

APPENDIX C - Isotope Study Plan



US Magnesium
Groundwater Discharge Permit Application
Isotope Study Plan

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Sign-off Sheet


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1.0 INTRODUCTION AND PURPOSE

The US Magnesium facility (Facility) processing plant produces a low-pH wastewater stream that is currently conveyed to unlined evaporation ponds, the Current Waste Pond (CWP) receives approximately 1100 gallons per minute (gpm) of process plant wastewater which overflows eastward into the Old Waste Pond (OWP) (refer to site map shown in **Figure 1**). An expanded and retrofitted wastewater evaporation pond (Retrofitted Waste Pond [RWP]) utilizing vertical hydraulic barrier wall technology is proposed for the Facility to meet requirements outlined in Utah Administrative Code R317-6.

This document has been created in response to comments and discussions with the Utah Department of Environmental Quality (UDEQ) Division of Water Quality (DWQ), United States Environmental Protection Agency (USEPA), and US Magnesium on the Groundwater Discharge Permit (GWDP) application submitted to DWQ on December 15, 2017. The purpose of this document is to present an isotope study plan designed to assess whether stable isotopes of hydrogen and oxygen may be suitable Facility wastewater tracers in the future.

2.0 FACILITY WASTEWATER TRACERS

Selection of appropriate parameters that will reliably indicate potential migration of Facility wastewater into groundwater surrounding the future hydraulic barrier wall is key to the compliance monitoring program. Considering the unique wastewater and groundwater (high total dissolved solids [TDS]) at the US Magnesium site, the most effective Facility wastewater tracers for groundwater and surface water should meet the following criteria:

- Exhibit distinctive signatures between Facility wastewater and native groundwater
- Be chemically conservative while being transported in groundwater (i.e. amount of measured tracer is not lost or added to groundwater via interaction with aquifer matrix)
- Have no other sources in the system, other than plant wastewater and native groundwater
- Can be detected analytically at low concentrations in a high total dissolved solids TDS matrix.

Groundwater at the US Magnesium site is classified as Class IV groundwater according to UDEQ standards, with total dissolved solids (TDS) concentrations ranging from 29,000 mg/L on the west side to 300,000 mg/L at the eastern edge of the Old Waste Pond (OWP) adjacent to Great Salt Lake. The neutral to basic pH of native groundwater at the site makes use of metals problematic as they are not chemically conservative in the subsurface. During subsurface migration from the plant to downgradient locations, the metals derived from the wastewater are likely to undergo sorption, desorption, and ion exchange reactions along the migration path, potentially altering their chemical mass during transport. In addition, mineral dissolution and precipitation may also change the chemical mass in the groundwater during transport.

Another site-specific challenge is the analytical uncertainty which results from the high TDS nature of the site waters. High dilution required to successfully analyze samples increases uncertainty in analytical results of major ions and metals, resulting in greater uncertainty when comparing samples through time and thus the ability to identify potential migration of wastewater to subsurface locations. In response to these factors, US Magnesium proposes using a set of organic constituents as interim compliance parameters as described in the *Interim Compliance Monitoring Plan* (Stantec, 2018), while simultaneously carrying out a proof-of-concept/feasibility study of the practicability of using stable isotopes as compliance parameters as outlined in this plan.

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3.0 PHASED ISOTOPE STUDY

US Magnesium will perform a study to determine whether stable isotopes of hydrogen and oxygen of the water molecule may be utilized as compliance parameters. This plan describes utilization of stable isotopes as groundwater tracers, expected isotopic fractionation processes at the US Magnesium site and describes a phased study to determine whether stable isotopes are a viable groundwater tracer at the US Magnesium site.

3.1 USE OF STABLE ISOTOPES AS TRACERS

Mass differences in the stable isotopes of oxygen (^{18}O and ^{16}O) and hydrogen (^2H (Deuterium [D]) and ^1H) cause isotopic fractionation during physical processes such as evaporation and condensation, and chemical processes such as reaction of water with minerals (precipitation and dissolution). Quantification of the isotopic ratios in the water molecule ($^{18}\text{O}/^{16}\text{O}$ and D/H) can be utilized to differentiate sources of water based on changes in these ratios due to the fractionation processes.

Isotopic ratios are generally plotted relative to the 'Global Meteoric Water Line', which is based on analysis of precipitation data from around the world and represents isotopic composition of water at a given land surface location prior to isotopic fractionation processes occurring (i.e. evaporation). If a distinct isotopic signature exists between the wastewater and unimpacted (native) groundwater and surface water, the stable isotopes can be considered ideal tracers as they measure properties of the water molecules themselves and therefore are not subject to mass addition/loss during subsurface migration (although some additional fractionation may occur, as described below). Furthermore, the laboratory isotope analysis is not affected by the high TDS groundwater at the site.

3.2 EXPECTED ISOTOPIC DIFFERENCES AT US MAGNESIUM

US Magnesium's utilization of solar evaporation for creation of brine for input and subsequent disposal of wastewater (via evaporation ponds), means the isotopic signature of the wastewater in both the channels and the ponds is likely to be distinct from that of the native groundwater in the area. Evaporation causes isotopic fractionation such that the isotopic composition of wastewater is expected to be distinct (greater $^{18}\text{O}/^{16}\text{O}$ and D/H ratios) compared to the native groundwater water (lower $^{18}\text{O}/^{16}\text{O}$ and D/H ratios) which experiences significantly less evaporation. Once wastewater enters the subsurface, isotopic fractionation due to evaporation is negligible, with changes in isotopic composition of water primarily due to mixing of native groundwater and wastewater.

The primary driver of isotopic fractionation in the system is expected to be evaporation, however interaction of groundwater with the aquifer matrix (mineral dissolution and precipitation), and groundwater equilibration with carbon dioxide produced during dissolution of carbonate containing minerals, has a potential to shift the isotopic composition of groundwater. The magnitude of these interactions on isotopic fractionation at this site is not known, but as long as the wastewater and native groundwater have distinct isotopic signatures the exact processes causing fractionation are not relevant.

If the fractionation processes described above result in distinct isotopic signatures between the wastewater and native groundwater, these signatures can be utilized to determine if a groundwater location is comprised of native groundwater, Facility-derived wastewater, or some combination of the two (**Figure 2**).

Downgradient surface water expressions may also have a distinct isotopic signature, but due to evaporation once exposed to the surface, the isotopic signature of the surface water expression may shift towards the signature of the wastewater and thus not be as distinct from the wastewater as the groundwater.

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3.3 ADVANTAGES AND DISADVANTAGES OF USING ISOTOPIC SIGNATURES AS TRACERS

As with all groundwater tracers, use of isotopes have advantages and disadvantages:

Advantages:

- *Analyses Unaffected by Water Matrix.* Isotope analyses are not affected by site water matrix (high TDS, low pH).
- *Simple to Interpret.* If signatures of native groundwater and wastewater are distinct, interpretation of results will be relatively straightforward.
- *Dependable Wastewater Tracers in Groundwater.* Evaporation used to produce plant influent solution (brine), and additional evaporation that occurs after waste disposal into the ponds drives the isotopic signature of the final wastewater. Stable isotopes of water are true tracers of water and do not rely on chemicals derived from US Magnesium processing; therefore, this tracer is still valid if the chemical signature of wastewater changes (due to implementation of the filtration plant or changes in processing methods).
- *Initial Conceptual Evaluation.* Can initially determine with a reasonably small sample set whether the isotopic tracer will be an effective approach for GWDP compliance monitoring at the Facility (focus on wastewater and native groundwater).

Disadvantages:

- *Initial Study Required.* Initial study is needed to assess the potential effectiveness of using isotopes as wastewater tracers for this Facility and to establish isotopic signatures of various waters across the site.
- *Dependent on Initial Study Results.* There is potential for the isotopic signatures between plant wastewater and native groundwater to not be distinct, and thus not suitable for use as tracers. Initial isotope sampling results will indicate whether stable isotope tracers are suitable for use as Facility wastewater tracers for GWDP compliance monitoring.
- *May Not Be Dependable Wastewater Tracers in Surface Water.* Isotopic signatures for downgradient surface water expressions may not be as distinctive as downgradient groundwater signatures. (Due to evaporation that would occur once groundwater emerges above ground surface, and/or dilution with potential fresh water precipitation.)

3.4 PHASED ISOTOPE STUDY

A two-phased approach will be used to assess whether stable isotopes may be appropriate parameters for long-term compliance monitoring at the US Magnesium site. If distinct isotopic signatures of the stable isotopes exist across the different waters (wastewater, groundwater) are detected, stable isotope parameters will be considered for future compliance monitoring. A summary of potential outcomes of the proposed Isotope Study is illustrated in **Figure 3**. Details of the two primary phases of study are presented in this section.

3.4.1 Isotope Study Phase I – Proof-of-concept Sampling

In order to confirm that stable isotopes are viable Facility wastewater tracers, a limited sampling event is proposed to be conducted in summer 2018. This study will aim to determine if a subset of the proposed compliance wells (listed

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in **Table 3-1**) and plant wastewater have isotopic signatures that are distinct enough to be utilized as effective groundwater tracers. Isotope proof-of-concept sampling is proposed to be conducted at surface water and groundwater sampling locations listed in **Table 3-1** and shown in **Figure 4**. Sampling in summer, before maximum evaporation has occurred, will provide a good indication of whether isotopic signatures will be distinct throughout the year.

If the results of Phase I indicate a distinct isotopic signature between the wastewater and groundwater from the proposed sampling locations (**Table 3-1**), the study will move to Phase II described in Section 3.5. If the results of Phase I do not indicate a distinctive isotopic signature between the wastewater and proposed compliance wells, US Magnesium will schedule a meeting with DWQ to discuss alternative long-term compliance parameters.

Table 3-1: Phase I – Proof-of-concept Sampling Locations

Locations	Number of Samples
Surface Water Locations	
Great Salt Lake Source Water (at Facility Inlet)	1
Star Pond	1
Facility Main Discharge Ditch (Main Ditch)	1
Northwest CWP (NWCWP)	1
Southeast CWP (SECWP)	1
Old Waste Pond (OWP)	1
Surface water downgradient of the OWP (HBD, SVDD)	2
Groundwater Locations	
MW-22B	1
PZ-6	1
MW-10	1
MW-11	1
Total	12

3.4.2 Isotope Study Phase II – Site-wide Baseline Study

If the results of the *Isotope Study Phase I – Proof-of-concept Sampling* indicate a distinct isotopic signature between Facility wastewater and groundwater in compliance wells, a site-wide surface water and groundwater isotope baseline sampling round will be performed during late summer 2018, when evaporation at the site is expected to be greatest and the isotopic signatures of the wastewater and native groundwater are expected to be most distinct.

If the results of a late summer 2018 sampling round confirm that the isotopic signatures of the wastewater and native groundwater are distinct enough for use in compliance monitoring, a second round of samples will be collected the following spring when evaporation is limited and the isotopic signatures between wastewater and native groundwater are expected to be more similar, a theoretical “worst case scenario”. **Figure 5** and **Table 3-2** list the proposed sample locations for these two rounds.

Table 3-2: Sampling Locations for Isotope Study Phase II – Site-wide Baseline Study and 5-Year Reviews

Locations	Number of Samples
Surface Water Locations	
Facility Main Discharge Ditch (Main Ditch)	1
Northwest Current Waste Pond (NWCWP)	1

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Table 3-2: Sampling Locations for Isotope Study Phase II – Site-wide Baseline Study and 5-Year Reviews

Locations	Number of Samples
Southeast Current Waste Pond (SECWP)	1
Old Waste Pond (OWP)	1
Surface water downgradient of the OWP (HBD, SVDD)	2
Great Salt Lake Source Water (at Facility Inlet)	1
Groundwater Locations	
Upgradient Wells: PMW-1S/1D, MW-2/PZ-3, PZ-4, MW-1	6
Upgradient Wells: PZ-1, MW-20B, MW-19B, PZ-18	4
CWP/OWP Divide Wells: MW-14, MW-15B, PZ-8, PZ-11, PZ-13, PZ-16, MW-13B, MW-21, MW-22A, MW-22B, MW-23	11
Downgradient Wells: MW-9, MW-10, MW-11, MW-12, PZ-7, PZ-29, PZ-5	7
Total	35

3.5 POTENTIAL PROPOSED COMPLIANCE SAMPLING FOR ISOTOPES

If the Site-wide Baseline Study (outlined above) concludes that stable isotopes are suitable groundwater compliance parameters, the following monitoring program is proposed.

- Routine Sampling. Conduct semiannual (fall and spring) sampling of the surface water and groundwater at approved compliance monitoring locations.
- Site-wide sampling. Conduct periodic (once every 5 years) site-wide sampling to re-establish site-wide isotopic signatures (**Figure 5** and **Table 3-2**).

3.6 ISOTOPE SAMPLING METHODS

Groundwater samples will be collected utilizing low flow techniques as described in Standard Operating Procedure 7 (Stantec, 2018a), which are the same as those previously approved by USEPA for the US Magnesium RI project. Groundwater levels will be recorded prior to the start of sampling as described in SOP-7. Field parameters will be measured and recorded prior to collection of groundwater samples as described in SOP-7, and will include temperature, pH, specific conductivity, dissolved oxygen, oxygen reduction potential and turbidity. ORP will be converted to eH utilizing the electrode solution based conversion per USEPA procedures (USEPA, 2017).

Surface water sampling will be performed in accordance with SOP-8, which has previously been approved by the USEPA for US Magnesium RI work (Stantec, 2018a). Field parameters will be recorded prior to collection of surface water samples as described in SOP-8 and will include temperature, pH, specific conductivity, dissolved oxygen, oxygen reduction potential, and turbidity. ORP will be converted to eH utilizing the electrode solution based conversion per USEPA procedures (USEPA, 2017).

Sampling procedures outlined in SOP-7 and SOP-8 will be followed as they relate to isotope sampling (i.e. decontamination, chain-of-custody), however no special preservation is required for isotope samples and therefore portions of the SOPs may not be relevant. Surface water and groundwater samples collected by Stantec will be analyzed by Isotech Laboratories (Champaign, IL) utilizing laser spectroscopy methods.

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4.0 REFERENCES

- ERM, 2016. *Draft Old Waste Pond/Current Waste Pond Area Hydrologic Conceptual Site Model*, US Magnesium NPL Site, June 2016.
- Stantec, 2017. *US Magnesium Groundwater Discharge Permit Application Preparation Field Data Collection Work Plan*. May 2017.
- Stantec, 2018. *US Magnesium Groundwater Discharge Permit Application Interim Compliance Monitoring Plan*. June 2018.
- Stantec, 2018a. *Groundwater Discharge Permit Application Standard Operating Procedures for Compliance Monitoring*. June 2018.
- USEPA, 2017. *Field Measurement of Oxidation-Reduction Potential (ORP)*. U.S. Environmental Protection Agency Region 4, Science and Ecosystem Support Division, April 2017.

**CONCEPTUAL GROUNDWATER
DISCHARGE CONTROL
DESIGN SUMMARY**

 Barrier wall

Extent of northern barrier
wall to be confirmed
during detail design

Northwest Current
Waste Pond

OLD
WASTE POND

CURRENT
WASTE
POND

Southeast Current
Waste Pond

Extent of southern barrier
wall to be confirmed
during detail design



Aerial Photography 2 March 2016



USmag®

**Proposed Extent of Retrofitted
Waste Pond
Figure 1**

Figure 2: Isotope Fractionation Due to Evaporation

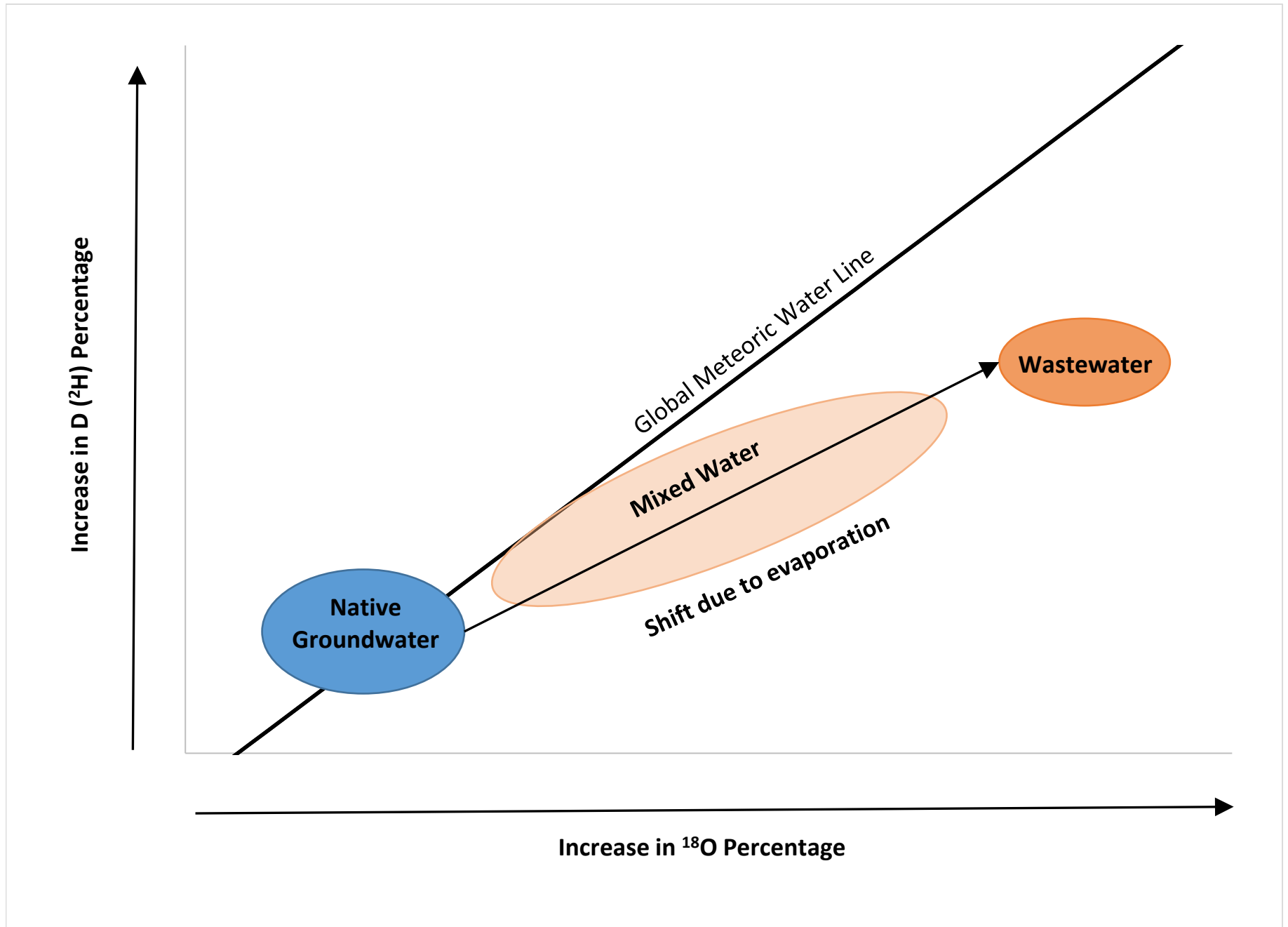
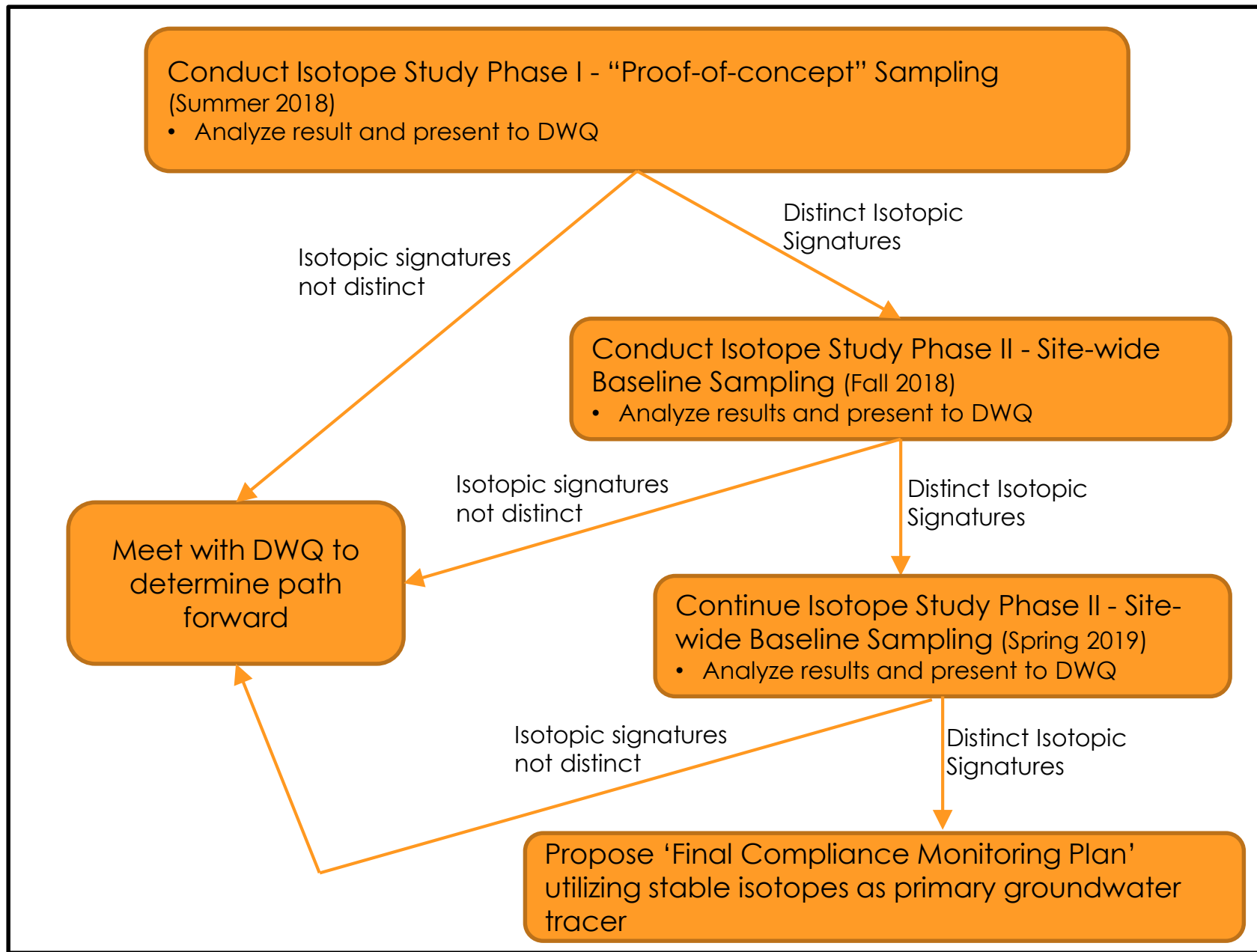
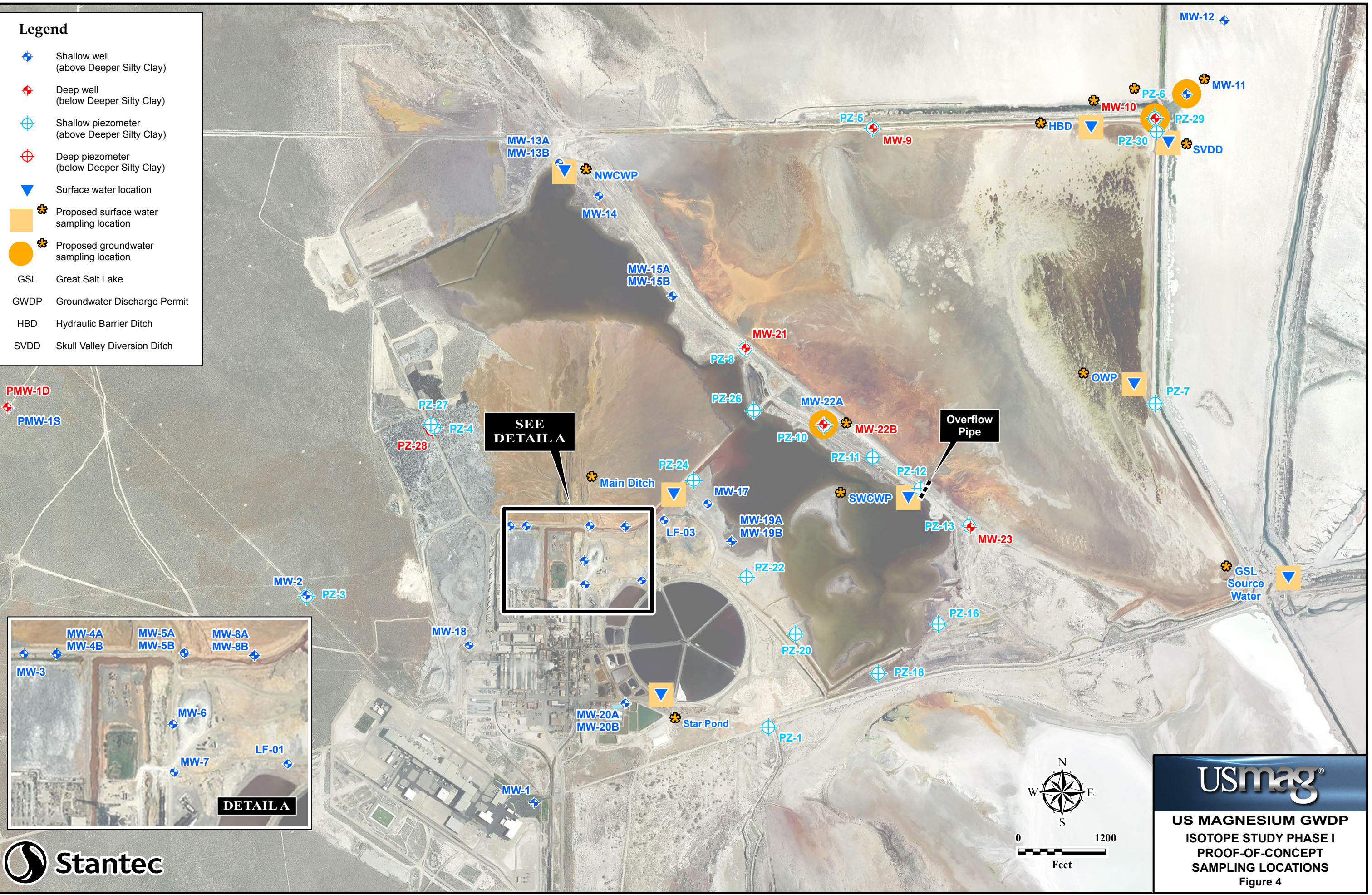


Figure 3: Potential Outcomes of Stable Isotope Study



Legend

- Shallow well (above Deeper Silty Clay)
- Deep well (below Deeper Silty Clay)
- Shallow piezometer (above Deeper Silty Clay)
- Deep piezometer (below Deeper Silty Clay)
- Surface water location
- Proposed surface water sampling location
- Proposed groundwater sampling location
- GSL Great Salt Lake
- GWDP Groundwater Discharge Permit
- HBD Hydraulic Barrier Ditch
- SVDD Skull Valley Diversion Ditch



US MAGNESIUM GWDP
ISOTOPE STUDY PHASE I
PROOF-OF-CONCEPT
SAMPLING LOCATIONS
Figure 4

