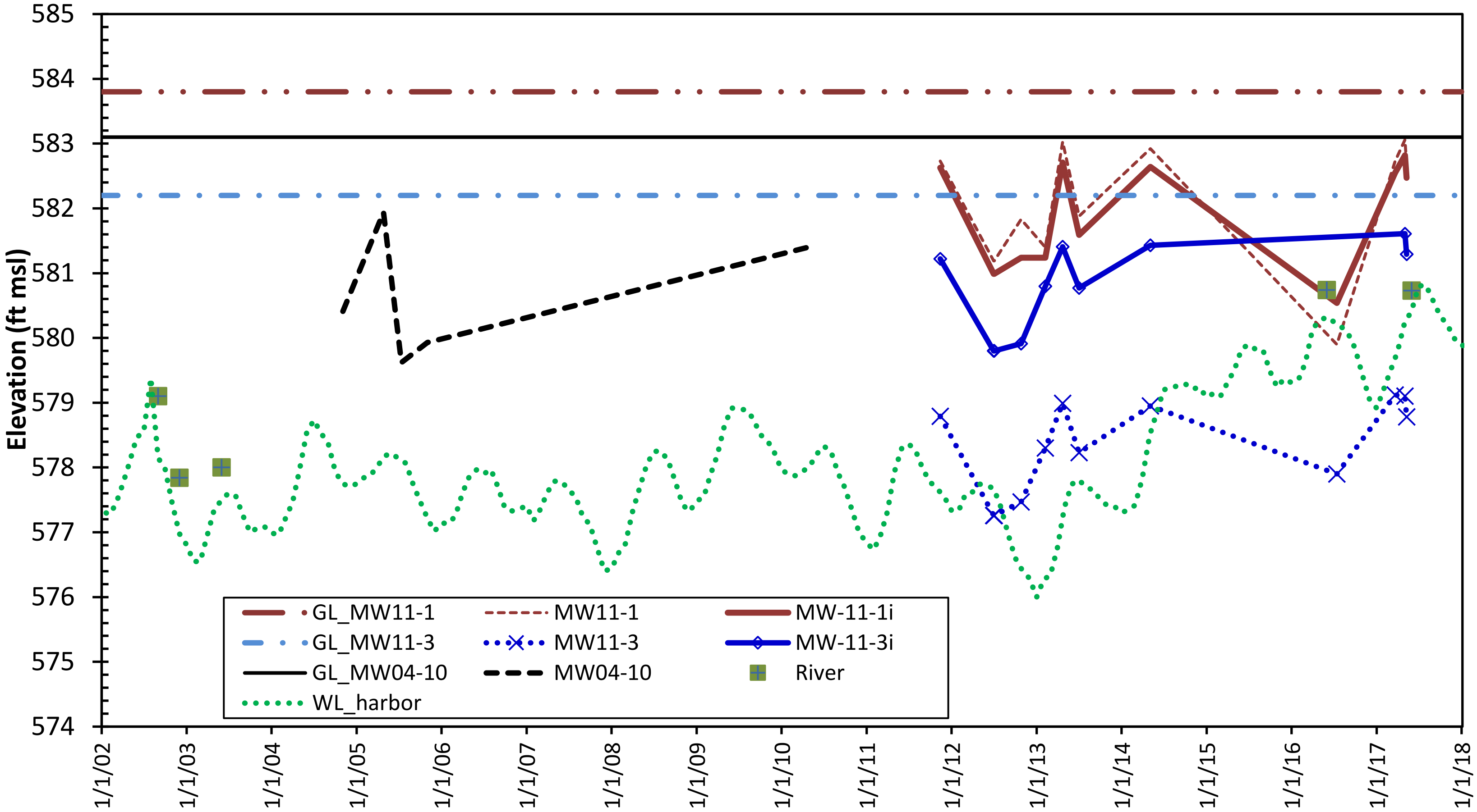


Fig. A- 11b Temporal variation of groundwater table observed at selected wells (note: GL_: ground level; MW11-1: shallow well; MW11-1i: intermediate well; MW11-3: shallow well,; MW11-3i: intermediate well; MW04-10: shallow well; River: surface water elevation in the Kewaunee River, WL_harbor: surface water elevation in the Kewaunee Harbor at NOAA station. Records collected in 2017 may not be at equilibrium state. Some of the extreme lower values are not plotted. Lines between points are plotted just for display purpose, not for prediction of the elevation.)

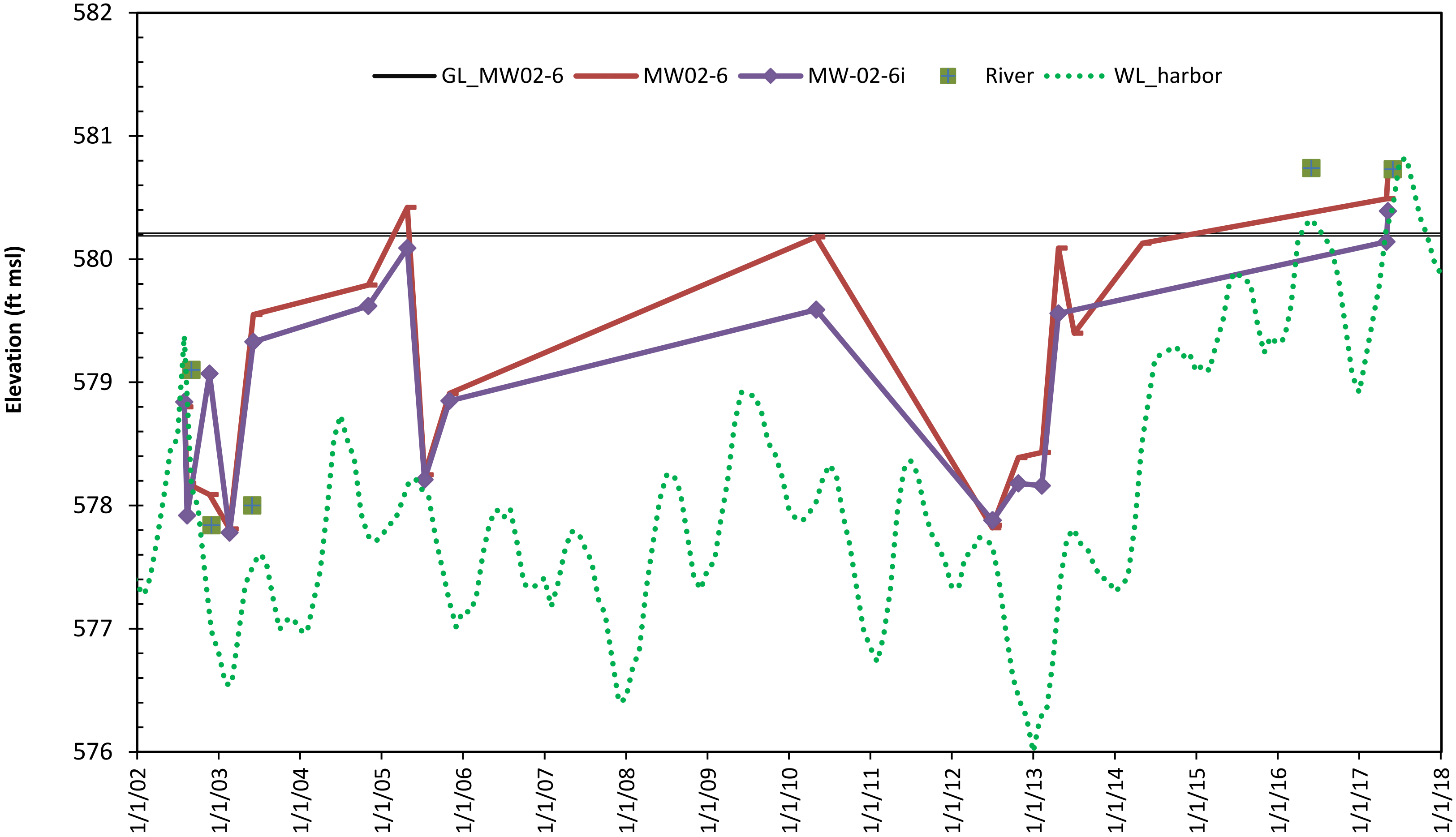


Fig. A- 11c Temporal variation of groundwater table observed at selected wells (note: GL_: ground level; MW02-6: shallow well; MW-02-6i: intermediate well; River: surface water elevation in the Kewaunee River, WL_harbor: surface water elevation in the Kewaunee Harbor at NOAA station. Records for collected in 2017 may not be at equilibrium state. Some of the extreme lower values are not plotted. Lines between points are plotted just for display purpose, not for prediction of the elevation.)

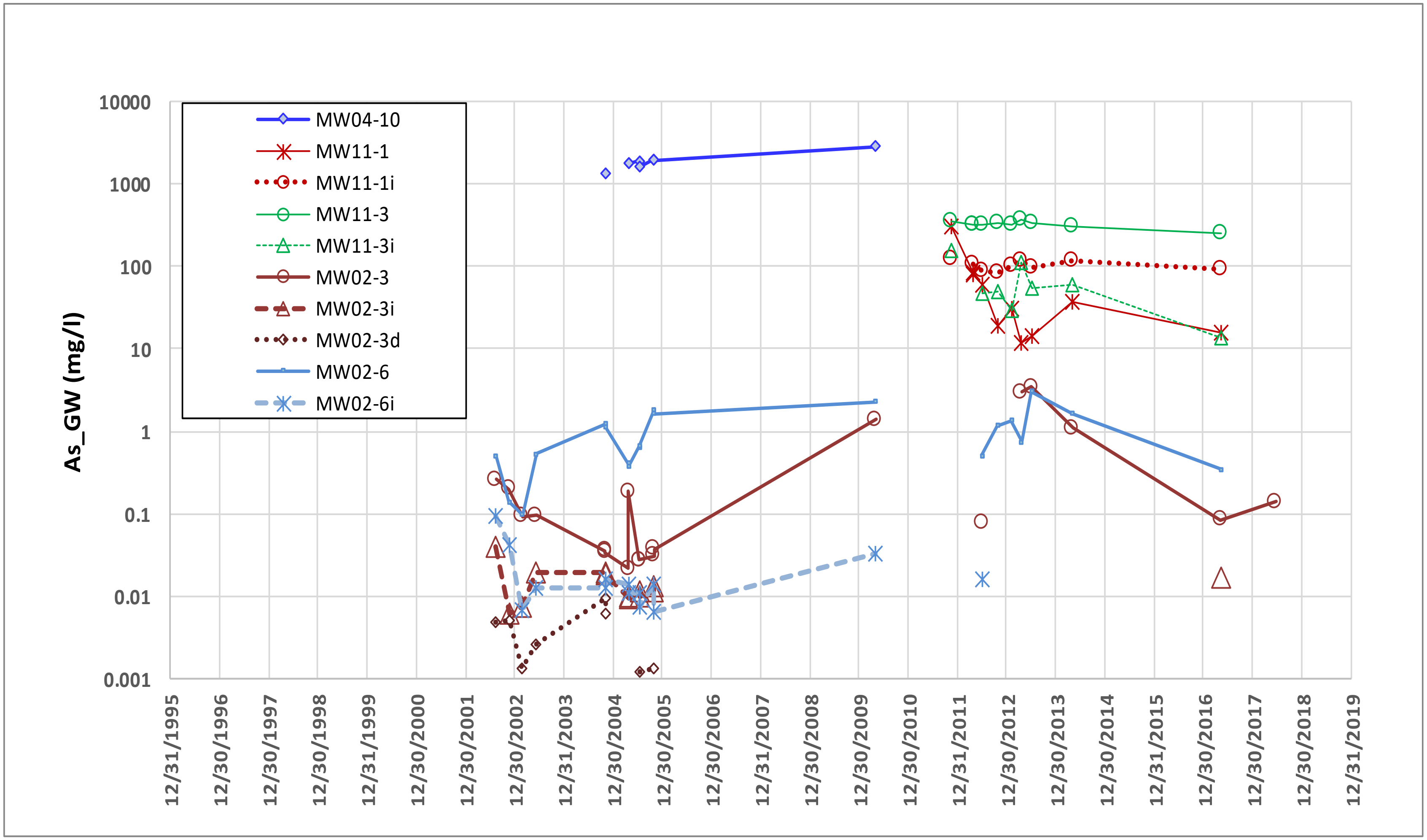
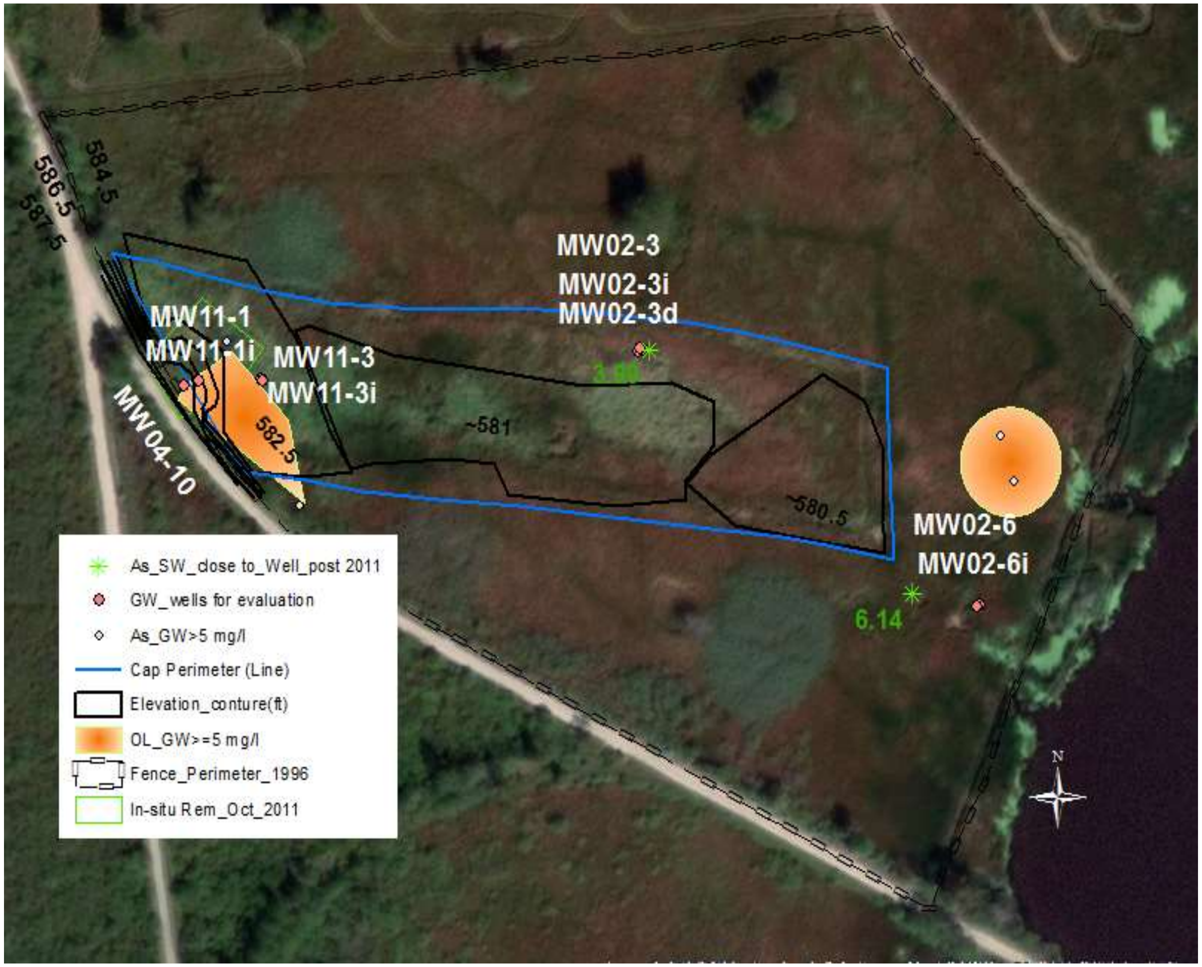
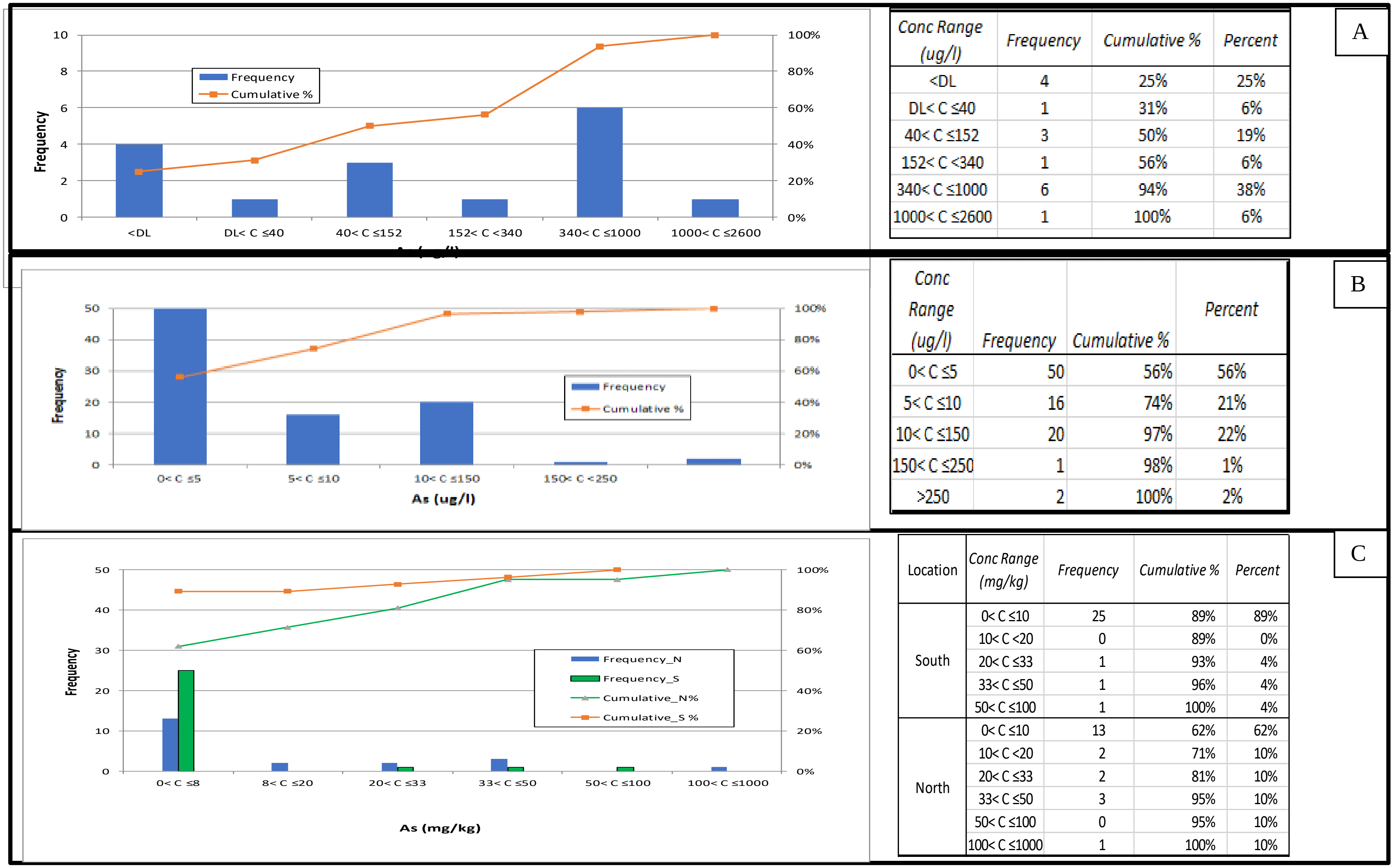


Fig. A-12a Arsenic concentration in GW samples from wells located on southeast transport pathway and adjacent to in-situ treated area



Well ID	Installed-date	Top of screening below ground surface (ft)	As Con in SW (mg/l)
MW11-1	10/18/2011	7.2	
MW11-1i	10/18/2011	12.5	
MW11-3	10/18/2011	7.2	
MW11-3i	10/18/2011	12.5	
MW02-3	07/18/2002	5.1	3.9
MW02-3i	07/18/2002	10	
MW02-3d	07/18/2002	18.8	
MW02-6	07/22/2002	5	6.1
MW02-6i	07/22/2002	10	

Fig. A-12b Spatial location of the wells selected for evaluation of arsenic concentration in GW samples post in-situ remediation (screening depth of the wells are summarized in the table along with arsenic concentration detected in the surface water with similar location. Also displayed is the elevation contour based on LIDAR)



A

Conc Range (ug/l)	*Frequency*	*Cumulative %*	*Percent*
<DL	4	25%	25%
DL< C ≤40	1	31%	6%
40< C ≤152	3	50%	19%
152< C <340	1	56%	6%
340< C ≤1000	6	94%	38%
1000< C ≤2600	1	100%	6%

B

Conc Range (ug/l)	*Frequency*	*Cumulative %*	*Percent*
0< C ≤5	50	56%	56%
5< C ≤10	16	74%	21%
10< C ≤150	20	97%	22%
150< C ≤250	1	98%	1%
>250	2	100%	2%

C

Location	*Conc Range (mg/kg)*	*Frequency*	*Cumulative %*	*Percent*
South	0< C ≤10	25	89%	89%
	10< C <20	0	89%	0%
	20< C ≤33	1	93%	4%
	33< C ≤50	1	96%	4%
	50< C ≤100	1	100%	4%
North	0< C ≤10	13	62%	62%
	10< C <20	2	71%	10%
	20< C ≤33	2	81%	10%
	33< C ≤50	3	95%	10%
	50< C ≤100	0	95%	10%
	100< C ≤1000	1	100%	10%

Fig. A-13. Statistical analyses of concentration distribution in SS samples collected from outside of the fence (Panels A: SW, B: GW and C: SS Frequency_S= Frequency in percent in samples collected from the southside of the fence, _N=northside of the fence)

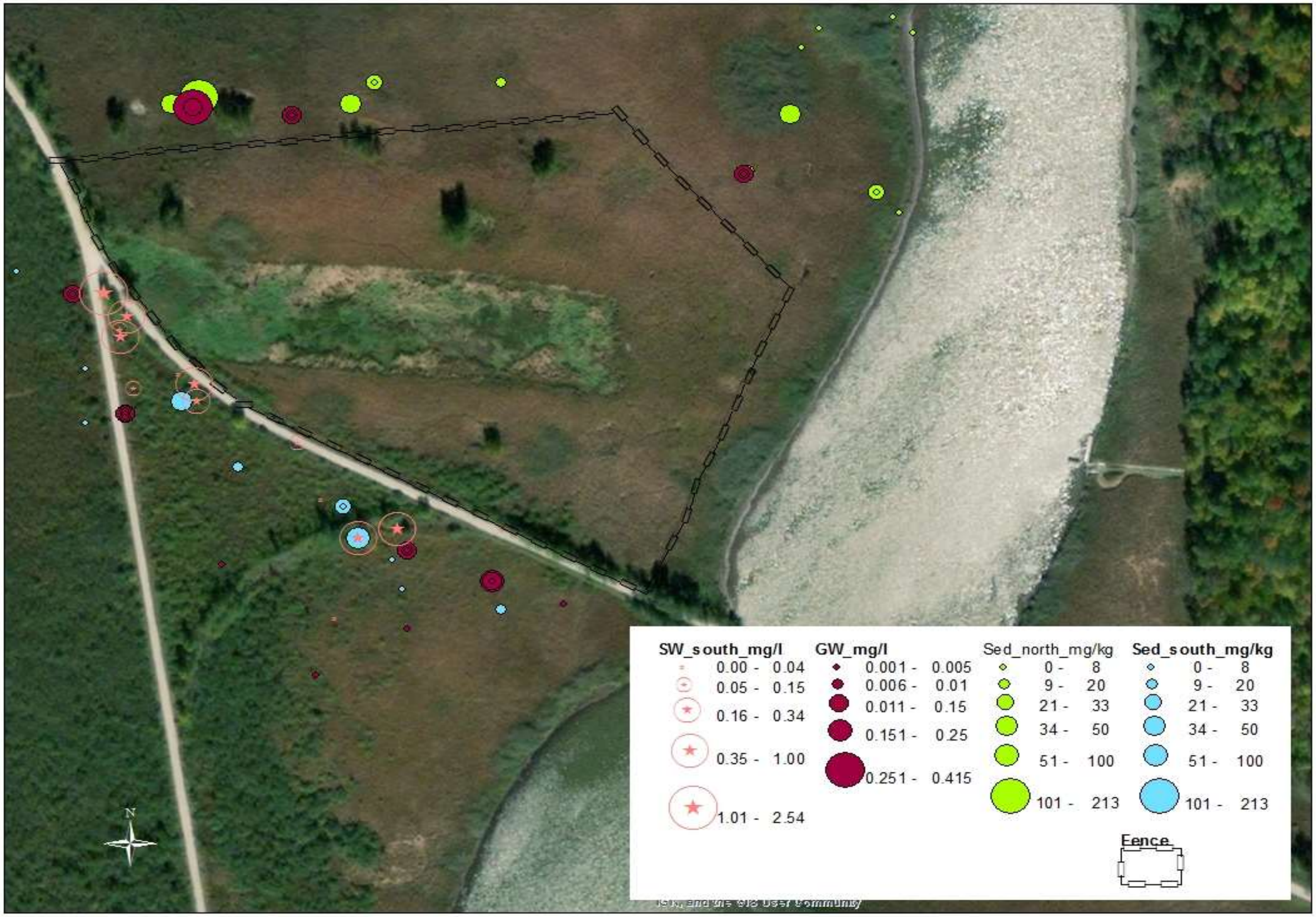


Fig. A-14 Distribution of arsenic concentrations in SW, GW, and SS samples collected outside of the fence

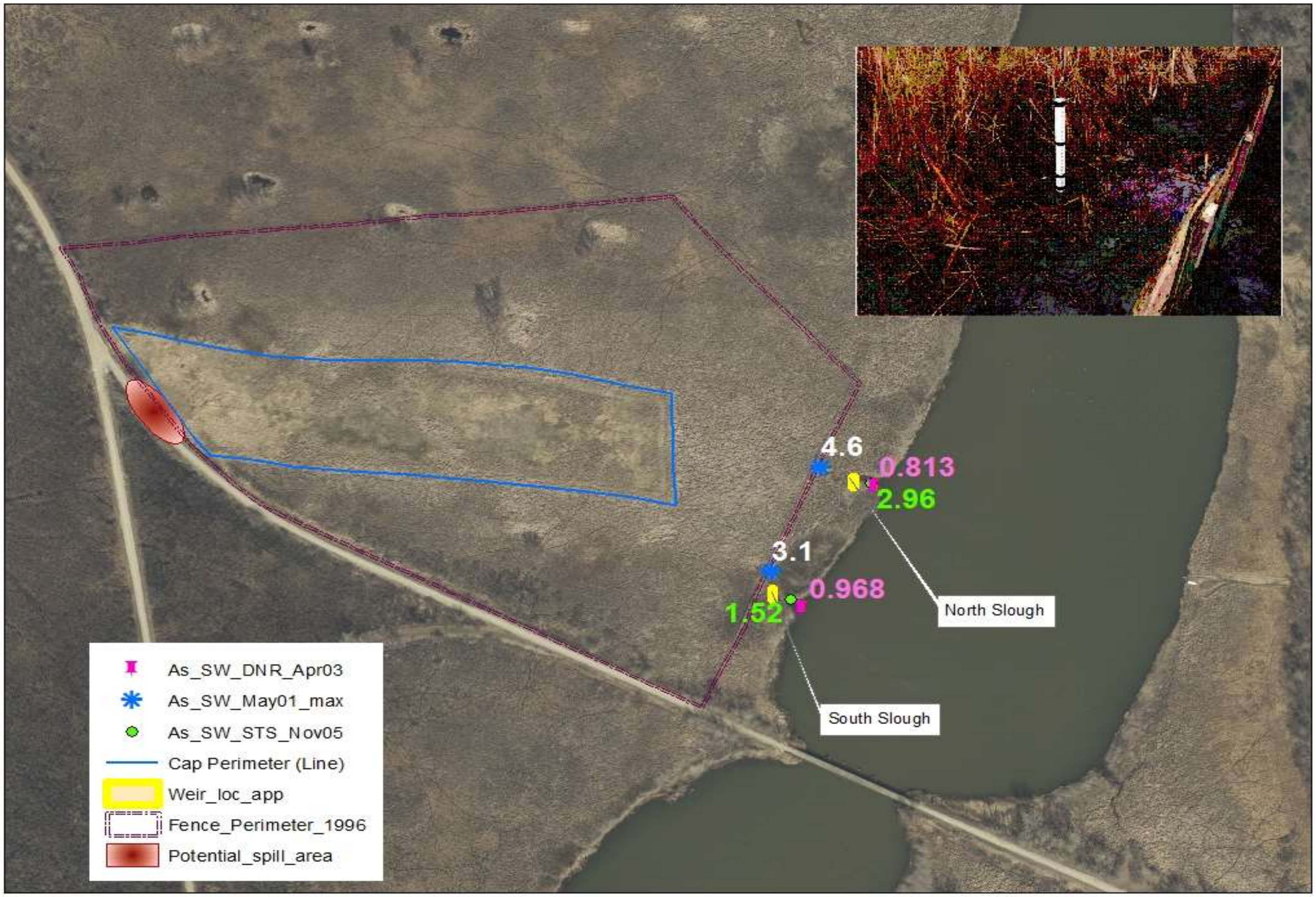


Fig. A-15 Location of weirs for flow monitoring by STS (2004) and concentration of arsenic detected in SW in mg/l (the data were used for discharging analyses)

Table A-1 Estimation of arsenic loading to the Kewaunee River via two sloughs*

Slough	Flow rate			Annual Discharge (Q_{base})		Mass loading at slough						Mass discharge at Fence		
	Q_{bi} (gal/min)		Q_{pi}	Q_{yr_min}	Q_{yr_max}	C_{As}	M_{dmin}/yr		C_{As}	M_{dmax}/yr		C_{As}	Md/yr	
				($Q_{ave}+Q_{p\_30d}$)	($Q_{max}+Q_{p\_75d}$)	Min	low	high	Max	low	high	Max-01	low	high
	Q_{ave}	Q_{max}	gal/min	gal/yr	gal/yr	ug/l	kg	kg	ug/l	kg	kg	ug/l	kg	kg
South	1.4	5.6	22	1,252,800	3,585,600	968	4.6	13.1	1,520	7.2	20.6	3,100	14.7	42.0
North	1.5	4.5	55	1,274,400	6,912,000	813	3.9	21.3	2,960	14.3	77.4	4,600	22.2	120.3
Sum	2.9	10.1	77	2,339,280	9,752,400		9	34		21	98		37	162

* Q_{bi} = base flow rate from monitoring by STS (2004); Q_{ave} = average base flow; Q_{max} = maximum flow rate observed; Q_{pi} = predicted peak flows by STS (2004); Q_{yr_min} and Q_{yr_max} = estimated minimum and maximum annual flow; $Q_{ave}+Q_{p\_30d}$ = assuming the marsh will discharge water under average base flow condition for 150 day and peak flow for 30 days per year; $Q_{max} + Q_{p\_75d}$ = assuming the marsh will discharge water under maximum base flow condition for 150 days and peak flow for 75 days; C_{As}= arsenic concentration detected in SW from sloughs or at the east side of the fence; M_{dmin}/yr and M_{dmax}/yr = predicted minimum and maximum annual loading of arsenic to the Kewaunee River. Within each concentration category, multiplying concentration with Q_{yr_min} and Q_{yr_max} resulted in a range of mass loading from low to high; Min = minimum; Max = maximum and Max-01 = maximum arsenic concentration detected at east side of the fence.

Table A-2. Estimation of potential arsenic mass spilled

Chemical name: **cacodylic acid or sodium cacodylic acid**
Atomic weight of arsenic: **75**
Molecular weight: **cacodylic acid: 138**
Molecular weight sodium **cacodylic acid**: **160**
% Arsenic: **47-54** by weight
Detailed car capacity: **70** tons
Total mass of arsenic: **32- 38** tons