ARCADIS U.S., Inc.
2999 Oak Road
Suite 300
Walnut Creek
California 94597
Tel 925 274 1100
Fax 925 274 1103

MEMO

To:
Yvonne Meeks, PG&E

Copies:
Virginia Strohl, PG&E
Ellery Kling, PG&E
Lisa Kellogg, ARCADIS
Janis Lutrick, ARCADIS
Kelli Jo Preston, ARCADIS

From:
The ARCADIS Risk Assessment Team

Date:
January 28, 2013

ARCADIS Project No.:
RC000753.0003

Subject:
Technical Memorandum
The Potential For Chromium Uptake by Arrowweed and Potential Exposure Pathways

1. Introduction and Overview of Conclusions

The purpose of this technical memorandum is to provide the results of a literature review and preliminary exposure pathway analysis conducted for the Pacific Gas and Electric (PG&E) Topock Compressor Station (TCS), located in San Bernardino County, California, 12 miles southeast of Needles (the site) and the surrounding area of potential effect (APE). The literature review and pathway analysis were conducted at the request of the California Department of Toxic Substances Control and U.S. Department of the Interior in response to stakeholder questions.

The potential exposure pathway being addressed is the potential for hexavalent chromium [Cr(VI)] and/or trivalent chromium [Cr(III)] uptake by plants [specifically arrowweed (*Pluchea sericea*)] as a component of the human and ecological exposure assessment at the site. Two aspects of this pathway are evaluated in this technical memorandum:

- **Potential for Chromium Uptake by Arrowweed** – A literature search was conducted and relevant articles reviewed to evaluate the potential for Cr(VI) or

Cr(III) uptake from growth media by arrowweed and/or other relevant plants that may be used to evaluate potential arrowweed uptake.

- **Potential for Arrowweed Exposure to Chromium** – Soil and groundwater data, and arrowweed locations were reviewed to evaluate if arrowweed near the site is in contact with Cr(VI) and/or Cr(III) at concentrations greater than background. Chromium concentrations at or below background that are co-located with arrowweed would not indicate potential site-related exposure.

The conclusions of the literature review and pathway analysis are discussed in detail in the last section of this technical memorandum; a brief overview is provided below.

The literature search did not identify any published articles on chromium uptake specifically in arrowweed. The literature review indicates that plants can take up Cr(VI) and Cr(III) from soil, but much of the Cr(VI) is converted to Cr(III) in the plant. Typically, little Cr(VI) is present in above-ground plant structures relative to the exposure concentration in growth media.

The exposure pathway analysis indicates little overlap between elevated total chromium and Cr(VI) (relative to background) and arrowweed. Total chromium and Cr(VI) above background concentrations in soil does not extend to the area where the arrowweed community is located. However, arrowweed may also be present as an understory plant (i.e., plant between the canopy and ground surface) in salt cedar community, and low concentrations above background were detected at two locations in the salt cedar community near the mouth of Bat Cave Wash. Both of the locations are difficult for human receptors to access due to very steep slopes and/or very dense vegetation. Total chromium and Cr(VI) have not been identified at concentrations greater than background in groundwater underlying the arrowweed and salt cedar communities. Arrowweed plants occur at the mouth of East Ravine and are located where sediment sampling is planned but has not yet been conducted. Therefore, current soil and groundwater data indicate that contact with arrowweed by either human or ecological populations is unlikely to result in chromium exposure exceeding background conditions for the following reasons:

- Arrowweed was not observed near locations with detectable Cr(VI) in soil (Russell 2012). Therefore, based on soil data collected to date, the human and ecological exposure to hexavalent chromium in soil via arrowweed uptake is insignificant.

- No groundwater concentrations above background were co-located with arrowweed and salt cedar communities.

- The magnitude of the soil concentrations exceeding background was modest (within three times background).

- Human access is deterred in the area where chromium concentrations exceeding background were detected in soil.

Additional soil sampling will be conducted (as planned in the Combined Part A and B Work Plan) and the results of that investigation will help to determine whether ecological populations are exposed. The remainder of this technical memorandum is organized as follows:

- **Literature Review** – provides the objectives of the review, properties and uses of arrowweed, approach to the literature search, and key findings of the review. The detailed results of the literature review are provided in Attachment 1 to this technical memorandum.

- **Pathway Analysis** – provides the approach, results, and key findings of the pathway analysis, identifying the location of arrowweed in the APE and co-located chromium concentrations in soil and groundwater.

- **Conclusions** – provides conclusions regarding the potential for exposure to Cr(VI) and/or Cr(III) via contact with arrowweed under current site conditions based on the key findings from the literature review and exposure pathway analysis.

2. Literature Review

The literature review was conducted to understand the potential for Cr(VI) and/or Cr(III) uptake into plant tissue as a component of human and ecological exposure assessment. As specifically requested, the literature search focused on arrowweed. In addition, this technical memorandum summarizes findings for other potentially relevant plant species as well. A discussion of California Environmental Protection Agency's (CalEPA's) most recent relevant draft guidance regarding soil-to-plant Uptake Factors (UFs; Office of Environmental Health Hazard Assessment [OEHHA] 2012) in plants that could be consumed by humans is also included in preparation for the human health risk assessment for soil.

2.1 Objectives

The primary purpose of this literature review was to ascertain whether there is evidence in the literature that arrowweed, a plant found in the southwestern part of the United States, is able to absorb and translocate chromium in the form of Cr(VI) and/or Cr(III) from soils[1] into plant tissue. In order to gain a better understanding of whether chromium in soils at the site could be taken up by arrowweed or other potentially relevant plants, a search of the scientific literature was conducted with the goal of answering the following questions:

1. Are plants, including arrowweed, able to take up chromium from their growth media (e.g., soils, agar, or hydroponic solutions)?

2. For plants that exhibit evidence of chromium uptake, what species of chromium [i.e., Cr(VI) or Cr(III)] is found in the plant?

3. For plants that exhibit evidence of Cr(VI) or Cr(III) uptake from their growth media, what parts of the plant contain detectable chromium, and what is the ultimate form of the chromium in the various plant tissues following translocation?

Through the literature search, articles were identified that describe the uptake of chromium, both Cr(VI) and Cr(III), in plants, and the results are presented following this general outline:

1. The properties of arrowweed, including habitat, scientific classification, and potential application or use is provided. This information is useful for identifying other relevant species that could provide information about chromium uptake into arrowweed. Arrowweed properties and uses may also provide initial information that can be discussed with the stakeholders to identify relevant potential exposure pathways, if applicable.

2. The approach used to identify relevant studies identified during the literature search is described.

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[1] In our literature search, we did not distinguish between soils and sediment as growth media.

3. The results and conclusions regarding potential uptake of Cr(VI) and Cr(III) that can be drawn from the literature search are summarized.

2.2 Properties and Uses of Arrowweed

Arrowweed (*Pluchea sericea)* is an upright shrub-like perennial plant of the sunflower family. The plant is tall (1 to 5 meters in height) with slender leafy stems (Baldwin et al. 2012). Arrowweed is an angiosperm (flowering plant), with a two-part seed (dicot). More specifically, it is classified as an asterales, which also includes other desert plants. *Pluchea*, also known as camphorweed, refers to the genus of arrowweed. The scientific classification of arrowweed is as follows:

Kingdom: Plantae – Plants
Subkingdom: Tracheobionta – Vascular plants
Superdivision: Spermatophyta – Seed plants
Division: Magnoliophyta – Angiosperms, or flowering plants
Class: Magnoliopsida – Dicots
Subclass: Asteridae – Asterid
Order: Asterales
Family: Asteraceae – Aster family
Genus: *Pluchea* – Camphorweed
Species: *Pluchea sericea* – Arrowweed

Arrowweed is commonly found in the southwestern United States desert and frequently grows between willows and mesquites along river channels (Uno 1999). The plant is a common component of streamside communities and often forms dense thickets along streams, in washes and canyons, and around springs (Uno 1999). Arrowweed is a salt-tolerant plant and typically grows in areas with low to moderate soil salinity; the soil pH requirements for arrowweed cultivation ranges from 7 to 9 (Wilson 2012). The roots of arrowweed are found most frequently in soil samples taken at depths up to about 3 feet (ft) below ground surface (bgs) (Hely and Peck 1964), but are reported to extend to up to 20 ft bgs (Alth et al. 1991).

Parts of arrowweed have been used medicinally by Native Americans. Among many medicinal treatments, the leaves may be chewed as a throat aid, the decoction of roots for antidiarrheal aid, the raw root may be chewed for gastrointestinal aid, and the roots have also been used as a wash for dermatological aid and eye medicine (UMD 2003). Other traditional uses of arrowweed include using the shaft as building material (e.g., roofing, thatching, and fences); for storage bins, animal cages, and baskets; for

cradleboard beds; and for arrow making (UMD 2003). Additionally, roots may be roasted and eaten, and the leaves or the stem tips may be brewed as a tea (UMD 2003). Arrowweed is also browsed by deer and sometimes by livestock (UMD 2003).

2.3 Approach to Literature Search

The approach to the literature search is described below, including the methods for identifying relevant articles (e.g., database searched and keywords used) and compilation of the search results.

2.3.1 Identifying Relevant Articles

The first step in the literature search was to identify studies that focused on understanding the potential for total chromium and/or Cr(VI) in soil and other media to be taken up into plants. To this end, an inventory of peer-reviewed studies was assembled. The resulting inventory contains studies published between the years of 1964 and 2012.

From April 23 through May 15, 2012, the following sources were searched to identify potentially pertinent studies:

- National Library of Medicine's PubMed
- World Health Organization's AGRIS (Agricultural Sciences and Technology)
- Wiley Interscience, an online service with access to more than 3 million articles across nearly 1,500 journals and 7,000 online books and major reference works
- ScienceDirect, an online service with access to over 10 million articles across more than 2,500 journals and 11,000 books
- American Chemical Society (ACS) Publications, with access to more than 35 journals
- Google Scholar

The searches were conducted using combinations of five groups of keywords:

- **Chemical name** [i.e., hexavalent chromium, trivalent chromium, Cr(VI), Cr(III), chromium, and heavy metals]

- **Plant species** (i.e., arrowweed, plant, and *Pluchea* [same genus as arrowweed])

- **Environmental medium** (i.e., soil, groundwater, and contaminated)

- **Route of uptake** (i.e., uptake, transpiration, kinetics, fate, transport, distribution, reduction, phytoremediation, accumulation, and translocation)

- **Method analysis** (i.e., x-ray, atomic spectroscopy, x-ray absorption spectroscopy, XAS, atomic absorption, and AAS)

The search string was refined during routine database searches. Bibliographies of relevant reviews and reports were also searched to identify additional studies and references.

2.3.2 Data Compilation and Management

The results of these searches, more than 2,800 articles, were reviewed to remove duplicates and articles not pertinent to the primary study objectives. Articles from the database were removed if they did not have an abstract, and aside from reviews, articles were removed if they did not report original research results (e.g., editorials and commentaries). The results of the searches were combined into EndNote™ (version X4; Thomson Reuters, Carlsbad, CA), a reference database management software program. In addition, articles in the following categories were removed as they were deemed not of primary relevance:

- Articles on bioremediation strategies using non-plant species (e.g., bacteria, yeast, animals, or animal waste)

- Articles solely focused on methods of detecting chromium and/or speciation of chromium

- Studies that used growth media other than soils, agar, or hydroponic solutions (e.g., effluent waste and activated sludge)

- Articles from journals not related to plants (e.g., Journal of Bacteriology)

- Articles that studied binding mechanisms of chromium to plants, but did not study actual uptake of chromium into plants.

Removal of duplicate and non-relevant articles yielded approximately 300 articles. Of these articles, abstracts were reviewed and categorized into Tiers I, II, and III, in order of obvious relevancy, with Tier I being the most informative in terms of answering the question of chromium uptake, translocation, and ultimate concentration in plant tissue. The initial categorization (see results discussion below) yielded approximately 65 Tier I articles, 15 Tier II articles, and 60 Tier III articles; the remainder were classified as non-informative. The full texts of the Tier I articles were then obtained and reviewed. Following the review of Tier I articles, Tier II and Tier III articles were reviewed for additional relevant information to help answer the primary question regarding uptake of hexavalent chromium into plant tissue. If articles in Tier II or Tier III provided relevant information in terms of chromium uptake and/or speciation in plants, they were considered Tier I and summarized in the Tech Memo, Table 1 summarizes the key Tier I articles identified during the literature search. Although a full critique of each article was not conducted for the purposes of this technical memorandum, a few caveats and comments regarding study methodologies and conclusions are presented in the last column of Table 1, to aid in interpretation of results.

2.4 Key Findings from the Literature Review

The literature search did not identify any published articles on chromium uptake specifically in arrowweed. However, some of the Tier I studies were based on plants scientifically classified in the same subgroups or live in similar habitats as arrowweed, as identified in Table 2. Mesquites, tumbleweed, creosote bush, and Mexican palo verde are all desert plants (Aldrich et al. 2003; Arteaga et al. 2000; Buendía-González et al. 2010; Gardea-Torresdey et al. 2005; Zhao et al. 2009, 2011); mesquites and creosote bush are also found in some areas of the Topock site. Therefore, it is reasonable to conclude that findings from the literature search are potentially applicable to site-specific plants.

Some Tier I studies indicate concerns with the reliability and precision of the analytical methods available to measure Cr(VI) and Cr(III) in plant tissue. As indicated by OEHHA, there are methodological challenges associated with estimating the actual speciation of chromium in biological tissues during analysis (OEHHA 2012). It has been suggested that chemical extractions may induce alterations on speciation results in samples (Lytle et al. 1998). For example, Gheju et al. (2009) used a strong acid solution to extract Cr(VI) from plant tissues. Some authors have noted that a strong

acid digestion could potentially alter the oxidation state of the chromium being measured (Espinoza-Quinones et al. 2009). It should be noted that due to the limitations of the types and number of studies measuring Cr(VI) in plant tissue, OEHHA, in its draft Hot Spots guidance, recommends that until the form of chromium found in edible plant portions of crops is able to be determined, the health protective assumption is that the (total) chromium found in crops due to root uptake is in the form of Cr(VI) (OEHHA 2012).

In general, the literature supports that plants have the ability to absorb both Cr(VI) and Cr(III) from soil, solution, and agar. The extent of this absorption varies due to many factors, some of which are described in more detail in the paragraphs of this section discussing study methodology and variations in findings. In summary, studies varied in their conclusions on what form of chromium is more likely to be taken up in plant roots, and the absolute quantity of Cr(VI) that is reduced to Cr(III) in plant tissue.

With a few exceptions, most notably the study by Sampanpanish et al. (2006) using *Pluchea Indica*, the Tier I studies support the finding that once absorbed by root tissues, it appears that most of the Cr(VI) is reduced to Cr(III) and retained by the roots in a tightly bound or insoluble form or in a soluble complex that is not translocated to a large degree to the above-ground plant parts (OEHHA 2012). Once Cr(VI) and Cr(III) are actually inside the plant, it is reported that Cr(VI) is more mobile while Cr(III) likely interacts with surrounding plant cells and components (Skeffington et al. 1976). A portion of absorbed chromium in the form of Cr(III) and/or Cr(VI) may migrate throughout the stem and leaves of the plant, interacting with plant biochemical species along the way, some of which may facilitate further reduction, oxidation, solubility, movement across cell membranes, or precipitation of chromium species. Buendía-González et al. (2010) concluded there was significant translocation of total chromium from roots to aerial parts, and Gardea-Torresdey et al. (2005) measured higher translocation of total chromium when Cr(VI) was supplied to plant in agar compared to Cr(III) supplied in agar. Zhao et al. (2009) also measured Cr(VI) and concluded complete reduction of Cr(VI) in all plant tissues. In a soil experiment, Zhao et al. (2011) showed that chromium supplied in either form increased translocation of total chromium over time into the stems of Mexican palo verde plants.

The study on chromium uptake in Indian camphorweed (*Pluchea indica*), which may be a useful comparison to arrowweed as they share the same genus, detected Cr(VI) in leaves after 30 and 60 days; however, Cr(VI) concentrations fell below the detection limit due to dilution by plant growth and, therefore, Cr(VI) was not detected in stems or

leaves at 90 or 120 days (Sampanpanish et al. 2006). A few of the caveats related to this study's design are described on the following page, as well as in Table 1.

The growth medium (i.e., soil, solution, or agar) for the study has an important impact on potential plant uptake of Cr(VI) and Cr(III), soil being the least facilitative for uptake. Variation in transport and accumulation of chromium in plants may depend on the chemical complexes that may form in the soil prior to being absorbed, as well as those formed inside the plant after absorption (Đogo et al. 2011; Gardea-Torresdey et al. 2005; Shanker et al. 2005). Differences in uptake and translocation may be explained by pH or oxidation-reduction reactions occurring in soil, along with organic matter and other ionic elements interacting with one another in the soil (Gardea-Torresdey et al. 2005; McGrath 1982). Aldrich et al. (2003) directly measured Cr(VI) and found partial reduction of Cr(VI) in roots and stems of plants grown in solution, but the Cr(VI) was fully reduced in the leaves, as well as in all plant tissues grown in agar medium. Additionally, it is important to note that hydroponic media used in some studies may not be a realistic representation of field conditions, because more soluble chromium is present in this media as opposed to in soil, where chromium may be adsorbed, complexed, reduced, or precipitated and, therefore, less available (Zayed and Terry 2003).

Studies reviewed from the literature search demonstrated variability in results based on plant types, plant age, cultivation times, extraction methods, sample preparation, growth media, pH conditions, concentration of chromium sources, oxidation conditions, presence of other chemical species in growth medium, and the extrapolation of laboratory experiments to natural habitats. Some of these issues have been described above. Due to these complexities, it is difficult to draw a simple conclusion regarding Cr(VI) and/or Cr(III) into arrowweed based on the literature available. Notable issues regarding study methodologies and issues impacting the variability in findings are summarized below to provide some additional perspective on the conclusions drawn from this evaluation.

In general, several studies failed to mention the presence of a plant control or method limit of detection; therefore, the results from these studies may not accurately represent actual concentrations of chromium in the plant.It was noted above that the one study identified using *Pluchea indica*, or Indian Camphorweed (Sampanpanish et al. 2006) could be useful in interpreting results for arrowweed since this is the most closely related plant studied. However, there are issues with study methododologies and conditions that bring into question the relevance of this study for the Topock site. At the end of the Sampanpanish study, the resulting pH of the soils was fairly acidic.

Specifically, the starting pH of the soil was 5.2, while the pH in the soil at the end of the study was 3.8. Typical soil pH conditions at Topock range from 7.48 to 10.49 (CH2M Hill 2011). Given the sensitivity of chromium speciation to pH conditions, it is questionable how relevant the results of this study are to the soil conditions at the Topock site. This is an important distinction because this study is one of the minority that did show uptake for and the ultimate presence of Cr(VI) in leaves. Additionally, some researchers have documented challenges associated with the method for alkaline extraction of Cr(VI) used by Sampanpanish et al. (2006) from biological matrices, due to interactions between metals or anions with organic components (Buckley et al. 2009). Further, as described in Table 1, a limit of detection for Cr(VI) was not reported in this study by Sampanpanish et al. (2006),

It is also important to note that the experimental conditions in this study exposed plants to high concentrations of chromium. Sampanpanish et al. (2006) supplied plants with 100 parts per million of Cr(VI), which is above the tolerance level for some species of plants. Therefore, uptake of chromium in plants at high initial concentrations may result in different accumulation and translocation patterns when compared to Cr(VI) at lower initial concentrations more typical of Topock soil and groundwater conditions in the areas where arrowweed is found.

Cr(VI) was also detected in the leaves of crops near a tannery by Elci et al. (2010). Tomato and fig leaves collected near the tannery contained 14% and 48% of total chromium as Cr(VI), respectively, while corn leaves and cotton leaves collected far from the tannery contained around 12% of total chromium as Cr(VI), respectively. However, during sample preparation, the leaves of the plants were not rinsed as was done in many other studies to eliminate debris or contamination from surface deposition. Therefore, while it is plausible that plants near tanneries contain elevated concentrations of Cr(VI), these concentrations may not accurately reflect concentrations of chromium accumulated specifically by absorption through roots.

The amount of time a plant is exposed or grown in soil or other media containing chromium may also affect the quantity of chromium accumulated by plant tissues. For example, Zhao et al. (2011) demonstrated that translocation of total chromium into stems of the plant increased with time. In contrast, Sampanpanish et al. (2006) observed a decreasing trend of total chromium and Cr(VI) concentrations in plants over time.

Plant age was also shown to play a role in the uptake of chromium. Choo et al. (2006) reported higher uptake of Cr(VI) in nine week old plants, followed by six and three week

old plants. Choo et al. (2006) also studied the effects of uptake when chromium was supplied alone in the growth media or in the presence of other metals. As a result, the presence of copper [Cu(II)] with Cr(VI) in solution resulted in decreased uptake and accumulation of Cr(VI). This presents an additional issue in generalizing results, because of the differences in solutions provided to plants.

3. Exposure Pathway Analysis – Location of Arrowweed and Chromium Concentrations in Soil and Groundwater

To assist in the evaluation of the potential for a complete human or ecological (upper trophic level) exposure pathway to chromium in arrowweed tissue, historical soil and groundwater results and the occurrence of arrowweed in the APE were reviewed. Additional soil sampling will be conducted (as planned in the Combined Part A and B Work Plan) and the results of that investigation will be used to determine whether ecological populations are exposed.

A geographic information system was used to evaluate the co-location of arrowweed and chromium in soil and groundwater. The purpose of the effort was to identify potentially complete exposure of arrowweed to chromium concentrations greater than background in either soil or groundwater, and to assess the significance of this potential exposure pathway to human and ecological receptors.

3.1 Approach to Exposure Pathway Analysis

The potential exposure area (i.e., the location of arrowweed) in the APE was identified using the Programmatic Biological Assessment (PBA) completed "to determine any potential effect on species protected under the federal Endangered Species Act (ESA) resulting from past, present, or planned remedial and investigative activities" (CH2M Hill 2007). The PBA provides data on the location of plant communities within the APE (i.e., the area surrounding the TCS that may be affected by investigation or remediation). The location of plant communities with arrowweed listed as a dominant or understory plant were selected to identify the potential exposure area.

The potential exposure depth for arrowweed was then identified to assess the likely vertical limit of exposure. The depth of arrowweed roots (up to 20 ft bgs) was previously identified in the approved *Human and Ecological Risk Assessment of Groundwater Impacted by Activities as Solid Waste Management Unit (SWMU) 1/Area of Concern (AOC) 1 and SWMU 2* (ARCADIS 2009). This depth was applied to identify representative soil and groundwater samples.

Soil samples collected in the exposure area were identified and total chromium and Cr(VI) data from the exposure area were summarized. Well locations within the area where arrowweed may occur were identified, and the screened interval of the wells was reviewed. Wells completed in the shallow zone, alluvial aquifer with screened intervals less than 20 ft bgs were identified, and recent total chromium and Cr(VI) data from these wells were summarized. Only recent groundwater data (from May 2011 to May 2012) were reviewed.

Chromium data from soil and groundwater within the exposure area were then compared with corresponding background values. Background values were obtained from the *Soil RCRA Facility Investigation/Remedial Investigation Work Plan* (CH2M Hill 2011) for soil and from the *Revised Final RCRA Facility Investigation/Remedial Investigation Report Volume 2. Hydrogeologic Characterization and Results of Groundwater and Surface Water Investigation* (CH2M Hill 2009a) for groundwater. Concentrations exceeding background were identified and the potential exposure pathway was discussed.

3.2 Results of Exposure Pathway Analysis

In the PBA, CH2M Hill reports two plant communities that include arrowweed: arrowweed and salt cedar communities (CH2M Hill 2007). Arrowweed community is located along the river, and is not located within the boundaries of site SWMUs or AOCs. Arrowweed is also reported to be present as understory in the dense monotypic stands of salt cedar (CH2M Hill 2007) that occur at the mouth of Bat Cave Wash and along the river east of National Trails Highway. During a recent reconnaissance of the occurrence of arrowweed near the mouth of Bat Cave Wash, no arrowweed was observed as understory in the tamarisk thicket southwest of National Trails Highway (Russell 2012). Figures 1 and 2 show the location of soil samples collected to date to characterize chromium concentrations as well as the occurrence of arrowweed and salt cedar communities in the APE, and the location of AOCs.

As shown on Figures 1 and 2, soil samples collected to investigate AOCs in the APE did not extend into the arrowweed community. The AOCs are not co-located with the arrowweed community. Further, additional proposed soil sampling locations identified during the data gaps evaluation, and also depicted on Figures 1 and 2, do not overlap with the arrowweed community because no source of site-related contamination has been identified or is expected in the arrowweed community. Arrowweed does occur in small stands outside the identified arrowweed community shown on Figures 1 through 4. This is confirmed by data that are now available from more current plant surveys

conducted in support of the Environmental Impact Report (EIR) (AECOM, 2011) mitigation measures (floristic survey report in preparation), as well as incidental observations of arrowweed near proposed sediment sampling location(s)[2]. Although no soil data gaps were identified in the arrowweed community, sediment data gaps were identified where arrowweed occurs in small stands but is not a dominant species (Russell, 2012). Data collected during the forthcoming soil/sediment investigation will be reviewed to evaluate the potential for a complete and significant exposure pathway via arrowweed tissue. Data gaps are discussed in Appendix C Part A of the *Soil RCRA Facility Investigation/Remedial Investigation Work Plan* (CH2M Hill 2011).

Soil samples were collected in several locations in or adjacent to salt cedar community where arrowweed may occur as understory (Figures 1 and 2). Both total chromium and Cr(VI) exceeded background in one sample at one location, AOC1-BCW6, and Cr(VI) exceeded background in one sample from a second location, AOC1-BCW4 (Figure 1). Total chromium at AOC1-BCW6 (71 milligrams per kilogram [mg/kg]) was less than twice the background value (39.8 mg/kg). Cr(VI) at AOC1-BCW6 (2.63 mg/kg) was slightly greater than three times the soil background value (0.83 mg/kg) at AOC1-BCW6, and less than twice background at AOC1-BCW4 (1.3 mg/kg). Access near AOC1-BCW6 is deterred by the density of the salt cedar and steep slopes bounding the wash. The concentration of Cr(VI) at AOC1-BCW4 is lower than at AOC1-BCW6, and the area is somewhat more accessible, though still in dense vegetation. Sampling at the remaining locations in the salt cedar community did not identify total or Cr(VI) in excess of background conditions. Current human exposure to arrowweed that may be present near AOC1-BCW4 and AOC1-BCW6 is not expected, given the very few and modest detections greater than background and that arrowweed was not observed in these areas during a recent reconnaissance (Russell 2012).

Based on data collected to date and the detailed data gaps evaluation conducted with the agencies and stakeholders, no significant current exposure pathway has been

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[2] More current vegetation maps (than those presented herein) based on data from recent vegetation surveys in the project area are in preparation. Figures in the RAWP Addendum 2 will provide more current and precise information about the distribution of arrowweed communities (arrowweed thickets and salt cedar/arrowweed thickets) in the project area. The more current vegetation survey data do not change the conclusions regarding the overlap between arrowweed communities and soil and groundwater data reviewed for this memorandum.

identified for human exposure to site-related chromium in arrowweed. This conclusion will be validated through additional soil sampling already planned in the salt cedar community at the north end of Bat Cave Wash (CH2M Hill 2011). Plant identification could be performed concurrent with the soil sampling to identify the extent of arrowweed and further refine the exposure assessment. While the pathway is currently judged to be insignificant in part due to limited accessibility, it should be noted that access to the area will be temporarily improved to allow soil sampling. The co-occurrence of chromium concentrations in groundwater with the root zone of arrowweed was also reviewed. The greatest density of arrowweed roots are typically found in the top 3 ft of soil (Hely and Peck 1964), although arrowweed roots may extend to 20 ft bgs (Alth et.al. 1991).

Wells with screened intervals within 20 ft bgs (shallow zone, alluvial aquifer) were identified based on well construction data provided in Appendix A3 of the RFI Volume 2 (CH2M Hill 2009b) and locations are depicted on Figures 3 and 4. Using this 20-ft depth criterion, wells constructed within or adjacent to arrowweed were identified and associated chromium data are provided on Figures 3 and 4. Total chromium and Cr(VI) were detected in wells screened within 20 ft of ground surface only in the East Ravine. Total chromium was detected in nine of the wells (meeting the depth criterion) that were sampled between May 2011 and May 2012, while Cr(VI) was detected in five of the wells. Both Cr(VI) and total chromium detections were very low (i.e., close to the detection limit that was typically 1 microgram per liter [µg/L]). Recent (May 2011 to May 2012) chromium data was compared with background concentrations for wells within the exposure area for arrowweed. Background concentrations were site Upper Tolerance Limits of the mean (UTLs) for total chromium (34.1 µg/L) and Cr(VI) (32 µg/L). Chromium was not detected at concentrations greater than background in recent groundwater samples from wells with screened intervals within 20 ft bgs *and* within or adjacent to arrowweed at the site (see Figures 3 and 4). Therefore, chromium concentrations available for uptake by arrowweed are considered insignificant.

3.3 Key Findings from the Exposure Pathway Analysis

Soil samples collected to investigate AOCs in the APE did not extend into the arrowweed community, but did extend into the salt cedar community where arrowweed may be present in the understory. Total chromium was detected at concentrations greater than background in one soil sample co-located with arrowweed in an area where access is deterred by steep slopes and dense salt cedar. Cr(VI) was detected at concentrations greater than background at the same location, and one additional location also in dense salt cedar. During a recent site reconnaissance, arrowweed was not observed in the areas where hexavalent chromium was detected in soil, but small

stands of arrowweed plants were observed at the mouth of East Ravine where sediment sampling is planned (Russell 2012). Groundwater wells were identified within the arrowweed exposure area. Chromium was not detected in recent groundwater samples (May 2011 to May 2012) from these wells at concentrations greater than background when compared with the site UTLs for total chromium and Cr(VI).

Based on review of current soil and groundwater data, and the detailed soil data gaps evaluation conducted with the agencies and stakeholders, no significant current exposure pathway has been identified for human exposure to site-related chromium in arrowweed. Additional soil data collection already planned in the salt cedar at the mouth of Bat Cave Wash and at the mouth of East Ravine will be done to validate this conclusion.

4. Summary of Conclusions

Based on the key findings presented above for the literature review and exposure pathway analysis, the conclusions regarding the potential for exposure to Cr(VI) and/or Cr(III) via contact with arrowweed under current site conditions are as follows:

- Although studies indicate that plants can absorb Cr(VI) and Cr(III) from soil, the extent of total chromium and Cr(VI) above background concentrations in site soil does not extend to the area where arrowweed community is located. In salt cedar community in Bat Cave Wash, total chromium and Cr(VI) was detected at one location at a concentration greater than background, and Cr(VI) was detected at a second distant location at a concentration greater than background. Both locations are difficult to access due to rugged terrain and/or very dense vegetation. Further, arrowweed was not observed in these areas during a recent site reconnaissance (Russell 2012). The potential exposure pathway to groundwater in AOC 11 and the mouth of the East Ravine remains to be evaluated and will be considered in the future.

- Total chromium and Cr(VI) have not been identified at concentrations greater than background in groundwater underlying the arrowweed and salt cedar communities.

- Current site data indicates that contact with arrowweed by either human or ecological populations is unlikely to result in exposure exceeding background conditions.

- Existing soil sampling data adequately define background conditions adjacent to the location of arrowweed community; therefore, additional soil sampling for Cr(VI) or Cr(III) is not needed to refine this potential exposure pathway.

- Soil sampling already proposed in the salt cedar community in Bat Cave Wash, and plant identification will validate the exposure pathway for chromium uptake by arrowweed in the understory.

- Based on the above, exposure to chromium in arrowweed does not represent a significant pathway under current conditions. However, based on the literature review, there is the potential for plant uptake of chromium. Consistent with the approved *Human Health and Ecological Risk Assessment Work Plan* (ARCADIS 2008) and subsequent discussions with the agencies and stakeholders, we will work with the stakeholders to identify appropriate modeling methods and relevant species to estimate current and future potential exposures using current and new information from pending soil sampling and porewater/sediment sampling.

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Tables

Figures

Attachments

Tables

Table 1: Summary of Articles Included in Technical Memorandum for Hexavalent Chromium Uptake in Plants

Author	Journal	Title	Year	Growth Medium (soil, solution, etc.)	Plant type(s)	Study Objective	Analytical Method and Sample Prep	Total Cr tested for?	Cr(VI) tested for?	Cr(VI) detected in plant?	Conclusions (as cited in literature)	Comments, critiques and caveats in study methodologies and conclusions
Aldrich et al.	Environ Sci Technol	Uptake and reduction of Cr(VI) to Cr(III) by mesquite (*Prosopis* spp.): chromate-plant interaction in hydroponics and solid media studied using XAS	2003	agar & hydroponics; added K2CrO7 to both agar and hydroponic	*Prosopis spp.* [mesquite]	To investigate the possibility that mesquite can remove Cr from the environment via active transport systems to the aerial portions of the plant.	XAS was used to determine the uptake and binding of Cr(VI) in live mesquite tissue	not studied	Yes	Yes in hydroponics; No in agar	The XAS results for both the hydroponic and the agar study showed some of the supplied Cr(VI) was uptaken by the mesquite roots. The data analyses of the plant tissues grown in agar demonstrated that it was FULLY reduced to Cr(III) in the roots, stems and leafs. in contrast, the plants grown in hydroponics showed a small percent of hexavalent chromium in the roots (1.2%) and stems (6.2%), but no CrVI in the leaves.	Mesquite is an indigenous desert plant; No CrVI detected in plant tissues in agar. No controls presented for speciation work, no information on instrument sensitivity. High concentrations (80ppm) may cause some Cr(VI) to be transported thru plant and also exceed biological capacity of plant's ability to reduce Cr(VI) to Cr(III).
Arias et al.	Environ Sci Technol	Plant Growth and Metal Distribution in Tissues of *Prosopis juliflora-velutina* grown on chromium contaminated soil in presence of *Glomus deserticola*	2010	Uncontaminated soil from El Paso; CrIII and CrVI soil added w/ seed	*Prosopis juliflora-velutina* seeds [mesquite]	Determine presence of Cr in mesquite; total amylase activity recorded as an indicator of stress.	ICP-OES	Yes	No	N/A	Inoculated Cr(VI) treated plants had 21% and 30% more Cr than uninoculated and EDTA treated roots, respectively, at 80 mg Cr kg 1 treatment. In the case of Cr(III), EDTA produced the highest Cr accumulation in roots. TAA was higher in inoculated plants grown with Cr(III) at 80 and 160 mg kg-1 and Cr(VI) at 40 and 160 mg kg-1.	Study examines uptake of CrVI, but measures only total Cr in plant tissue (i.e., no speciation to determine the form of chromium in the plant tissue).
Arteaga et al.	Hazardous Waste Research	Spectroscopic Confirmation of Chromium Uptake by Creosote Bush (*Larrea tridentata*) Using Hydroponics	2000	hydroponic; supplied with Cr(VI) only	*Larrea tridentata* [Creosote Bush]	To gain a better understanding of the processes through which creosote bush accumulates Cr(VI) and Cr(III) ions, and ascertain the functional chemical groups responsible for Cr binding.	Plants separated into roots, stems, leaves; digested using EPA 200.3; then Total Cr analyzed by FAAS; Cr speciation also in plant by XAS	Yes	Yes	Yes	Results indicate the roots absorbed Cr(VI) from solution, but was partially reduced to Cr(III)(that is, some of the Cr in the roots remained as CrVI). Some Cr(VI) and the reduced Cr(III) were transported through the stems (and thus there was some CrVI in the stems), and finally accumulated as Cr(III) in the leaves of the plant.	Note that only Cr(VI) was supplied; but authors measured both Cr(VI) and Cr(III) in plant tissue. This study demonstrates that high concentrations (520ppm) may exceed plant's biological capacity to reduce Cr(VI) to Cr(III). Time of exposure to Cr(VI) may also be a potential factor in how much is reduced (if experiment continued past 48 hours, would plant contain Cr(VI) in roots?). No information on instrument sensitivity; oven drying/rinsing of plant may contribute to changes in Cr oxidiation.
Banerjee et al.	Environ Pollut	Uptake studies of environmentally hazardous 51Cr in Mung beans	2008	Sand; added nutrient solution containing K2 ^{51}Cr207 and ^{51}CrNO3	*V. radiata* [mung bean]	To study the accumulation behavior of a common plant, Mung bean (*Vigna radiata*) towards Cr(III) and Cr(VI) to have an insight on the migration and bio-magnification of Cr.	The amount of 51Cr(VI) and 51Cr(III) accumulated by 10 days old seedlings was determined by gamma spectroscopic techniques.	Yes	No	N/A	The transfer of Cr(VI) from sand to plant is of the order of only about 5% (4.5-7.5 mg) and transfer does not depend on the presence or absence of phosphate ion. The accumulation of 51Cr(VI) in the Mung bean seedlings has been found mainly in the root. Cr(VI) migration as total chromium is higher than that of Cr(III).	Study examines uptake of CrVI, but measures only total Cr in plant tissue (i.e., no speciation to determine the form of chromium in the plant tissue).
Bonfranceschi et al.	J Hazard Mater	Study of the heavy metal phytoextraction capacity of two forage species growing in an hydroponic environment	2009	hydroponic + CrVI	*Sorghum bicolor* [Sorghum] and *Medicago sativa* [alfalfa]	To evaluate the metal extraction capacity of sorghum and alfalfa growing in hydroponic conditions, focusing the case of Cd (II), Ni(II), Cr(VI), and Cr(III), made partially soluble by complexing (simulating what occurs in nature) with EDTA.	Metal contents in plant tissues was determined after by acidic digestion with HNO3 (c)/H2SO4 (c). The measurement of the metal content in the extracts was accomplished through AAS.	Yes	No	N/A	In alfalfa, the increases in the concentration of Cr(VI), Cd(II) and Cr(III)/EDTA, favored the translocation of total chromium to the aerial parts of the plants. In sorghum, Cr(VI) increases in the metal solution concentration lead to higher translocation of this metal.	Study measures uptake of CrVI, but measures total Cr in plant tissue.
Buendia-Gonzales et al.	Bioresource Technol	*Prosopis laevigata* a potential chromium (VI) and cadmium (II) hyperaccumulator desert plant	2010	solution + CrVI	*Prosopis laevigata* [smooth mesquite]	The aim of this work was to investigate the in vitro ability of P. laevigata (mesquite), a widely distributed species in the semi-arid and arid regions in Mexico, to remove two different heavy metals in different concentrations from the culture media, and to assess the effect of these metals uptake on the growth, morphology and survival of the plant.	The metals concentration was analyzed from those samples using an Atomic Absorption Spectrometer	Yes	No	N/A	Heavy metals did not stop germination, but smaller plants with fewer leaves and secondary roots were produced. Seedlings showed an accumulation of 8176 and 21,437 mg/kg Cd and of 5461 and 8090 mg Cr/kg dry weight, in shoot and root, when cultured with 0.65 mM Cd(II) and 3.4 mM Cr(VI), respectively. These results indicated that significant translocation from the roots unto aerial parts took place. A bioaccumulation factor greater than 100 for Cd and 24 for Cr was exhibited by the seedlings.	Study examines uptake of CrVI, but measures only total Cr in plant tissue (i.e., no speciation to determine the form of chromium in the plant tissue).
Cary et al.	J Agricultural and Food Chem	Control of Cr concentrations in food plants. I. Absorption and translocation of Cr by plants.	1977	Solution: added CrVI and CrIII; Soil: added K2CrO7	Wheat (*Triticum aestivum*), corn (*Zea mays*), potato (*Solanum tuberosum*), tomato (*Lycopersicon esculentum*), pea (*Pisum sativum*), red kidney bean (*Phaseolus vulgaris*), Barley (Hordeum uulgare), beet (Beta vulgaris), buckwheat (Fagopyrum esculentum), rutabaga (Brassica napus), snap beans (Phaseolus spp.), spinach (Spinacia oleracea), and Swiss chard (Beta cicla)	The primary objective was to provide a basis for designing crop production practices that might increase the Cr concentration in food and feed crops.	Used ^{51}Cr and gamma ray spectrometry	Yes	No	N/A	There was very little translocation of any 51Cr from the roots to the tops in any species treated with the nutrient solution; CrEDTA was apparently readily translocated from the roots to the tops, but the roots removed very little Cr from the nutrient solution. For the soil experiment, CrVI only was added the soil and levels of chromium were measured in the leaves and stems of a variety of plants (e.g., spinach, Swiss chard, rutabaga, buckwheat) after between 70 and 100 days after seeding. chromium was detected in leaves and stems of plants.; SOIL: Total CR was measured in all plants; leafy vegetables appear most effective at translocating Cr to aerial parts (spinach, turnip leaves), very low transport into seeds.	Document cited in 2012 Hot Spots Draft plant uptake factor derivation for Cr. The leafy UF of 0.3 was based on this study based on a sample size of 3. Hot Spots document took the leafy UF of 0.3 and multiplied it by a factor of 10 to give us the root UF of 3.

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Choo et al.	Chemosphere	Accumulation of chromium (VI) from aqueous solutions using water lilies (*Nymphaea spontanea*)	2006	aqueous solution + potassium dichromate (CrVI)	*Nymphaea spontanea* [tropical water lilies]	Investigate the effectiveness of using water lilies to remove Cr(VI) from aqueous solutions and electroplating waste and assess the effect of Cr(VI) on some of the plant biochemical processes	Samples were digested in a mixture of HNO3 and HClO4 in the ratio of 4:1 to determine metal contents (Pickford's wet ashing method)	Yes	No	N/A	Water lilies are capable of accumulating substantial amount of Cr(VI), up to 2.119 mg g 1 from a 10 mg l 1 solution. The roots of the plant accumulated the highest amount of Cr(VI) followed by leaves and petioles, indicating that roots play an important role in the bioremediation process. The maturity of the plant exerts a great effect on the removal and accumulation of Cr(VI). Plants of 9 weeks old accumulated the most Cr(VI) followed by those of 6 and 3 weeks old. The results also show that removal of Cr(VI) by water lilies is more efficient when the metal is present singly than in the presence of Cu(II) or in waste solution.	Age of plant may play role in uptake and accumulation. Researchers concluded Cr(VI) was taken up by plant but study did not measure actual Cr(VI) concentration, but just supplied the plant with Cr(VI). Concentrations reported assume that Cr(VI) accumulated.
Dogo et al.	J Serb Chem Soc	Analysis of the bioavailability of Cr(III) and Cr(VI) based on the determination of chromium in Mentha piperita by graphite furnace atomic absorption spectrometry	2011	soil + Cr(NO3) for CrIII, and Dichromate (CrVI)	*Mentha piperita (L*. Lamiaceae) [peppermint]	Plants cultivated in the presence of varying levels of Cr(III) and Cr(VI) in order to determine its capacity to control chromium uptake and its tolerance limit.	Total Cr measured by GFAAS	Yes	No	N/A	Total chromium content in plant in general increased with soil concentration of the metal. Relatively low uptakes of Cr for all soil types and at all investigated pH values. High mobility of Cr(VI) through the plants tissues, low mobility of chromium in Cr(III) contaminated plants.	Study measures uptake of CrVI, but measures total Cr in plant tissue.
Elci et al.	J Hazard Mater	Selective extraction of chromium(VI) using a leaching procedure with sodium carbonate from some plant leaves, soil and sediment samples	2010	soil + Cr(VI)	Leaves of tomato, fig, corn, and cotton plants near tannery	To speciate chromium in various environmental samples like various vegetable plants, soil and sediment near and far from a tannery in Denizli, Turkey	Total Cr in plant: acid/H2O2 digestion; CrVI species: alkaline digestion to extract CrVI (USEPA 3060A); then analyze by GFAAS	Yes	Yes	Yes	Cr(VI) is accumulated by the plants. The contents of Cr(VI) and total chromium for growing plant leaves, such as tomato and fig leaves, in soil of land close to the leather tanning industry region are highest. No more than 14% of the total Cr present in the plant leaves, except for fig sample, under examination in this study are Cr(VI) compounds.	Note that this study is a field study, not a controlled experimental study. As stated by the authors, the study shows that some plant leaves collected near the old tannery industry used for a very long time, still have elevated levels of chromium and CrVI. Results are based on assumption that analytical method accurately extracts Cr(VI); other researchers have documented difficulties with this method. Also note: researchers did not wash leaves - potential Cr on leaf surfaces
Espinoza-Quionones et al.	Water Research	Root uptake and reduction of hexavalent chromium by aquatic macrophytes as assessed by high-resolution X-ray emission	2009	hydroponic + CrVI (as CrO3) and CrIII (as CrNO3)	ROOTS*: Salvinia auriculata* [eared water moss]*, Pistia stratiotes* [water lettuce]*, and Eichornia crassipes* [water hyacinth]	To investigate the Cr(VI) reduced by root-based biosorption in a chromium uptake experiment, using a high-resolution XRF technique.	Used only plant roots; analytical method: X-ray spectroscopy	Yes	Yes	No	High-resolution X-ray fluorescence emission spectroscopy provided information about the bioreduction phenomenon by measuring the Cr-Kb emission lines which involve transitions from valence states. The comparison of the high-energy region of the Cr-Kb spectra of treated plants with that of Cr(VI) and Cr(III) reference compounds showed that there is no contribution of the hexavalent oxidation state in Cr(VI)-treated plants. This indicates that reduction of hexavalent chromium occurred for all the studied living aquatic macrophytes.	Roots were exposed to low (3ppm) CrVI concentrations for 27 days; may be partial reason why results showed complete reduction of Carve to CrIII. However, no LOD for Cr is listed. Authors note how often-used chemical extraction techniques introduce probable alterations on the speciation results. Thus, X ray spectroscopy is used, which avoids this disadvantage. Also, note that it appears that only the roots were measured, not the aerial parts of the plants.
Gardea-Torresdey et al.	Arch Environ Contamin Toxicol	Differential Uptake and Transport of Trivalent and Hexavalent Chromium by Tumbleweed (*Salsola kali)*	2005	agar: added K2CrO7 and Cr(NO3)3 (both CrVI and CrIII) in a nutrient solution	*Salsola kali* [Tumbleweed] (same class as arrowweed)	To determine the differential absorption of Cr species by tumbleweed (*Salsola kali*) as well as the effect of this heavy metal on plant growth and nutrient uptake.	oven dried, then acid digestion of pure HNO3. analysis by ICP/MS	Yes	No	N/A	Uptake of Cr was affected by species of Cr and metal concentration in medium. Hexavalent Cr resulted in concentrating of total Cr in plant tissues 10 to 20 times than if CrIII was supplied. Hexavalent form moves more easily from stems to leaves than trivalent form.	Tumbleweed is the same kingdom, phylum and class as arrowweed; found in deserts. Cr uptake could potentially be compared to arrowweed. Note however the aggressive chemical digestion step which could alter speciation.
Gheju et al.	Ovidius University Annals of Chemistry	Analysis of hexavalent chromium uptake by plants in polluted soils	2009	soil: added Cr(VI) (as K2Cr2O7 solution)	*Zea mays* [corn]	Concentration levels of Cr(VI) in contaminated soil and in Zea mays (corn) plant parts were determined and Cr(VI) bioaccumulation and bioconcentration capacity of this plant were discussed.	Dried plant parts were ashed in a furnace (600 degrees) and then digested with HCL/HNO3. Total Cr in plants and soil was then measured using a spectrophotometer	Yes	No	N/A	Total Cr concentrations in plant organs decreased in the following order: roots > stems > leaves; Zea mays roots have the greatest tendency to concentrate Cr(VI), the concentration in these plant parts being 11.7 times greater than in the surrounding soil. The translocation factor (TF), bioaccumulation factor (BAF) and the bioconcentration ratio (BCR) were determined and indicate that Cr(VI) was slowly translocated within the plant from the roots to stems, and very slowly further translocated to leaves.	Note the acid digestion technique and ashing process could potentially impact speciation? Interesting that the calculated UF (or BAF) for above ground vegetation (shoot) of 0.33 is greater than the UF recommended by OEHHA of 0.07 for protected produce (which is where corn would be classified).

Table 1: Summary of Articles Included in Technical Memorandum for Hexavalent Chromium Uptake in Plants

Author	Journal	Title	Year	Growth Medium (soil, solution, etc.)	Plant type(s)	Study Objective	Analytical Method and Sample Prep	Total Cr tested for?	Cr(VI) tested for?	Cr(VI) detected in plant?	Conclusions (as cited in literature)	Comments, critiques and caveats in study methodologies and conclusions
Hauschild, M	Ecotoxicology and Environmental Safety	Putrescine as an indicator of Pollution-induced stress in higher plants: Barley and Rape stressed with Cr(III) or Cr(VI)	1993	Nutrient solution + CCl3 (CrIII) or CrO3 (CrVI)	*Hordeum vulgare* [Barley seeds] and *Brassica napus* [Rape seeds]	To study the behavior of putrescine under simulated soil pollution stress, and measure chromium content in the plant.	Plant leaf or stem digested in HNO3, analyzed by AAS	Yes	No	N/A	Differences between chromium concentrations were found in plants stressed with CrVI vs. CrIII. In rape plants, chromium concentrations were 10-500 times higher when exposed to Cr(VI) than Cr(III). Concentrations of chromium found in stems of CrVI stressed rape were lower or similar to concentrations found in leaves, suggesting rapid transport of chromium to the leaves. Considering large concentrations were found in leaves of CrVI exposed rape plants, it is likely that parts of this chromium has reached the leaves in the form of CrVI and that the strong chlorotic symptoms observed are caused in part by oxidative attack on the leaf cells.	Study examines uptake of CrVI, but measures only total Cr in plant tissue (i.e., no speciation to determine the form of chromium in the plant tissue).
Howe et al.	Environ Sci Technol	Localization and speciation of chromium in subterranean clover using XRF, XANES, and EPR spectroscopy	2003	hydroponic + different variations of CrIII and CrVI depending on pH	Trifolium brachycalycinum *[subterranean clover]*	To localize Cr and determine the oxidation state and possible complexation mode of Cr in intact plant tissue by means of XANES, synchrotron XRF microprobe spectroscopy, and EPR spectroscopy.	XANES, synchrotron XRF microprobe spectroscopy, and EPR spectroscopy	Yes	Yes	Yes	The uptake, translocation, and form of Cr in the plant were dependent on the form and concentration of supplied Cr. Cr was found predominately in the +3 oxidation state, regardless of the Cr source supplied to the plant, though at high Cr(VI) treatment concentrations, Cr(VI) and Cr(V) were also observed (i.e., CrVI in the roots, and CrV in roots and leaves). At low Cr(VI) concentrations, the plant effectively reduced the toxic Cr(VI) to less toxic Cr(III), which was observed both as a Cr(III) hydroxide phase at the roots and as a Cr(III)- organic complex in the roots and shoots. At low Cr(VI) treatment concentrations, Cr in the leaves was observed predominately around the leaf margins, while at higher concentrations Cr was accumulated at leaf veins. The following Cr species were identified in subterranean clover following growth in Cr(VI): (i) Cr(VI) (by XANES) in the roots at high Cr(VI) concentration in solution, (ii) Cr(V) (by EPR) in the roots and leaves at high Cr(VI) concentration, and (iii) Cr(III)-organic complexes (by EPR) in roots and leaves.	Nondestructive techniques, such as EPR spectroscopy, XANES, and synchrotron X-ray fluorescence (SXRF) microprobe spectroscopy, are useful for investigation of speciation, complexation, oxidation state, and spatial distribution of Cr. These procedures eliminate possible artifacts in the oxidation state and chemical bonding that can occur as a result of homogenization or extraction procedures. Study supports that not ALL Cr (VI) is reduced in the roots; some stays as Cr(VI) in the roots. Time of exposure is a possible variable, along with exceedance of biological capacity of plant's ability to reduce Cr(VI) to Cr(III) (in this case, 0.04mMol); any CrVI leftover may contribute to plant toxicity. No LOD provided but controls were used.
Liu et al	Bioresource Technol	Hexavalent chromium uptake and its effects on mineral uptake, antioxidant defense system and photosynthesis in Amaranthus viridis L.	2008	Hydroponic solution, with other metals, EDTA, and after 2 weeks, CrVI (Dichromate) was added	*Amaranthus viridis* L (slender amaranth)	Investigate the effects of different concentrations of CrVI on mineral uptake, activities of antioxidant enzymes, and photosynthetic parameters.	Wet digestion; total chromium measured by ICP-AES	Yes	No	N/A	Chromium accumulated primarily in roots; Cr content increased in roots and shoots with increasing CrVI concentrations, and induced decrease absorption of other metals.	Study examines uptake of CrVI, but measures only total Cr in plant tissue (i.e., no speciation to determine the form of chromium in the plant tissue).
Lytle, CM	Environ Sci Technol	Reduction of CrVI to CrIII by Wetland plants: potential for in situ heavy metal detoxification	1998	Solution: added CrVI (as dichromate)	*E. crassipes* [Water Hyacinth], from San Joaquin River), and other wetland plants	Can this plant or other wetland plants reduce CrVI to CrIII and accumulate detoxified Cr into leaf and roots?	Plants were grown; given nutrient solutions w/ CrVI; plant tissues analyzed with XAS	not studied	Yes	No	This plant can absorb CrVI, and reduce it to CrIII which accumulates in plant tissues, especially in roots; authors conclude very fast reduction to CrIII, because Cr(VI) was not detected in plant tissues.	Study examines uptake of CrVI, but measures only total Cr in plant tissue (i.e., no speciation to determine the form of chromium in the plant tissue).
McGrath, SP	New Phytol	The Uptake and Translocation of Tri and Hexavalent chromium and effects on the growth of oat in flowing nutrient solution and soil	1982	Solution of CrIII and CrVI with seed; Soil with CrVI and CrIII added along w/ seeds	*Avena sativa* [Oat]	Measure uptake and translocation of CrVI and III at equal concentrations and determine relative toxicities.	Harvested after 35 days; total Cr determined by AAS; CrVI in solution determined by absorptiometric method	Yes	No	N/A	Toxicity to plants occurs when CrVI is present and pH is high; or in low pH, CrVI can be reduced to CrIII which equilibrates with soil solution (implies that CrIII is also toxic)	Study examines uptake of CrVI, but measures only total Cr in plant tissue (i.e., no speciation to determine the form of chromium in the plant tissue).
Micera, G	Journal of Inorganic Biochemistry	Chromium Adsorption by Plant Roots and Formation of Long-Lived CrV species - an ecological hazard?	1988	Hydroponic + CrIII nitrate or potassium dichromate (CrVI)	*Allium sativum* [garlic]	To determine mechanism of reduction in plants	Electron Spin Resonance (ESR) Spectroscopy	Yes	Yes	Yes	Plant roots absorb CrVI but then it is partially reduced in the roots to CrIII by components inside plant (sugars, phenolics, or organic acids perhaps)	Study suggests theory of exceedance in biological capacity of plant's ability to reduce Cr(VI) to Cr(III); no LOD or controls provided. ESR may not provide accurate quantitative measurements of Cr(VI). Also mentions CrV (intermediate species)
Mishra, S	Food and Chemical Toxicology	Studies on Uptake of Trivalent and Hexavalent Chromium by Maize	1995	Soil and sand, separately (added water with CrVI and CrIII)	*Zea maize* [Corn]	To quantify amount of chromium uptake by maize (zea mays) in soil and sand, to understand key elements of oxidation and reduction and mobilization of CrIII.	Pot culture: soil and seeds, irrigated with water w/ known amounts of CrVI and CrIII in water; used radiotracers (51Cr) to measure total chromium.	Yes	No	N/A	CrIII does get taken up in roots; perhaps gets oxidized to CrVI and translocated to various parts of plant and perhaps changes back into CrIII (evidence for reduction to CrIII).	Study examines uptake of CrVI, but measures only total Cr in plant tissue (i.e., no speciation to determine the form of chromium in the plant tissue).
Mishra, S	Agriculture Ecosystems and Environment	A study on uptake of trivalent and hexavalent chromium by paddy (oryza sativa): possible chemical modifications in rhizosphere	1997	Quartz sand and soil each, + nutrient solution w/ CrIII and CrVI salts	*Oryza sativa* [Paddy or rice]	Study uptake of CrIII and CrVI through irrigation water in paddy	Grow plants for 120 days in soil/sand; add Cr salts, after 7 days, harvest plant; Used radiotracer tagged chromium (51Cr) and analyzed roots, shoot and grain for chromium via gamma spectrometric assay methods.	Yes	No	N/A	CrIII is taken up less than CrVI. CrVI and complexed CrIII can be translocated, but very small amounts make it to aerial parts of plant.	uptake patterns of chromium under submerged (anaerobic) conditions thought to be different than those in soil.

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Author	Journal	Title	Year	Growth Medium (soil, solution, etc.)	Plant type(s)	Study Objective	Analytical Method and Sample Prep	Total Cr tested for?	Cr(VI) tested for?	Cr(VI) detected in plant?	Conclusions (as cited in literature)	Comments, critiques and caveats in study methodologies and conclusions
Montes-Holguin et al.	Environ Toxicol Chem	Biochemical and spectroscopic studies of the response of Convolvulus arvensis L. to chromium(III) and chromium(VI) stress	2006	hydroponic: Cr(III) (as CrNO3) or Cr(VI) (as dichromate)	*Convolvulus arvensis L.* [field bindweed or morning glory]	To determine the oxidative stress caused by Cr(VI), the chromium (Cr) uptake, and the Cr speciation in plants grown in hydroponics media containing either Cr(VI) or Cr(III)	Total Cr determination by ICP/OES; Cr speciation in plant by XAS	Yes	Yes	No	Results show that the plant absorbs Cr(VI) and reduces it to a less toxic species. No Cr(VI) detected in plant tissues.	Time is potential variable - how long does it take for the plant to reduce Cr(VI) once Cr(VI) is absorbed? No LOD information, but used controls. Results suggest plants have biological capacity to reduce Cr(VI) to Cr(III), as no Cr(VI) was detected in plants, so plant may have been able to reduce all CrVI that it was exposed to in this study.
Peralta et al.	Bull Environ Contam Toxicol	Uptake and effects of five heavy metals on seed germination and plant growth in alfalfa (*Medicago sativa L.*)	2001	agar + Cr(VI)	*Medicago sativa L.* [alfalfa]	Investigate the ability of alfalfa seeds to germinate and grow in media containing Cd(III), Cr(VI), Cu(II), Ni(II), and Zn(II) ions.	heavy metal content analyzed by FAAS	Yes	No	N/A	Heavy metal content strongly correlated with the heavy metal content in the media. In general, the ratio of the amount of metal in the shoots to the amount of metal in the roots increased with the dose; the corresponding ratios for total chromium after treatment with Cr(VI) were 27.3%, 18.4%, and 43.1%, respectively.	Study examines uptake of CrVI, but measures only total Cr in plant tissue (i.e., no speciation to determine the form of chromium in the plant tissue).
Sampanpanish	Water, Air, and Soil Pollution: Focus	Chromium removal from soil by phytoremediation with weed plant species in Thailand	2006	Uncontaminated soil near tannery in Thailand; added K2CrO7 at 3 concentrations	Pluchea indica (same genus as arrowweed) and other weeds	Planted seeds in pots; add CrVI water; plant harvested @ 30, 60, 90 days; alkaline digestion and Atomic absorption	FAAS for total Cr; alkaline digestion (EPA 3060A) followed by colorimetric method (EPA 7196A) for Cr(VI) measurement	Yes	Yes	Yes	Describes CrVI specifically in pluchea; CrVI and CrIII accumulation in roots at 30, 60, 90 and 120 days; provides evidence for transport in root, stem, and leaves. Accumulations of both CrVI and CrIII reached the highest values in roots on day 30 (30mg/kg and 150mg/kg, respectively), and gradually decreased on days 60, 90 and 120. Concentration of CrVI was higher in leaves than roots at day 30 and 60 (roots: ~30mg/kg; leaves: 70mg/kg for both time periods); but no CrVI was measured in leaves at 90 or 120 days.	Difficult to extract Cr(VI) using this method. Experiment ended at a low pH (around 4) which may impact speciation of chromium (CrIII is more likely to be present at lower pH). No plant controls or LODs were presented for CrVI, although total Cr LOD was reported as 30mg/kg; high concentrations were used that may be toxic to plant.
Sawalha et al.	Microchemical J	Determination of adsorption and speciation of chromium species by saltbush (*Atriplex canescens*) biomass using a combination of XAS and ICP–OES	2005	Aqueous solutions of CrIII and CrVI added to plant material	*Atriplex canescens* [saltbush]	To determine the effect of pH on chromium (Cr) binding by native, esterified, and hydrolyzed saltbush (Atriplex canescens) biomass. In addition, X-ray absorption spectroscopy studies were performed to determine the oxidation state of Cr atoms bound to the biomass.	ICP–OES was used to analyze the samples resulted from the pH and Cr binding capacity studies. XANES was used to provide information about possible changes in the oxidation of Cr atoms bound to the biomass.	Yes	Yes (see comment)	Yes (see comment)	The results of the XAS experiments showed that Cr(VI) was reduced in some extend to Cr(III) by saltbush biomass at both pH 2.0 and pH 5.0.	This was only a binding study, conducted to understand the chemical bonding mechanism of chromium atoms in plant tissue. Many factors could affect binding. This research does not study uptake of chromium into plant tissue.
Skeffington et al.	Planta	Chromium Uptake and Transport in Barley Seedlings (*Hordeum vulgate L.*)	1976	solution + radioisotope of potassium dicrohmate or CrCl3 (CrIII)	*Hordeum vulgare* [barley] seedlings	To investigate the kinetics of Cr uptake by barley seedlings, the form of chromium within the root, and discuss the apparent block in Cr transport from roots to shoots.	Plant material dried, ashed at 450C, taken up in 2N HCL; total Cr concentration measured using an atomic absorption spectrophotometer	Yes	No	N/A	Transport of Cr up the root is very slow, accounting for the low levels of Cr in the shoots. Chromate is transported better than Cr(III) though still to a very limited extent. Apparent uptake of Cr(III) was greater than that of CrO4 2- in the roots, but more Cr appeared in the shoots when the plants was fed CrO4 2-. 51CrO,~2- for 24 h, the only Cr species extractable from the roots was CrO42-. When plants were fed 51Cr(III) under the same conditions, however, CrO4 2- was again the only species detected. Further experiments showed that this effect occurred independently of Cr(III) concentration, nor was the feeding solution the source of the CrO4 2- as none could be detected in it. These results indicate that some Cr(III) can be converted to CrO4 2- after entering the tissues. However, when roots from plants not previously supplied with Cr were ground in the presence of Cr(III) and/or CrO4 2- and the aqueous ethanol fraction subjected to electrophoresis, the Cr 3+ again could not be detected, presumably as it was adsorbed onto the residue, whereas CrO4 2- was unaffected. This strongly suggests that the apparent absence of Cr 3+ in the Cr(III)	Study examines uptake of CrVI, but measures only total Cr in plant tissue (i.e., no speciation to determine the form of chromium in the plant tissue).
Sorensen, M. A. et al.	Environmental Pollution	Effects of pollutant accumulation by invasive weed salt cedar (Tamarix ramosissima) on the biological control agent Diorhabda elongata (Coleoptera: Chrysomelidae)	2009	Solution: 2mg/L CrVI (as CrO3)	*Tamarix ramosissima* [Salt cedar]	To quantify D. elongata (beetle) larval growth while feeding on T. ramosissima plants grown in the presence of various pollutants, including CrVI.	Salt cedar grown from cuttings, in nutrient solution; treatment solution added; acid and H2O2 digestion of plant material; analyzed using GFAAS	not studied	No	N/A	Treatment of 2mg/L of CrVI resulted in 1.90 mg/kg total Cr in plant tissue.	Study was used for GWRA HRA.
Vazquez, MD	Annals of Botany Company	Chromium VI induced structural and ultrastructural changes in bush bean plants	1987	Nutrient solution with Na2CrO4 (which is CrVI)	*Phaseolus vulgaris* [Bush Bean plants]	To establish if CrVI induced changes in structure of plant organs are consistent with hypothesis of a direct toxic action of Cr on roots and indirect effect on leaves	Bean plants grown in nutrient solution, with and without Cr; plant material analyzed by Light Microscopy and TEM (transmission electron microscopy)	See comment	See comment	See comment	CrVI in direct contact with plant cells causes membrane damage; small amounts of CrVI may reach upper parts of plant/leaves, since less damage was seen there, and Cr may exist as CrIII in these parts. Evidence for reduction in plant tissue.	Indirectly measured accumulation of CrVI by observing damage to plant organs. Did not directly measure concentrations of Cr in plant; used TEM images to assess damage to organs and therefore if CrVI or CrIII was present.

Table 1: Summary of Articles Included in Technical Memorandum for Hexavalent Chromium Uptake in Plants

Author	Journal	Title	Year	Growth Medium (soil, solution, etc.)	Plant type(s)	Study Objective	Analytical Method and Sample Prep	Total Cr tested for?	Cr(VI) tested for?	Cr(VI) detected in plant?	Conclusions (as cited in literature)	Comments, critiques and caveats in study methodologies and conclusions
Zayed and Terry	Plant and Soil	Chromium in the environment: factors affecting biological remediation	2003	soil and hydroponics (review article)	Various (review article)	-- (review article)	-- (review article)	Review	N/A	N/A	Chromium may be absorbed as Cr(III) or Cr(VI) by roots. Studies have shown that after Cr is absorbed by roots from nutrient solution as Cr(III) or Cr(VI) it is poorly translocated elsewhere and largely retained in the roots. Shoot concentrations of Cr barely exceeded one-hundredth of those in roots, regardless of the Cr species supplied. The restriction in the translocation of both Cr forms in plants to the same degree, despite the differential accumulation in roots and shoots, suggests that conversion of Cr(VI) to Cr(III) is almost certain to occur in roots. Since the predominant species of Cr in roots is Cr(III), very little translocation of Cr to the shoot is expected to occur when plants are supplied with either forms of Cr.	Used for general information
Zayed et al.	Planta	Chromium accumulation, translocation an chemical speciation in vegetable crops	1998	hydroponic	beet (Beta vulgaris L. var. crassa (Alef.) J. Helm), broccoli (Brassica oleracea L. var. Italica Plenck), cantaloupe (Cucumis melo L. gp. Cantalupensis), cucumber (Cucumis sativus L.), lettuce, radish (Raphanus sativus L.), spinach, tomato (Lycopersicon lycopersicum (L.) Karsten), and turnip (Brassica rapa L. var. rapifera Bailey)	To determine the extent to which various vegetable crops absorb and accumulate Cr(III) and Cr(VI) into roots and shoots and to ascertain the different chemical forms of Cr in these tissues.	Total Cr in plant extract measured by direct aspiration into ICP; also conducted Cr speciation in plant by XAS	Yes	Yes	No	Results suggest that plant tissues are able to convert Cr(VI) species to Cr(III) species, a conversion that almost certainly occurred in the root tissues since no Cr(VI) species were observed in roots of plants that were previously supplied with Cr(VI). There is also evidence that no conversion occurs for Cr species in the nutrient solution before absorption by plant roots. Speciation analysis indicates that Cr(VI) is converted in the root to Cr(III) by all plants tested (no CrVI was detected). Translocation of both Cr forms from roots to shoots was extremely limited and accumulation of Cr by roots was 100-fold higher than that by shoots, regardless of the Cr species supplied. In studies of Cr supplied to plants in irrigation water, uptake of both Cr species increased as the concentration of Cr in irrigation water increased with a strong correlation between plant Cr concentrations and the level of Cr in irrigation water.	Study supported by grants from PG&E and the Electric Power Research Institute. No CrVI was detected in plant roots; all CrVI was reduced to CrIII.
Zhao et al.	Metallomics	Use of synchrotron-and plasma-based spectroscopic techniques to determine the uptake and biotransformation of chromium(III) and chromium(VI) by *Parkinsonia aculeata*	2009	hydroponic + CrVI and CrIII	*Parkinsonia aculeata* [Mexican Palo Verde], a desert plant	Inductively coupled plasma optical emission spectroscopy was used to determine the total amount of Cr, micro, and macro nutrients taken up; and to determine the oxidation state and coordination environment of Cr taken up by plants treated with Cr(III) and Cr(VI).	use XAS to determine the Cr oxidation state	Yes	Yes	No	XAS data showed that Cr(VI) was reduced to Cr(III) in/on the plant roots and transported as Cr(III) to the stems and leaves. The XANES spectra demonstrate that, irrespective of the supplied Cr form, Palo Verde plant samples contained Cr(III), and no CrVI was detected.	Only CrIII was detected in plant roots, stems, and leaves (no CrVI detected), indicating all was reduced.
Zhao et al.	Int J Phytoremediation	Use of plasma-based spectroscopy and infrared microspectroscopy techniques to determine the uptake and effects of chromium(III) and chromium(VI) on *Parkinsonia aculeata*	2011	soil watered with CrNO3 (CrIII) or potassium dichromate (CrVI)	*Parkinsonia aculeata* [Mexican palo verde tree]	Objectives of this study was to determine the effects of both Cr ions on the seedlings' vigor at an early critical stage in plant development and to determine Cr uptake and tolerance by Mexican palo verde.	The total Cr and macro- and micro-nutrient uptake by MPV plants at different Cr concentrations were measured by ICP-OES. In addition, infrared microspectroscopy was employed to analyze tissue changes on Cr(III) and Cr(VI) treated plants.	Yes	No	N/A	Results of this research have shown that in MPV roots, the uptake of Cr from Cr(III) did not increase after the first month of growth; however, in Cr(VI)-treated plants, Cr in roots increased for up to three months of growth. In both cases the translocation of Cr into the stems increased with time. Results have also shown that the uptake of nutrient elements varied with time and Cr ion.	Study examines uptake of CrVI, but measures only total Cr in plant tissue (i.e., no speciation to determine the form of chromium in the plant tissue).

NOTES:
ET-AAS = electrothermal atomic absorption spectrometry
FAAS = flame atomic absorption spectrometry graphite furnace atomic absorption spectrometry
GFAAS = graphite furnace atomic absorption spectrometry
ICP = inductively couple plasma
OES = optical emission spectroscopy
XANES = X-ray absorption near edge structure
ESR = Electron Spin Resonance Spectroscopy

Table 2. Scientific Classification of Arrowweed and Other Plant Species

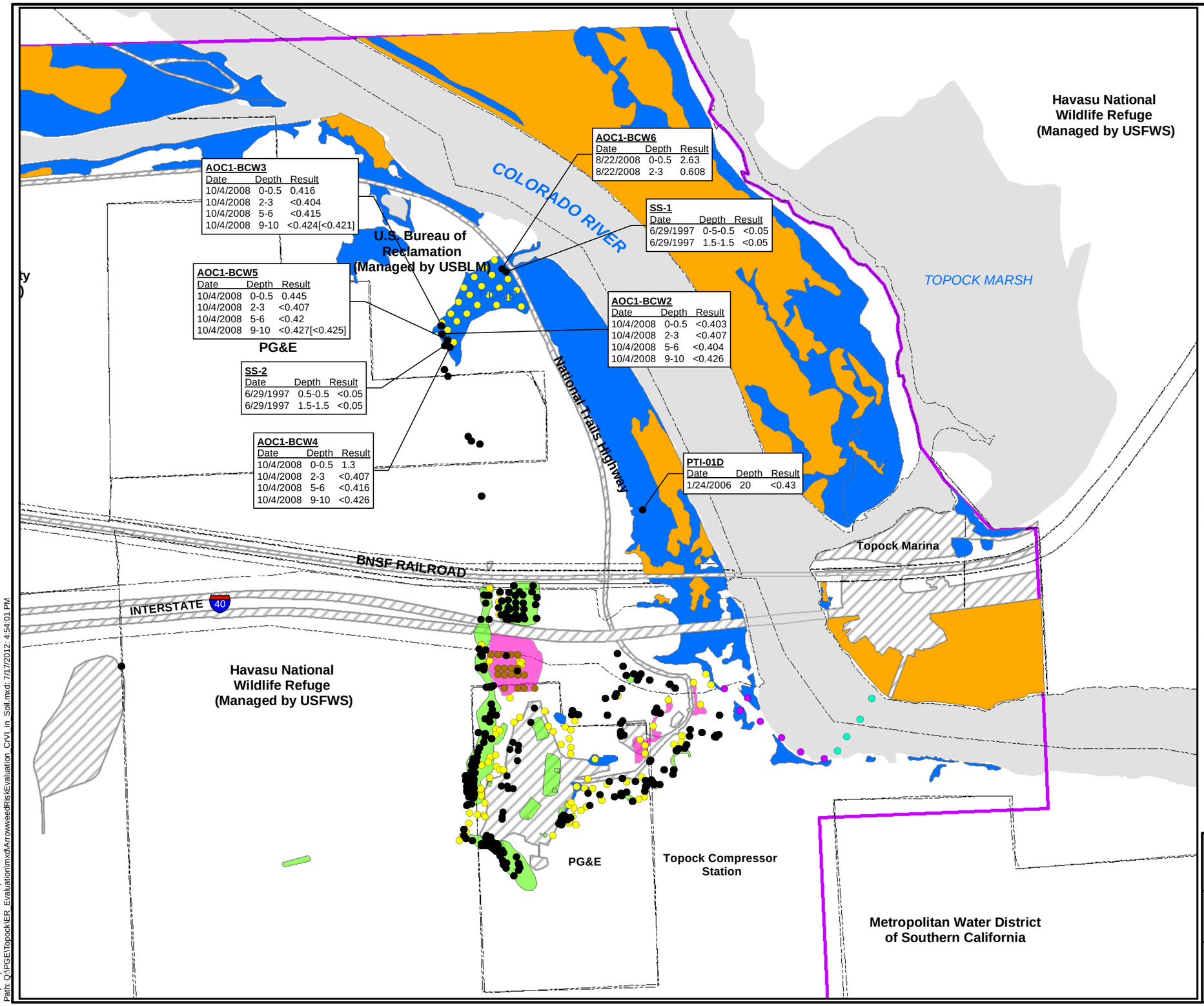
Arrowweed

Kingdom:	Plante - Plants
Subkingdom:	Tracheobionta - Vascular plants
Superdivision:	Spermatophyta - Seed plants
Division:	Magnoliophyta - Flowering plants
Class:	Magnoliopsida - Dicots
Subclass:	Asteridae
Order:	Asterales
Family:	Asteracea
Genus:	Pluchea - Camphorweed
Species:	Serica - Arrowweed

Other Plant Species	Classification Group Comparison to Arrowweed	Source of Information	Authors	Comment
Peppermint (*Mentha piperita*)	Subclass (Asteridae)	USDA	Dogo et al. (2011)	
Tumbleweed (*Salsola kali*)	Class (Magnoliopsida)	USDA	Gardea-Torresdey et al. (2005)	Also desert habitat. Found in most of United States (except South).
Oat (*Avena sativa*)	Division (Magnoliophyta)	USDA	McGrath (1982)	
Mung bean (*Vigna radiata*)	Class (Magnoliopsida)	USDA	Banerjee et al. (2008)	
Crops (including beets, broccoli, cucumber, radish, spinach, turnip, kidney bean, apples)	Class (Magnoliopsida)	USDA	Zayed et al. (1998), Cary et al. (1977a)	
Crops (tomatoes, potatoes)	Subclass (Asteridae)	USDA	Zayed et al. (1998), Cary et al. (1977a)	
Barley (*Hordeum vulgare*)	Division (Magnoliophyta)	USDA	Hauschild (1993)	
Rape seed (*Brassica napus*)	Class (Magnoliopsida)	USDA	Hauschild (1993)	
Slender amaranth (*Amaranthus viridis*)	Class (Magnoliopsida)	USDA	Liu et al. (2008)	
Sorghum (*Sorghum bicolor*)	Division (Magnoliophyta)	USDA	Bonfranceschi et al. (2009)	
Alfalfa (*Medicago sativa*)	Class (Magnoliopsida)	USDA	Bonfranceschi et al. (2009), Peralta et al. (2001)	
Creosote bush (*Larrea tridentata*)	Class (Magnoliopsida)	USDA	Arteaga et al. (2000)	Also desert habitat. Southwestern portion of the United States.
Paddy or rice (*Oryza sativa*)	Division (Magnoliophyta)	USDA	Mishra et al. (1997)	
Water lilies (*Nymphaea spontanea*)	Class (Magnoliopsida)	USDA	Choo et al. (2006)	
Maize or corn (*Zea maize*)	Division (Magnoliophyta)	USDA	Cary et al. (1977a), Gheju et al. (2009)	
Indian camphorweed (*Pluchea indica*)	Genus (Pluchea)	USDA	Sampanpanish et al. (2006)	
Mesquite (*Prosopis spp*.)	Class (Magnoliopsida)	USDA	Aldrich et al. (2003)	Desert habitat; indigenous desert species, found in southwestern United States.
Mesquite, smooth (*Prosopis laevigata*)	Class (Magnoliopsida)	USDA	Buendía-Gonzáles et al. (2010)	Desert hyperaccumulator plant; found in Texas.
Eared watermoss (*Salvinia auriculata*)	Subkingdom (Tracheobionta)	USDA	Espinoza-Quiononnes et al. (2009)	
Water lettuce (*Pistia stratiotes*)	Division (Magnoliophyta)	USDA	Espinoza-Quiononnes et al. (2009)	
Water hyacinth (*Eichornia crassipes*)	Division (Magnoliophyta)	USDA	Espinoza-Quiononnes et al. (2009), Lytle (1998)	
Subterranean clover (*Trifolium brachycalycinum*)	Class (Magnoliopsida)	USDA	Howe et al. (2003)	
Morning glory (*Convolvulus arvensis*)	Subclass (Asteridae)	USDA	Montes-Holguin et al. (2006)	
Garlic (*Allium sativum*)	Division (Magnoliophyta)	USDA	Micera and Dessì (1998)	
Saltbush (*Atriplex canescens*)	Class (Magnoliopsida)	USDA	Sawalha et al. (2005)	Desert shrub; found in western United States.
Bush bean (*Phaseolus vulgaris*)	Class (Magnoliopsida)	USDA	Vazquez et al. (1987)	
Mexican palo verde (*Parkinsonia aculeata*)	Class (Magnoliopsida)	USDA	Zhao et al. (2009, 2011)	Desert shrub/tree; found in southern United States.
Saltcedar (*Tamarix ramosissima)*	Class (Magnoliopsida)	USDA	Sorensen et al. (2009)	Desert tree; found in southwestern United States.

Note:
Plants highlighted in yellow share similar habitats to arrowweed (i.e., are found in deserts or are drought tolerant).

Figures



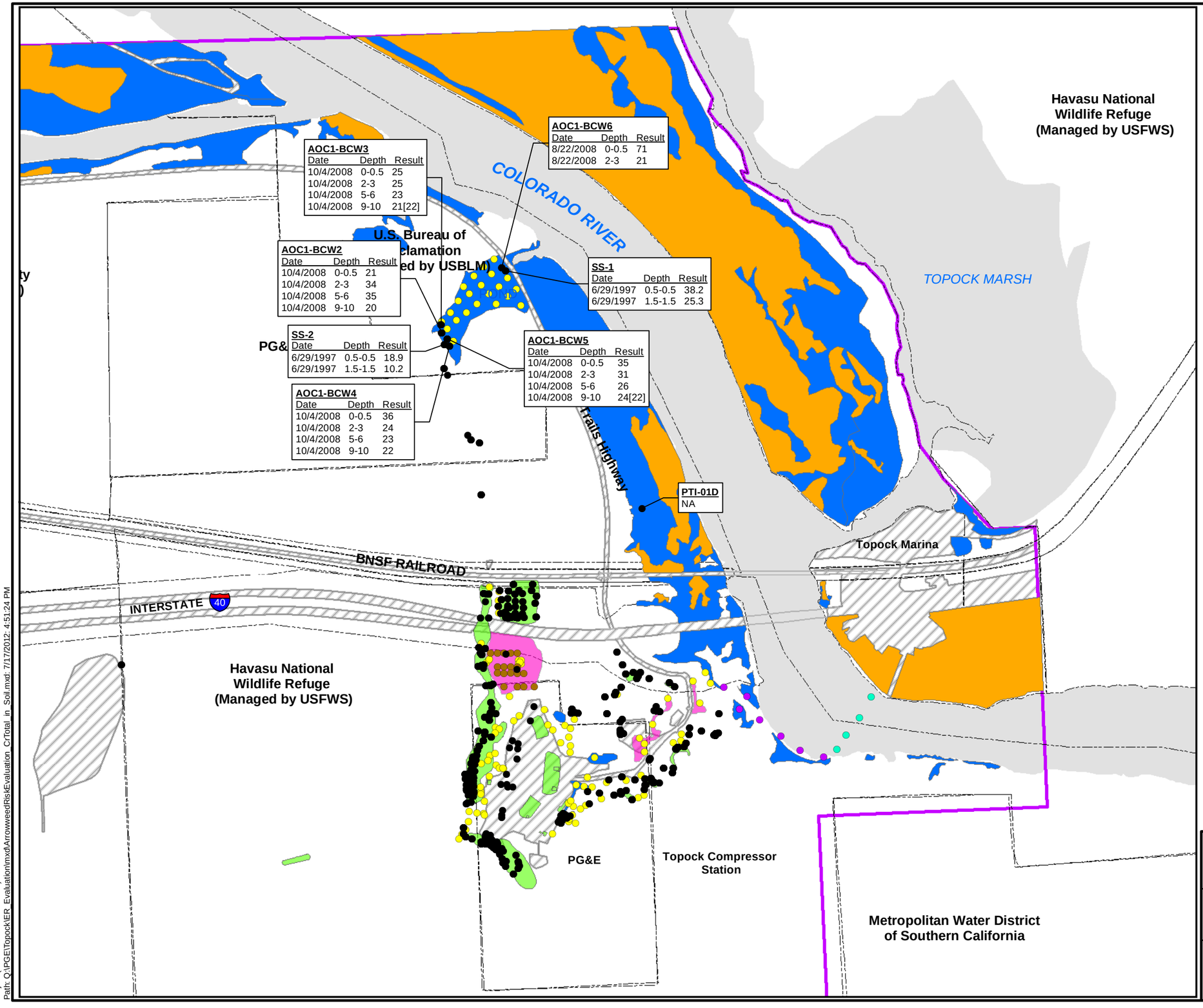
PG&E TOPOCK COMPRESSOR STATION
NEEDLES, CALIFORNIA

HEXAVALENT CHROMIUM CONCENTRATIONS IN SOIL CO-LOCATED WITH ARROWWEED

ARCADIS

FIGURE
1

[WC-95 VJR] SANF-95 EGH
Project (RC000689.0002 Task 2)
Path: Q:\PGE\Topock\ER_Evaluation\mxd\ArrowweedRiskEvaluation_CrVI_in_Soil.mxd: 7/17/2012; 4:54:01 PM



Legend:

- Soil Sample Location
- 2006 Porewater/Sediment Sample Location
- Contingency Sample Location
- Proposed Sediment and Porewater Sample Location
- Proposed Soil Sample Location
- AOC/SMWU Areas
- Other Investigation Areas
- Arrowweed
- Salt Cedar
- Property Boundaries
- Area of Potential Effects
- Developed Area

Notes:

1. Extent of vegetation communities from Figure 6 of the Programmatic Biological Assessment for Pacific Gas and Electric Topock Compressor Station Remedial and Investigative Actions report (CH2MHILL, 2007).
2. All total chromium concentrations are in milligrams per kilogram (mg/kg).
3. Depth of soil sample is in feet (ft).
4. Soil total chromium concentrations are only shown for samples collected from locations in or along the edge of the arrowweed or salt cedar plant communities.

[ ] - indicates duplicate sample result
NA - Not analyzed

0 730 1,460 Feet

GRAPHIC SCALE

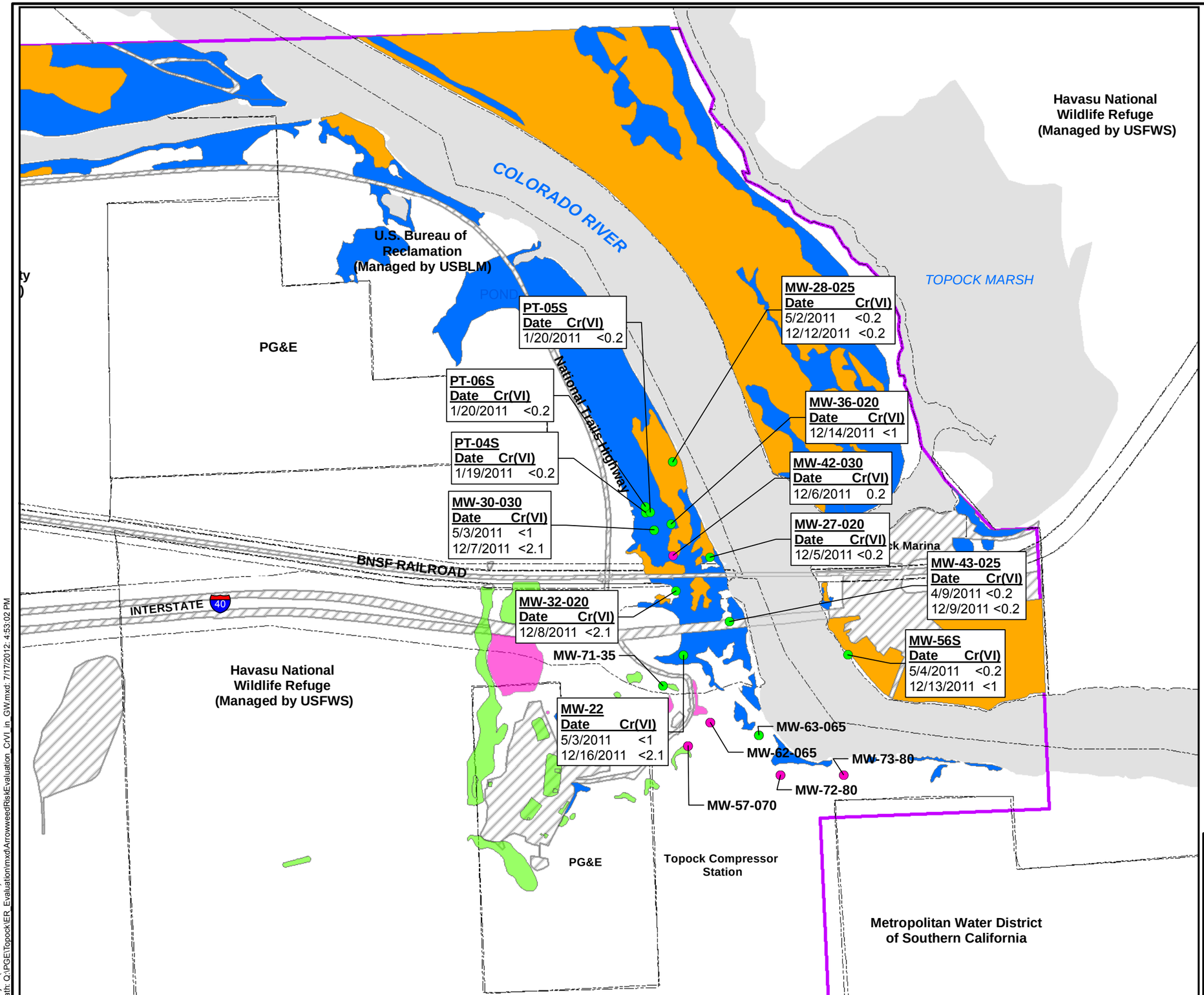
PG&E TOPOCK COMPRESSOR STATION
NEEDLES, CALIFORNIA

TOTAL CHROMIUM CONCENTRATIONS IN SOIL CO-LOCATED WITH ARROWWEED

ARCADIS

FIGURE 2

[WC-85 VJR] SANF-85 EGH
Project (RC000689.0002 Task 2)
Path: Q:\PGE\Topock\ER_Evaluation\mxd\ArrowweedRiskEvaluation_CrTotal_in_Soil.mxd: 7/17/2012: 4:51:24 PM



Legend:

Hexavalent Chromium Concentration (µg/L)

- Detected
- Non-Detect
- AOC/SMWU Areas
- Other Investigation Areas
- Arrowweed
- Salt Cedar
- Property Boundaries
- Area of Potential Effects
- Developed Area

Notes:

1. Extent of vegetation communities from Figure 6 of the Programmatic Biological Assessment for Pacific Gas and Electric Topock Compressor Station Remedial and Investigative Actions report (CH2MHILL, 2007).
2. Monitoring wells shown are screened at depths no greater than 20 feet below ground surface.
3. Hexavalent chromium groundwater concentrations are only shown for samples collected from wells that are located in or along the edge of the arrowweed or salt cedar plant communities.
4. The water table elevation in the flood plain is influenced by and mimics the water level in the Colorado River, which rises in the summer and falls in the winter due to Colorado River water management actions.
5. Analytical data shown are all available data from May 2011 to May 2012.

µg/L = micrograms per liter
Cr(VI) = Hexavalent Chromium
< - Indicates non-detect

0 730 1,460 Feet

GRAPHIC SCALE

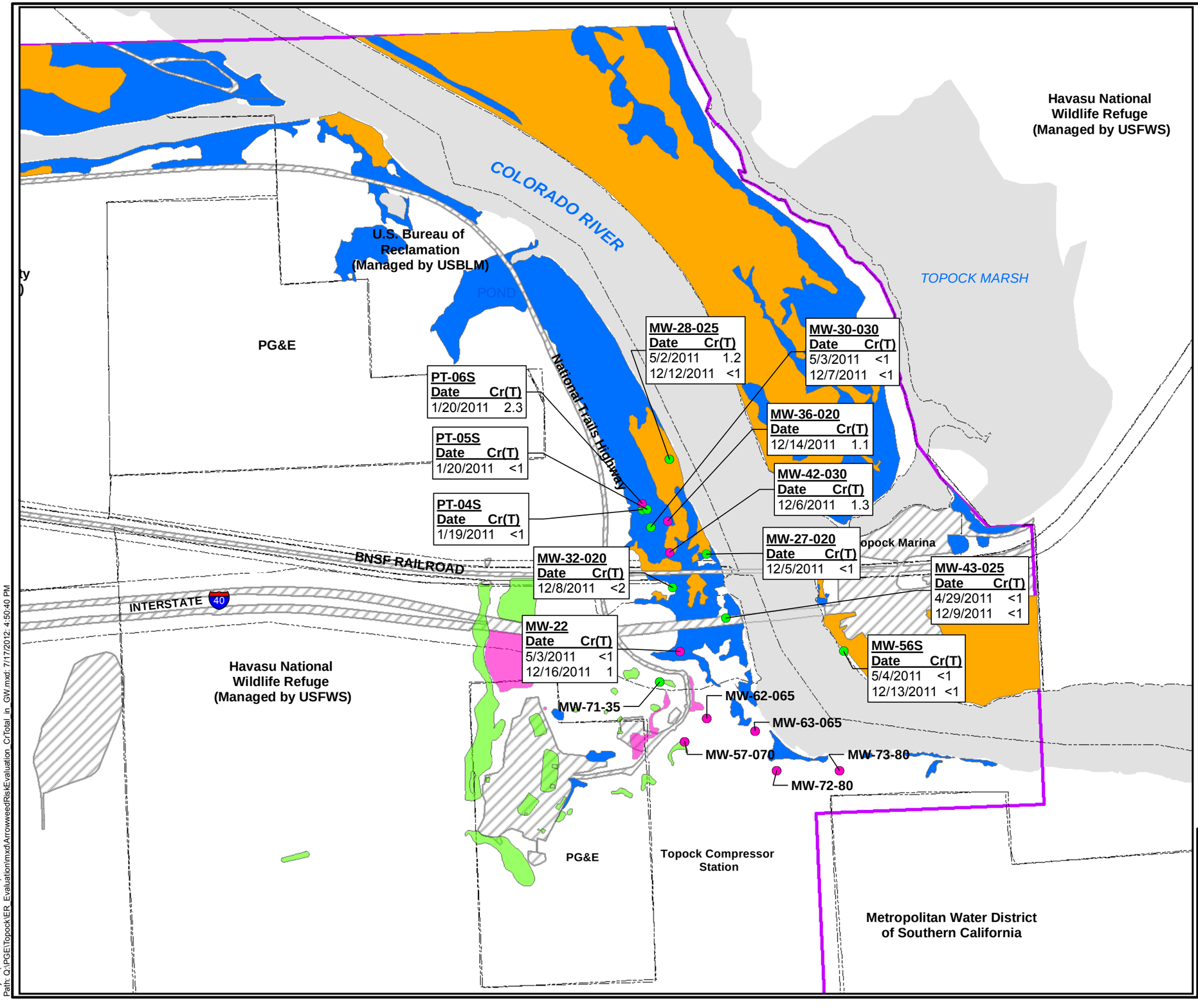
PG&E TOPOCK COMPRESSOR STATION
NEEDLES, CALIFORNIA

HEXAVALENT CHROMIUM CONCENTRATIONS IN GROUNDWATER CO-LOCATED WITH ARROWWEED

ARCADIS

FIGURE 3

[WC-85 VJR] SANF-85 EGH
Project (RC000689.0002 Task 2)
Path: Q:\PGE\Topock\ER_Evaluation\mxd\ArrowweedRiskEvaluation_CrVI_in_GW.mxd: 7/17/2012; 4:53:02 PM



Legend:

Total Chromium Concentration (µg/L)

- Detected
- Non-Detect
- AOC/SMWU Areas
- Other Investigation Areas
- Salt Cedar
- Arrowweed
- Property Boundaries
- Area of Potential Effects
- Developed Area

Notes:

1. Extent of vegetation communities from Figure 6 of the Programmatic Biological Assessment for Pacific Gas and Electric Topock Compressor Station Remedial and Investigative Actions report (CH2MHILL, 2007).
2. Monitoring wells shown are screened at depths no greater than 20 feet below ground surface.
3. Total chromium groundwater concentrations are only shown for samples collected from wells that are located in or along the edge of the arrowweed or salt cedar plant communities.
4. The water table elevation in the flood plain is influenced by and mimics the water level in the Colorado River, which rises in the summer and falls in the winter due to Colorado River water management actions.
5. Analytical data shown are all available data from May 2011 to May 2012.

µg/L = micrograms per liter
Cr(T) = Total Chromium
< - Indicates non-detect

0 730 1,460 Feet

GRAPHIC SCALE

PG&E TOPOCK COMPRESSOR STATION
NEEDLES, CALIFORNIA

TOTAL CHROMIUM CONCENTRATIONS IN GROUNDWATER CO-LOCATED WITH ARROWWEED

ARCADIS

FIGURE 4

[WC-85 VJR] SANF-85 EGH
Project (RC000689.0002 Task 2)
Path: Q:\PGE\Topock\ER_Evaluation\mxd\ArrowweedRiskEvaluation_CrTotal_in_GW.mxd: 7/17/2012: 4:50:40 PM

Attachment 1

Literature Review Results

1. Results of Literature Search

Relevant findings from the literature search were categorized by analytical methods used, the types of media used for plant growth, the types of plants studied, the source and type of chromium used in the study, and what type of chromium was ultimately detected in plant tissues. These findings are summarized below, including an overall discussion of the potential for chromium uptake in plants.

1.1 Analytical Methodologies

The literature search indicates that researchers used a variety of analytical methods in order to study the distribution of chromium in plants. Some analytical methods claimed that they were able to differentiate and quantify the species of chromium (hexavalent chromium [Cr(VI)] or trivalent chromium [Cr(III)]) in the plant, while other methods only quantified total chromium in plant tissues. Sample preparation also differed between research studies, including the form of chromium supplied to the plant, the growth media, cultivation time, method of extraction of chromium from the plant, and the part of the plant that was used in the analysis. Understanding these experimental components aided in interpretation of a study's results and conclusions. The following paragraphs provide an overview of analytical methods and experimental conditions reviewed during the literature search.

1.1.1 Analytical Methods for Total Chromium Determination in Plants

The methods used to determine total chromium concentration in environmental samples are atomic spectroscopic methods, such as atomic absorption (AAS), atomic emission (AES), and elemental mass spectrometry (MS). Methods commonly used in the relevant studies identified in the literature search include flame atomic absorption spectrometry (FAAS), graphite furnace atomic absorption spectrometry (GFAAS), inductively coupled plasma atomic emission spectrometry (ICP/AES), and inductively coupled plasma mass spectrometry (ICP/MS). FAAS and ICP/AES offer similar detection limits, whereas GFAAS and ICP/MS can provide a lower detection limit capability. The majority of studies identified as relevant relied on one of these types of AAS as the method for quantifying the total amount of chromium present in the plant.

Samples analyzed for total chromium generally involve an extraction step, to ensure that all chromium is separated from plant tissue before concentrations of total chromium are quantified by the analytical methods listed above. The extraction procedures vary,

but usually involve acid digestion, oxidative acid digestion (i.e., hydrogen peroxide addition), and addition of heat (Peralta et al. 2001). Some researchers believe that these chemical extraction techniques may not consistently solubilize all chromium present in the sample, which may result in lower yield (Buckley et al. 2009).

Additionally, a less common technique utilized by a few authors consisted of addition of radiotracer tagged chromium (^{51}Cr) to experimental media and subsequent analysis via gamma spectrometric assay methods (Cary et al. 1977a; Mishra et al. 1995). This technique, as with those mentioned above, provides information on total chromium in the sample.

1.1.2 Analytical Methods for Chromium Speciation in Plants

In addition to total chromium determinations, speciation measurements are important to determine whether chromium exists as Cr(VI) or Cr(III) in plant tissues. Because the bioavailability and translocation of chromium is dependent on its chemical form, the development of reliable methods for identification and quantification of trace element species is critical. As indicated by the Office of Environmental Health Hazard Assessment (OEHHA), there are methodological challenges associated with estimating the actual speciation of chromium in biological tissues during analysis (OEHHA 2012). As a result, most studies only measure total chromium content of plant parts. Of the methods available, X-ray absorption spectroscopy (XAS) is a common technique for determining the speciation of chromium [e.g., Cr(VI) vs. Cr(III)] in plant tissue.

Additionally, some researchers employed other methods of speciation, which involved a Cr(VI)-specific extraction process, such as the alkaline digestion, as described in U.S. Environmental Protection Agency (USEPA) Method 3060A (Elci et al. 2010; Sampanpanish et al. 2006). According to USEPA, alkaline extraction is a procedure for extracting Cr(VI) from soluble, adsorbed, and precipitated forms of chromium compounds in solid matrices such as soils, sludges, or sediments (USEPA 1996). In this method, after Cr(VI) is separated from the sample matrix material, the concentration of Cr(VI) is determined using the analytical methods mentioned above (i.e., GFAAS or ICP/MS), or by using a colorimetric spectrophotometry method as described in USEPA Method 7196A (USEPA 1992). The concentration of Cr(III) can then calculated by subtracting Cr(VI) from total chromium concentrations (Sampanpanish et al. 2006). It has been suggested that chemical extractions may induce alterations on speciation results in samples (Lytle et al. 1998). Because of the complexity involved with chemical extraction, many authors prefer to use XAS, as this method eliminates disadvantages

and potential errors induced by extraction of Cr(VI) (Espinoza-Quinones et al. 2009; Lytle et al. 1998).

1.2 Plant Species

The literature search did not identify any published articles on chromium uptake specifically in arrowweed. The strategy, therefore, was to review literature on chromium uptake in other plants, so that information on plants that may be related to arrowweed, either in terms of their scientific classification or use (e.g., desert plants and edible/medicinal plants), could be obtained and assessed for future relevancy at the site. The scientific classification of arrowweed is listed above, and Table 2 of the Technical Memorandum presents the similar scientific classifications between plant species that were used in the studies reviewed and arrowweed for contextual purposes.

Referring to the scientific classification shown above, arrowweed is an asterid, a large subgroup of flowering plants, which include many shrubs, trees, and some familiar crops. Some articles reviewed performed experiments on plants in the asterid subgroup, while other studies used plants from the broader category of *Magnoliopsida*, or dicot flowering plants. One study on chromium uptake was conducted using Indian camphorweed (*Pluchea indica*), which may be a useful comparison to arrowweed as they share the same genus and are closely related (Sampanpanish et al. 2006).

In addition, a few plants in even broader categories, such as the seed plants, shared another characteristic with arrowweed: habitat (as highlighted in Table 2 of the Technical Memorandum). For example, studies were identified and reviewed on mesquites, tumbleweed, creosote bushes, and Mexican palo verde, which are all desert/drought-tolerant plants and may share common biological mechanisms with arrowweed (Aldrich et al. 2003; Arias et al. 2010; Arteaga et al. 2000; Buendía-González et al. 2010; Gardea-Torresdey et al. 2005; Zhao et al. 2009, 2011). Further, mesquite, creosote bush, and salt cedar are plants that are found in some areas at the Topock Site along with arrowweed, and are included in the discussion below.

The findings regarding chromium uptake in various plant species provide an indication of potential uptake into arrowweed. Information on chromium uptake into produce was also noted and is presented on Table 1 (of the Technical Memorandum), as there have been questions posed by different stakeholders about uptake into homegrown produce. In addition, the U.S. Department of the Interior specifically requested that the risk assessment incorporate the assumption that their land could be used in the future for

growing fruits and vegetables [and these exposure pathways were incorporated into the conceptual site model in the RAWP (ARCADIS 2008)].

Additionally, the study involving the invasive weed salt cedar (*Tamarix ramosissima*) presented in Appendix I of the *Human and Ecological Risk Assessment of Groundwater Impacted by Activities as Solid Waste Management Unit (SWMU) 1/Area of Concern (AOC) 1 and SWMU 2* (i.e., Groundwater Risk Assessment [GWRA]) (ARCADIS 2009) was reviewed for relevant content. This study was used in the GWRA as a tool for estimating uptake of Cr(VI) in groundwater into potentially relevant plant species.

1.2.1 Media for Plant Growth and Source of Chromium Used in Relevant Studies

Uptake of chromium into plant tissue is dependent on chemistry of naturally occurring chromium and various chromium compounds in soil. Chromium exists predominately in the trivalent or hexavalent form in soil. Although Cr(VI) is more soluble than Cr(III) and, therefore, more available for uptake into plants, Cr(VI) is not thermodynamically stable in soil (unless in an oxidizing environment) and is readily reduced to Cr(III) (Cary et al. 1977b). This reduction likely occurs by redox reactions with aqueous inorganic species or soil organic matter under most soil conditions (James and Bartlett 1983, as cited in Amarillo National Resource Center for Plutonium [ANRCP] 1998). Investigators have also reported that most soil systems, especially soils in high inorganic matter, can reduce Cr(VI) to Cr(III), even at pH values around and above neutrality (Bartlett and Kimble 1976; Bartlett and James 1983, as cited in Kožuh et al. 2000).

As the source of chromium (i.e., total chromium, trivalent, or hexavalent) and environmental media in which plants were grown may potentially impact results of the study, the growth media and source of chromium were identified during review of the articles. The majority of the relevant studies used soil or a hydroponic solution (see various studies in Table 1 of the Technical Memorandum) as the growth media for plants; a few studies used agar (Aldrich et al. 2003; Gardea-Torresdey et al. 2005; Peralta et al. 2001) or sand (Banerjee et al. 2008; Cary et al. 1977a, 1977b; Mishra et al. 1997).

Many of the relevant studies identified through the literature search took place in a laboratory setting, where the amount of chromium in the growth media was a known concentration or a known concentration was added to the growth media. Most relevant studies added Cr(VI) to the media in the form of potassium chromate or Cr(III) to the media, while other studies added radiolabeled ^{51}Cr to the growth media. A field study by

Elci et al. (2010) examined concentrations of chromium in plants growing in soil near a tannery, a potential source of chromium for the surrounding area (Elci et al. 2010).

1.2.2 Evidence for Chromium Uptake in Plants

From the collection of selected articles, plants were generally found to absorb chromium from the different growth media at various concentrations. Some studies specifically tested only Cr(VI) uptake and translocation, while other studies conducted experiments with Cr(VI) and Cr(III) together as total chromium, and also separately. Additionally, researchers either measured the specific form of chromium [Cr(VI) or Cr(III)] or total chromium in plant tissues, depending on their study objective and analytical method. In order to organize the information and results from the Tier I studies, these studies are categorized by the form of chromium used in the media for the plant and the form of chromium ultimately found in plant tissue. Results from the studies are presented in Table 1 of the Technical Memorandum and summarized below in two categories: 1) studies measuring only total chromium in plant tissue, and 2) studies where Cr(VI) was specifically measured in plant tissue.

1.2.3 Total Chromium in Plants Following Treatment with Cr(III) and/or Cr(VI)

Articles described in this category studied uptake of chromium [either Cr(III) or Cr(VI) or both], but ultimately measured total chromium in the plant. In other words, the results discussed below are reported as total chromium in plant tissues after uptake.

Five studies provided information regarding the relative concentration of total chromium in plant tissues depending on the form of chromium in soil, sand, agar, and solution. Đogo et al. (2011) grew peppermint plants in the presence of Cr(VI) and Cr(III) soils and found that uptake of either form of chromium was low from the soil. Results from this study also showed that plants cultivated in soil with Cr(III) had even lower concentrations of total chromium in aerial plant tissues than plants cultivated with Cr(VI) (Đogo et al. 2011). Gardea-Torresdey et al. (2005) also reported that Cr(VI) uptake by tumbleweed resulted in higher accumulation of total chromium in upper plant tissues when compared to Cr(III) uptake. Consistent with these results, an experiment on mung beans in sand by Banerjee et al. (2008) showed total chromium migration from roots to shoots was higher when plants were supplied with Cr(VI) compared to Cr(III). Hauschild et al. (1993) also detected higher total chromium concentrations in plants exposed to Cr(VI) compared with Cr(III) in an experiment with barley and rape seeds in solution;

however, McGrath (1982) reported almost equal uptake into oat plants of the two chromium species from solution.

Several studies examined the translocation of total chromium from roots to aerial plant tissues in plants exposed to either form of chromium. Results from Đogo et al. (2001) and Banerjee et al. (2008), mentioned above, observed poor translocation of total chromium from the roots to the aerial portions of the plant. Many other authors who measured total chromium in plant tissues also concluded primary accumulation of total chromium in the roots compared to aerial portions (Arteaga et al. 2000; Bonfranceschi et al. 2009; Gheju et al. 2009; Hauschild et al. 1993; Liu et al. 2008; Mishra et al. 1997; Zayed et al. 1998). Research suggests that roots of vascular plants may provide a binding mechanism for chromium absorption and adsorption, which may explain decreased concentrations of chromium in aerial portions of plants (Wallace et al. 1976). Further, consistent with results from Đogo et al. (2011), Banerjee et al. (2008) reported the amount of total chromium in the roots represented only about 5% of the Cr(III) or Cr(VI) originally supplied.

Differences in uptake based on concentrations of Cr(VI) and/or Cr(III) supplied in media were also investigated by some authors. For example, Peralta et al. (2001) and Liu et al. (2008) reported that the ratio of total chromium in shoots to chromium in roots generally increased with dose of Cr(VI) in agar and nutrient solution, respectively. Some researchers, however, reported no difference in uptake of chromium when concentrations were increased in experimental media (Buendía-González et al. 2010).

A few other researchers conducted experiments using hydroponic media and measured total chromium in plant tissues. Choo et al. (2006) found that mature water lilies take up a substantial amount of Cr(VI) from hydroponic solution, with 50 to 60% of total chromium accumulation in the roots, and the rest in leaves and petioles. These researchers also concluded that the age of the plant may play an important role in uptake of Cr(VI); three, six, and nine week old lilies were collected and exposed to a Cr(VI) solution for seven days, resulting in higher Cr(VI) concentrations in roots, petioles, and leaves of the nine week old lilies than the six and three week old plants (Choo et al. 2006).

A study by Buendía-González et al. (2010) in a desert hyperaccumulator plant (smooth mesquite) observed significant translocation of total chromium to aerial portions of the plant after treating seedlings in Cr(VI) solution for 50 days. Another hydroponic study on salt cedar conducted by Sorensen et al. (2009) found that after supplying 2 milligrams

per liter of chromium trioxide solution to plants, an average concentration of 1.89 milligrams per kilogram (mg/kg) of elemental chromium was detected in plant tissue.

Cary et al. (1977a) investigated total chromium uptake from solution in a variety of food crops. These researchers found that several crops (e.g., wheat, potato, barley, spinach, and others) are able to take up both Cr(VI) and Cr(III) anywhere from 2 to 73% of the original concentration in solution, depending on the chemical complex, concentration of chromium treatment, and plant species. The ratio of total chromium detected in the tops of the plant compared to the roots, however, was very small (between 0.01 and 0.03), which is consistent with the overall conclusions from studies mentioned above. The study by Cary et al. (1977a) was used by OEHHA in developing the uptake factors presented in OEHHA's Air Toxic Hot Spots Risk Assessment Guidelines (OEHHA 2012)[3]. Additionally, OEHHA cites a study by Srivastava et al. (1994), which concluded that 10% of Cr(VI) supplied to plant roots was found in aerial portions of the plant as total chromium and, therefore, OEHHA recommends that the uptake factor (UF) for the root is 10 times that of the leafy UF (OEHHA 2012). The percentage of total chromium that exists as Cr(VI) in plant tissues is currently not accounted for in the OEHHA guidance; specifically, the recommendation in the OEHHA guidance is that the UFs that were calculated for total chromium be applied to Cr(VI).

Based on studies mentioned above, plants have the ability to absorb chromium from their growth media, perhaps at higher concentrations when supplied in the form of Cr(VI). Generally, data indicate that absorbed chromium, Cr(III) or Cr(VI), is poorly translocated to aerial portions of plants as relatively higher concentrations of total chromium were detected in roots. Although the articles discussed in this section did not determine the species of chromium in the plant tissues, it has been suggested that one reason for poor translocation is due to reduction of Cr(VI) to Cr(III), which is considered less mobile than Cr(VI) due to chemical interactions and ion exchange within the plant (Becquer et al. 2003; Elci et al. 2010; Skeffington et al. 1976; Zayed and Terry 2003).

1.2.4 Uptake, Translocation, and Ultimate Measurements of Cr(VI) in Plant Tissues

This section describes articles in which Cr(VI) was specifically measured in plant tissues. Concentrations of Cr(VI) were supplied in soil or solution, and then analytical

[3] Note that the OEHHA (2012) Hot Spots Guidance document is still in DRAFT form.

methods were used to measure levels of Cr(VI) in plant tissues. Additionally, some of these researchers determined the concentration of Cr(III) concentrations in plant tissues, because Cr(VI) is said to reduce to Cr(III) as mentioned above.

A field study by Elci et al. (2010) using crops located near a tannery in Turkey detected concentrations of Cr(VI) in leaves of tomato and fig plants (percentages of total chromium and Cr[VI] were 14 and 48%, respectively). The same study, however, also tested cotton and corn leaves farther from the tannery, which contained much lower concentrations of Cr(VI) (Elci et al. 2010). This result may be due to the close proximity of the crops to chromium contamination from the tannery or differences in plant species.

As mentioned previously, one of the articles in the literature review includes a study conducted on *Pluchea indica*, or Indian camphorweed (Sampanpanish et al. 2006). This particular study is potentially more relevant for understanding chromium uptake in arrowweed because *Pluchea indica* shares the same genus as arrowweed (*Pluchea sericea*). Sampanpanish et al. (2006) grew *Pluchea indica* in uncontaminated soil from a Thailand tannery, added 100 parts per million Cr(VI) solution, and analyzed roots, stems, and leaves for Cr(VI) (using alkaline digestion and spectrophotometry), Cr(III), and total chromium. No initial Cr(VI) was detected in soil background before addition of Cr(VI) solution, suggesting that total chromium existed as Cr(III). Results showed total chromium accumulated in the roots, stems, and leaves at day 30 at 27%, 38%, and 35% of the total chromium mass uptake, respectively. Cr(VI) concentrations increased from roots to leaves (maximum concentration occurred at 30 days at around 30 and 73 mg/kg in roots and leaves, respectively). Over time, however, Cr(VI) concentrations fell below the detection limit due to dilution by plant growth and, therefore, Cr(VI) was not detected in stems or leaves at 90 or 120 days (Sampanpanish et al. 2006). Consistent with studies mentioned above, Cr(III) was detected at much lower concentrations in all samples of leaves than Cr(VI), indicating that the plant's ability to translocate Cr(III) is not as efficient as for Cr(VI) (Sampanpanish et al. 2006). As discussed below, it is important to note that the ultimate pH conditions of the soil in this study were fairly acidic (i.e., 3.8). Such acidic soils may not be representative of the natural soil conditions at the site which range from 7.48 to 10.49. Consequently, the applicability of this study to the site is questionable.

A few studies in the literature review included plants that share similar habitats to arrowweed (i.e., are desert habitants or drought-resistant). For example, in a hydroponic study on creosote bush (which is a plant found in some areas of the Topock site), Arteaga et al (2000) treated the plant with Cr(VI) and subsequently analyzed roots,

stems, and leaves for Cr(VI) using XAS (total chromium was also measured using FAAS, mentioned previously). Data indicated that stems of the plant contained some Cr(VI) and Cr(III), but the leaves contained only Cr(III) (Arteaga et al. 2000). In another study, mesquite, an indigenous desert plant also found in some areas at the Topock site, researchers concluded that although the mesquite roots absorbed Cr(VI) from hydroponic solution, only a small percent of Cr(VI) was present in plant roots (1.2%) and stems (6.2%), and no Cr(VI) was detected in the leaves (Aldrich et al. 2003). According to several sources, a plausible explanation for this observation is that a percentage of Cr(VI) is likely reduced to Cr(III) in the roots, and Cr(III) is considered less mobile than Cr(VI) due to chemical interactions and ion exchange within the plant (Becquer et al. 2003; Elci et al. 2010; Shanker et al. 2005; Skeffington et al. 1976; Zayed and Terry 2003).

Partial reduction of Cr(VI) to Cr(III) in other plant species studied by researchers has also been documented. These observations are based on detections of both Cr(VI) and Cr(III) in subterranean clovers (Howe et al. 2003) and garlic (Micera and Dessì 1988). Vazquez et al. (1987) analyzed bush bean plant tissue using transmission electron microscopy and concluded that small amounts of Cr(VI) may reach aerial portions of the plant; however, Cr(III) was believed to be the primary form in aerial parts. This author, however, did not directly measure the concentration of chromium, but rather assessed presence of Cr(VI) in the plant by observing damage to plant tissues (Vazquez et al. 1987). Sawalha et al. (2005) conducted a binding study by adding Cr(VI) and Cr(III) to plant biomass (as opposed to cultivating plants in chromium-treated media). Analysis of plant material by XAS showed partial reduction of Cr(VI) to Cr(III). Although this study does support reduction of Cr(VI) to Cr(III) in plant tissue, the results do not consider interactions that may occur between soil and roots. Results from Micera and Dessi (1988), Howe et al. (2003), Arteaga et al. (2000), and Aldrich et al. (2003) also suggest the potential for a threshold mechanism, where plants can reduce Cr(VI) to Cr(III) up to a certain concentration.Additionally, several hydroponic studies were identified where only Cr(III) was detected in plant tissues in plants cultivated with Cr(VI) and/or Cr(III). For example, an experiment on wetland plant roots supplied with both Cr(VI) and Cr(III) in solution reported no detection of Cr(VI) in plant root tissue (Espinoza-Quinones et al. 2009). Lytle et al. (1998) studied Cr(VI) uptake and reduction in water hyacinth, another wetland plant, in solution. Data from XAS analysis indicated the presence of only Cr(III) in leaf, petiole, and root tissues. Zayed et al. (1998), in addition to measuring total chromium as mentioned above, also used XAS in hydroponic solution for various crops and concluded that all Cr(VI) was reduced to Cr(III) in the roots as no Cr(VI) was detected in the roots. Zayed et al. (1998) also reported that translocation from roots to

shoots among a variety of vegetable plants was extremely low, because Cr(III) is not as mobile as Cr(VI). Similar observations were reported by Montes-Holguin et al. (2006) – no Cr(VI) was detected in morning glory plants grown in a hydroponic solution supplied with either Cr(III) and Cr(VI). Further, two studies in this category were conducted in mesquite and Mexican palo verde, which are both desert plants. Aldrich et al. (2003) analyzed uptake of Cr(VI) by mesquite in agar as well as hydroponic solution (mentioned above) by XAS. Although plants grown in the hydroponic solution contained small amounts of Cr(VI) in stems and roots, no Cr(VI) was detected in any plant tissues grown in agar. Similarly, Zhao et al. (2009) did not detect Cr(VI) in Mexican palo verde plant tissues; only Cr(III) was found in plant roots, stems, and leaves.

In summary, according to the review of the articles in this section, most of the studies support that the majority of Cr(VI) that was actually taken up by the plant did not migrate to aerial parts of the plant, but was mostly present in the roots. Further, chromium in the roots was largely present as Cr(III), and in some cases, plant tissues contained Cr(III) only. The quantity of Cr(VI) that a plant is able to reduce to Cr(III) depends on several factors including pH of medium, concentration of chromium in medium and plant, presence of enzymes and other ions, soil type, and plant type.

A few articles reviewed reported oxidation of Cr(III) to Cr(VI) in soil and possibly in plants in small amounts (Bartlett and James 1988; Mishra et al. 1995; Skeffington et al. 1976). As pointed out by Barlett and James (1988), depending on availability of organic acids from plant roots, oxidation of Cr(III) to Cr(VI) may increase absorption by plant roots, as Cr(VI) is more mobile.

1.3 Data Used in CalEPA's OEHHA Air Toxic Hot Spots Program Risk Assessment Guidelines

As mentioned above, OEHHA's draft guidance on UFs for Cr(VI) in edible plants (i.e., homegrown produce) is based on several published articles that quantify chromium uptake (OEHHA 2012). In the previous guidance document (2000), OEHHA used transfer coefficient data from Baes et al. (1984) and adjusted for the wet weight of the plant part and wet weight of soil by Clement Associates (1988) to derive plant UFs. Baes et al. (1984) estimated a soil-to-plant transfer coefficient for total chromium based principally on analysis of literature references and comparisons of observed and predicted elemental concentrations in foods. For chromium, the soil-to-plant transfer coefficients were derived from three different studies: one with pumpkins and pumpkin vines from East Tennessee; one with leaves, seeds, roots, and stems from sedge grass

and nut grass; and one with sweet corn, field corn, and grain from fields where sewage sludge had been applied. The recommended root UF was 0.001, and the recommended leafy UF was 0.0008 in the previous guidance document. Although the empirical data from these studies measured only total chromium (no speciation), OEHHA recommended these values be applied to Cr(VI) as well.

In the updated February 2012 draft document, OEHHA created a database to assemble the data and calculate UFs (document does not indicate why they now created this database). The references cited in the new draft document for Cr(VI) UFs are not mentioned in the previous document. The updated leafy UF of 0.3 was based on a study by Cary et al. (1977a) based on observations using lettuce, spinach, and buckwheat that were grown for extended periods in Cr(VI)-supplemented nutrient solutions. Only total chromium was ultimately measured in the different tissues. The root UF is not based on any quantitative data; OEHHA used the leafy UF of 0.3 and multiplied it by a factor of 10 to derive a root UF of 3. OEHHA cites Srivastava et al. (1994) as the basis of the factor of 10, where it was observed that roughly 10% of the chromium added as Cr(VI) to soil was incorporated in the above-ground plant parts, with the remainder incorporated into roots and bulbs and that the difference between above-ground and root chromium was also reflected by a 10-fold greater concentration of chromium in roots compared to above-ground plant parts.

Plant Tissue	Previous OEHHA UF	New OEHHA UF
Root	0.001	3
Leafy	0.0008	0.3
Ratio Root to Leafy	1.25	10

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