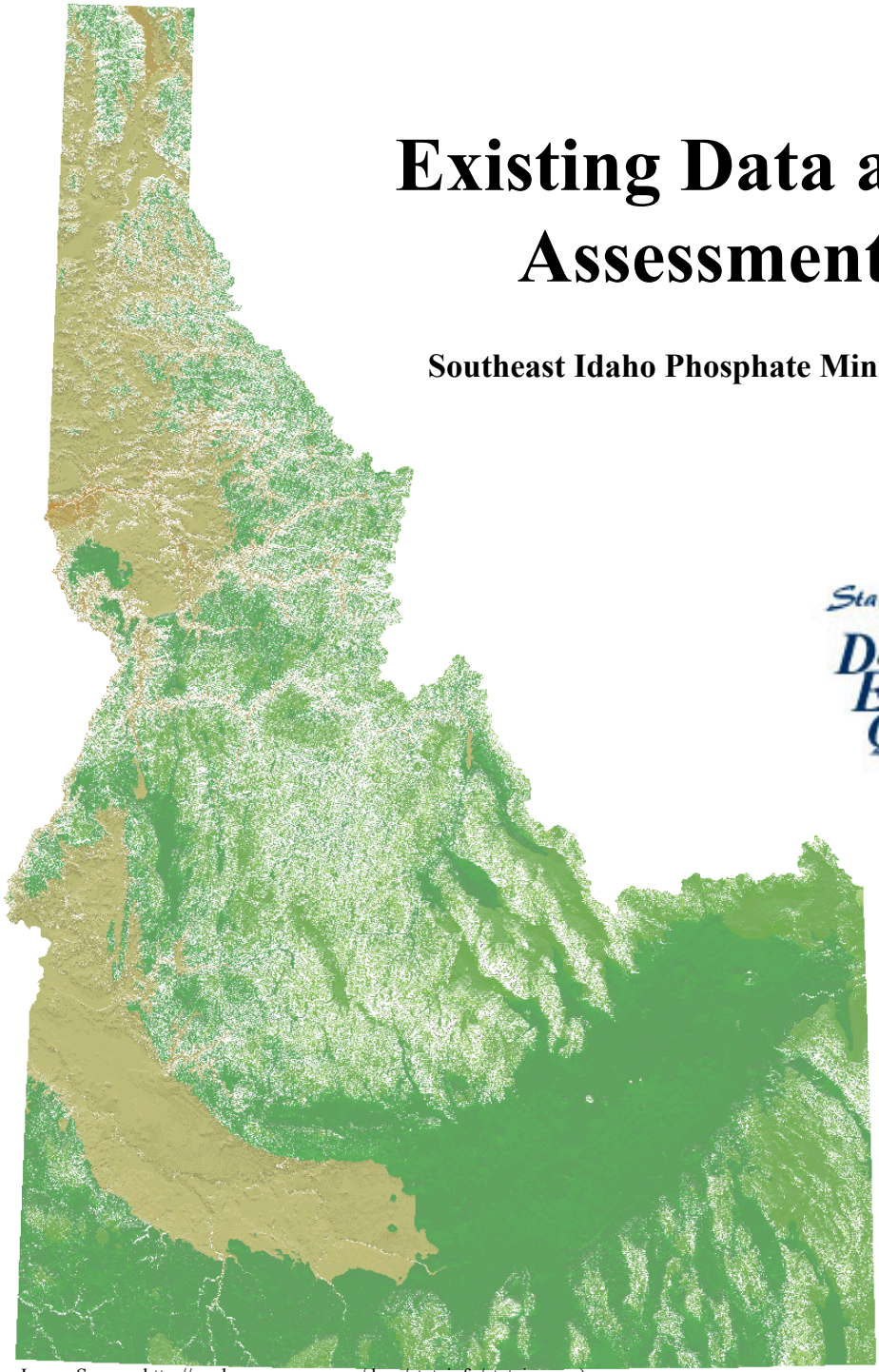
Final

Existing Data and Risk Assessment Review

Southeast Idaho Phosphate Mining Resource Area

October 2001



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State of Idaho Department of Environmental Quality

TETRA TECH EM INC.

AREA WIDE INVESTIGATION
SOUTHEAST IDAHO PHOSPHATE MINING RESOURCE AREA
Contract Number C023
Task Order AWI-00-01

Prepared for

IDAHO DEPARTMENT OF ENVIRONMENTAL QUALITY
Remedial Project Manager
Mr. Richard Clegg, P.E.
Pocatello, Idaho

FINAL

EXISTING DATA AND RISK ASSESSMENT REVIEW

Selenium Project

Southeast Idaho Phosphate Mining Resource Area

October 2001

Prepared by

TETRA TECH EM INC.
2309 Mountain View Drive, Suite 190
Boise, Idaho 83706
(208) 376-1986

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ACRONYMS AND ABBREVIATIONS

mg/kg	milligram per kilogram
mg/l	milligrams per liter
µg/g	microgram per gram
AES	Atomic emission spectrometry
AOAC	Association of Official Analytical Chemists
AOC	Administrative Order of Consent
ASA	American Society of Agronomy
ASTM	American Society of Testing and Materials
BIA	U.S. Bureau of Indian Affairs
BLM	U.S. Bureau of Land Management
BMP	Best management practice
CEC	Cation exchange capacity
COPC	Contaminant of potential concern
COPEC	Contaminant of potential ecological concern
CSM	Conceptual site model
DQO	Data quality objective
EDL	Estimated detection limit
ED	Exposure duration
EPA	U.S. Environmental Protection Agency
EPC	Exposure point concentrations
ERA	Ecological risk assessment
FMC	FMC Corporation
FS	U.S. Forest Service
FWS	U.S. Fish and Wildlife Service
HF	Hydrofluoric acid
HG	Hydride generation
HHRA	Human health risk assessment
HI	Hazard index
HQ	Hazard quotient
ICP	Inductively coupled plasma
IDEQ	Idaho Department of Environmental Quality
IDFG	Idaho Department of Fish and Game
IDHW	Idaho Department of Health and Welfare
IDL	Instrument detection limit
IMA	Idaho Mining Association
IRIS	Integrated Risk Information System
M	Molar
MCAWW	Methods for chemical analysis of water and wastes
MCL	Maximum Contaminant Level

MDL	Method detection limit
MOU	Memorandum of Understanding
MW	Montgomery Watson
N	Nitrogen
NAWQC	National Ambient Water Quality Criteria
NOAEL	No observed adverse effects levels
Nu-West	Nu-West Mining, Inc.
ORNL	Oak Ridge National Laboratory
PDF	Probability density function
PHHRA	Preliminary human health risk assessment
PRA	Probabilistic risk assessment
PRG	Preliminary remediation goal
QA	Quality assurance
QC	Quality control
RAGS	Risk Assessment Guidance for Superfund
RfD	Reference dose
SD	Standard deviation
SDHD	Southeastern District Health Department
SeAWAC	Selenium Area Wide Advisory Committee
SeWG	Selenium Work Group
SOP	Standard Operating Procedure
SRM	Standard reference materials
SUF	Site use factor
TRV	Toxicity reference value
TtEMI	Tetra Tech EM, Inc.
U of I	University of Idaho
UCL	Upper confidence limit
USDA	U.S. Department of Agriculture
USGS	U.S. Geological Survey
UTB	Upper tolerance bound

EXECUTIVE SUMMARY

The Idaho Department of Environmental Quality (IDEQ) retained Tetra Tech EM Inc. (TtEMI) to perform an independent review of the existing area-wide investigations and preliminary risk assessments compiled by the Idaho Mining Association (IMA) Selenium Committee. The emphasis of this review is to assess the adequacy of the existing characterization data and preliminary risk assessments. This information will be used to guide the development of final human health and ecological risk assessments associated with phosphate mining operations in southeastern Idaho.

The Selenium Project was initiated in the late 1990s to assess potential risks associated with phosphate mining in southeastern Idaho. As part of this effort a broad range of environmental media (surface water, groundwater, soils, plant and animal tissue) were collected and analyzed to characterize the nature and extent of contamination in the project area. The data collection protocols associated with the Selenium Project are generally consistent with industry standards for environmental investigations. The laboratory analytical methods produced high quality data, although the detection limits for some constituents may not have been appropriate relative to some toxicological standards. The issues associated with detection limits are important and influence many aspects of the preliminary human health and ecological risk assessment.

Overall, the investigation was approached from a phased perspective, whereby the results of preliminary sampling efforts were used to define the course of future investigations. Consequently, the number of samples was sometimes limited resulting in less than optimum sample sizes for supporting statistical analyses and risk conclusions.

The preliminary constituent of potential ecological concern (COPEC) screening process in 1997 identified six elements as candidates for additional study, including selenium, cadmium, manganese, nickel, vanadium, and zinc. Subsequent analyses of environmental media and reassessment in 1998 reduced the list of COPECs to selenium and cadmium. The soundness of the COPEC selection process was confounded by issues of limited sample size, the fact that only the results from surface water samples were considered in the 1997 assessment, and potentially inappropriate laboratory detection limits in the 1998 assessment. Therefore, the list of contaminants that pose a potential risk represents a fundamental deficiency in both the human health and ecological risk assessments.

The ecological and human health risk assessments were preliminary in nature and generally followed established U. S. Environmental Protection Agency (EPA) guidance. However, issues were noted relative to the development of the conceptual site model (CSM), assessment and measurement endpoints,

exposure assessment parameters, and toxicity factors. The principal concerns associated with the ecological risk assessment were the limited problem formulation and the degree of conservatism of the factors used in the assessment relative to standards that are generally applied in screening level risk assessments. These issues, while important, can only be resolved once the COPEC screening is fully supported by data developed using appropriate detection limits.

The conclusions of the preliminary human health risk assessment (PHHRA) are affected by the uncertainties of the COPECs screening process as they relate to the selection of the constituents of potential concern (COPC) for human health. Beyond the fundamental concern associated with the COPCs, the primary issue for the deterministic human health risk assessment (HHRA) is related to the lack of consideration for sensitive populations, such as children, or those with unique exposure potentials such as Native Americans or subsistence groups. The probabilistic HHRA did not follow EPA guidance and needs additional documentation.

Even though technical deficiencies have been identified in the existing investigations and preliminary risk assessments developed for the Selenium Project, those efforts provide a foundation for developing a definitive plan to assess risks associated with phosphate mining in southeastern Idaho.

1.0 INTRODUCTION

The Idaho Department of Environmental Quality (IDEQ) retained Tetra Tech EM Inc. (TtEMI) in October 2000 to perform an independent review of the existing data and preliminary risk assessment compiled and published by the Idaho Mining Association (IMA) Selenium Committee. TtEMI will also assist the IDEQ in the development of final human health and ecological risk assessments associated with past phosphate mining operations in the Southeast Idaho Phosphate Mining Resource Area (Resource Area) to support future agency risk management decisions for the region. This work is being carried out as part of an Area Wide Scope of Work referenced in the July 2000 *Interagency Memorandum of Understanding concerning Contamination from Phosphate Mining Operations in Southeastern Idaho* (MOU) negotiated between IDEQ and the tribal/federal agencies with jurisdictional responsibilities in the region. The MOU specified IDEQ as the lead agency for coordinating the future activities of the area wide investigation and for establishing regional cleanup guidance to assist lead agencies in implementing future site-specific remedial efforts. The area wide investigation is incorporated as part of an Administrative Order of Consent (AOC) negotiated with the responsible mining companies.

1.1 BACKGROUND

Phosphate mining has been practiced in southeastern Idaho throughout most of the 20th century, starting with the Waterloo mine in 1907. The major phosphate mines in this region are open pit or contour strip operations that were developed near surface exposures of the Phosphoria Formation. The phosphate ore is transported by truck, rail and slurry pipeline to local processing facilities in Soda Springs and Pocatello, Idaho. Production from this region represents a significant source of phosphorous for industrial and agricultural applications. Nearly 40 percent of the United States (U.S.) phosphate reserves occur in the Phosphoria Formation in southeastern Idaho, northern Utah, and western Wyoming.

In 1996, isolated livestock losses associated with excessive selenium uptake prompted concerns about potential ecological and human health impacts from past mining operations (Montgomery Watson [MW] 1999b). In response to these concerns, five companies operating mines in the region formed an "*ad hoc*" Selenium Committee with the IMA to characterize the environmental risks and identify mitigation measures associated with phosphate mining. The IMA Selenium Committee, composed of the companies listed in Table 1-1, was formed in 1997 to voluntarily and jointly address mining related environmental issues from a regional basis. An Interagency/Phosphate Industry Selenium Working Group (SeWG) was subsequently established to facilitate communication and participation by cooperating federal, state, local, and tribal entities. The SeWG consisted of voluntary representatives, including:

- IDEQ
- Idaho Department of Lands
- Idaho Department of Fish and Game (IDFG)
- Idaho Department of Health (IDH)
- Shoshone-Bannock Tribes
- Southeastern District Health Department (SDHD)
- U.S. Forest Service (FS)
- U.S. Bureau of Land Management (BLM)
- U.S. Bureau of Indian Affairs (BIA)
- U.S. Fish and Wildlife Service (FWS)
- U.S. Environmental Protection Agency (EPA)
- U.S. Geological Survey (USGS)
- Other Interested Stakeholders (i.e. ranchers, Greater Yellowstone Coalition, etc.)

Table 1-1. List of Area-Wide Mines and Operators, Southeast Idaho (MW 1999b)

Company	Mines	
	Active	Inactive
Astaris Production LLC	Dry Valley Mine	Gay Mine[1]
J.R. Simplot Company	Smoky Canyon Mine	Lanes Creek Mine Conda Mine Gay Mine[1]
Nu-West	Rasmussen Ridge Mine[2]	Mountain Fuel Mine Champ Mine North Maybe Canyon Mine South Maybe Canyon Mine[3] Georgetown Canyon Mine
P4 Production LLC[4]	Enoch Valley Mine	Henry Mine Ballard Mine
Rhodia Inc.		Wooley Valley Mine

Notes:
[1]Gay Mine was leased by FMC Corporation and J.R. Simplot Company, individually and jointly.
[2]Rasmussen Ridge Mine is leased by Nu-West Industries, Inc., an affiliated company of Nu-West Mining, Inc.
[3]South Maybe Canyon Mine is not included in the scope of the Selenium Project. It is being currently addressed under a consent order with Nu-West and the FS.
[4]P4 Production LLC is joint venture between Monsanto and Solutia, Inc.

In August 2000, the IDEQ was specified as the lead agency for coordinating the future activities of the area wide investigation and for establishing regional cleanup guidance to assist lead agencies in implementing future site-specific remedial efforts. The IDEQ subsequently established an Interagency Technical Group to coordinate their activities with the other jurisdictional and administrative agencies.

The IDEQ also established the Selenium Area Wide Advisory Committee (SeAWAC) to continue to solicit input from the mining companies, project stakeholders, and other participants in the former SeWG.

Much of the characterization and risk assessment work conducted under the auspices of the IMA Selenium Committee is documented in a series of reports prepared by MW (MW 1998a, MW 1998b, MW 1999a, MW 1999b, MW 2000). The IMA Selenium Committee implemented a phased approach for investigating potential impacts from phosphate mining activities (MW 1999b). Because of the broad similarities in mining operations and material characteristics, those investigations and the corresponding risk assessments were approached from an area-wide perspective. The focus of the investigations is a 2,500 –square mile area in southeastern Idaho that comprises portions of Caribou, Bear Lake, Bonneville, and Bingham counties (Figure 1). This region contains 15 mines previously owned or operated by FMC Corporation, J.R. Simplot Company, Nu-West Industries, Inc. and Nu-West Mining, Inc. (Nu-West), Rhodia, Inc., and P4 Production LLC (Table 1-1), as well as numerous "orphaned" mine sites primarily of underground design. One of the 15 mines, the South Maybe Canyon Mine, is being addressed separately under a consent order between Nu-West and the FS and is not included in the scope of the Selenium Project.

According to MW (1999b), the overall objectives of the investigations were to:

- Characterize the extent and magnitude of selenium and other target element releases from phosphate mine waste rock in a broad range of environmental media including surface water, sediments, groundwater, soil, and vegetation.
- Characterize the threat of releases of chemical constituents from waste rock including selenium and other target elements to human health, livestock, and aquatic and mammalian wildlife.
- Initiate a Management Study to develop and identify Best Management Practices (BMP) for mitigating potential releases of selenium or other target elements associated with historic, current, and future phosphate mine facilities.

Additional studies of the general geology of the Phosphoria Formation and site-specific investigation of selenium biogeochemistry have been or are being conducted by the various entities in the SeWG (e.g., USGS, FS, IDFG, FWS, and individual mine operators). These investigations are described in more detail, as appropriate, later in this report.

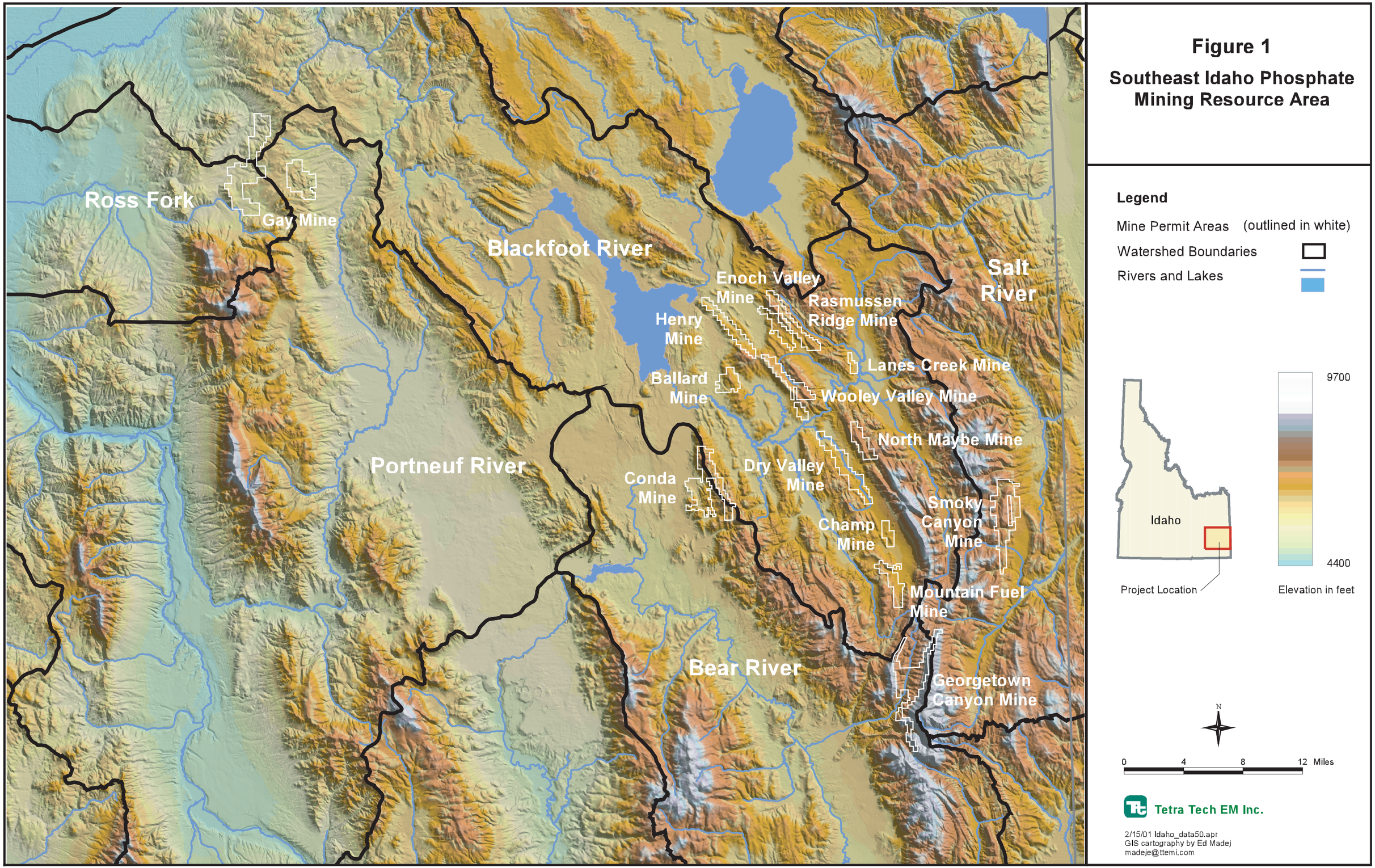

Figure 1

Southeast Idaho Phosphate Mining Resource Area

1.2 OBJECTIVES

This report, prepared by TtEMI, represents the initial task of a multi-task process outlined in Contract No. CO23 and Task Order No. AWI-00-01 (Area Wide Data Review/Risk Assessment). The major objectives of this project are to:

- Review and assess the existing data and preliminary risk assessment work
- Establish the data requirements to support area-wide ecological and human health risk assessments
- Develop sampling and analysis plans and studies to fill potential data gaps
- Finalize area-wide ecological and human health risk assessments

The emphasis of this particular report is to assess the adequacy of the existing characterization data and risk assessment. In general, it is easy in hindsight to be critical when conducting a comprehensive technical review. TtEMI recognizes the inherent difficulties and practical considerations associated with characterizing potentially hazardous constituents in multiple media and over a large geographical area. Additionally, the unique and complex chemistry of selenium and the generally imprecise understanding of its reaction in the environment further complicate the assessment of risk. The intent of this critique is to provide a basis for further discussion. The goal of all project stakeholders is the ultimate development of operationally viable mitigation measures. The data review and gap analysis, timely collection of critical data needs and the prudent completion of a final risk assessment will allow the supporting agencies to make the necessary risk management decisions required to formulate remedial action goals and objectives.

The existing reports developed by the IMA Selenium Committee have numerous and significant positive attributes. TtEMI recognizes the level of effort that is required to develop clear and concise reports. It is evident that some of the analysis was completed using best available information, which is a common and practical approach for phased investigations of this nature. The work reported by the IMA Selenium Committee represents a worthwhile undertaking and forms the written record for further study. It should be understood, TtEMI's identification of deficiencies is an attempt to maintain a balance between practicality, scientific rigor, and the need to address the concerns of a diverse group of stakeholders. In general, the decision to identify a deficiency was based on whether TtEMI's interpretation of the data was significantly different than that presented by MW, and whether the written record and/or scientific basis for the resulting conclusions would satisfy or withstand the scrutiny of the many interested parties.

Normal scientific controversy aside, this typically implies that the data or the fundamental understanding of the processes needs to be enhanced to support the interpretation.

Section 2 of this report provides an evaluation of the pertinent sources of data and Sections 3 and 4 provide a review of the ecological and human health risk assessments, respectively. Appendix A includes the data quality evaluation report. Specific recommendations for future investigations will be included in a Data Gaps Technical Memorandum scheduled for development following this initial review document and finalization of a conceptual site model (CSM). Appendix B is a review of literature related to selenium in the environment.

2.0 EXISTING DATA REVIEW

One of the key aspects of risk assessment is the characterization of the nature and extent of contaminants in the environment. Risks associated with potentially hazardous substances are dictated by the form, quantity, and location of the material with respect to the likelihood of exposure to a target population. For example, risks associated with hazardous materials dispersed at low concentrations over a large unpopulated area are less than if the material is concentrated in a smaller or more populated area. In many situations, the chemical form, physical condition (particle size), and environmental setting (acid versus alkaline soils) are important since these factors may affect mobility and bioavailability of the material in the environment.

This section discusses evaluation of the methods and existing data used in the preliminary risk assessment with emphasis on the work that is documented in three MW reports:

- Fall 1997 Interim Surface Water Survey Report (MW 1998a)
- 1998 Regional Investigation Report (MW 1999b)
- 1999 Interim Investigation Data Report (MW 2000)

The data are evaluated from both a quantitative and qualitative perspective, as appropriate, and are discussed in the following sections.

2.1 OVERVIEW OF PREVIOUS INVESTIGATIONS

This section provides a brief overview of the data contained in the primary investigations conducted in the Resource Area that form the basis for the current risk assessments. A wide range of environmental media and facilities were sampled and analyzed including biotic and abiotic media. Table 2-1 lists the types of media and number of locations sampled as part of the area-wide investigations. Table 2-2 summarizes the range of analytical results for selected analytes for each media type from the 1997, 1998, and 1999 investigations. Overall, the investigations were conducted using a phased approach where preliminary sampling was used to help define the requirements for future investigations. The results of these investigations are discussed in more detail in other sections of this report, where appropriate.

Table 2-1. Summary of Media Analyzed to Support the Selenium Project

Media	Location Type	Locations Sampled by Year[1]		
		1997	1998	1999
Surface Water	Streams	31	41	12
	Background Streams	6	16	--
	Waste Dump Seeps	5	5	--
	French Drains	1	2	--
	Stock Ponds	2	7	--
	Tailings Ponds	1	5	--
	Misc. Facilities	24	2	--
Sediment	Streams	--	38	--
	Background Streams	--	16	--
	Waste Dump Seeps	--	5	--
	French Drains	--	2	--
	Stock Ponds	--	7	--
Soil and Vegetation	Waste Dumps	--	9	--
	Waste Dump Seeps	--	5	--
	Background	--	3	--
Groundwater	Private Wells	--	1	--
	Stock Wells	--	3	--
	Mine Wells	--	14	--
Trout Fillets	Streams	--	3	--
Trout Eggs	Streams	--	--	Blackfoot River and Henry's Lake
Bird Egg		--	--	Area-wide
Elk Tissue		--	--	Area-wide
Beef Tissue		--	--	Henry Mine

Notes:
[1]Represents the total number of locations that were sampled each year. A few of the locations were sampled every year while other locations were sampled only once. At some locations, multiple samples were collected.

Fall 1997 Interim Surface Water Survey: The 1997 survey represents the initial effort to assess surface water quality in the Resource Area. The objectives of the survey were to:

- Assess the surface water quality at selected locations resulting from potential selenium releases from phosphate-mining operations in southeast Idaho.
- Provide an initial indication as to whether livestock health could be impacted by selenium releases from phosphate-mining operations.
- Obtain high-quality preliminary surface water data and background data to evaluate the need for replicate sampling for future work.

Table 2-2. Analytical Results of Samples from Selected Media Collected in the Selenium Project Area

Media and Location Type	Total Number of Samples Collected[1]	Range of Analytical Results[2]											
		Selenium		Cadmium		Manganese		Nickel		Vanadium		Zinc	
		Min	Max	Min	Max	Min	Max	Min	Max	Min	Max	Min	Max
Surface Water (mg/l):	**238**												
Streams	128	-0.00089	0.583	-0.0035	0.0047	-0.0041	0.53	-0.017	0.03	-0.034	0.18	-0.009	0.13
Background Streams	37	-0.00089	0.002	-0.0034	0.004	-0.00053	0.33	-0.01	0.026	-0.028	0.021	-0.0078	0.065
Waste Dump Seeps	14	0.00106	2.0	-0.0022	0.03	0.00057	0.51	0.003	0.48	0.0076	0.062	-0.0013	1.5
French Drains	5	-0.00028	0.24	0.0004	0.0059	0.056	1.5	0.022	0.048	0.0075	0.025	0.0023	0.23
Stock Ponds	15	0.00052	0.12	-0.0014	0.0052	0.0031	0.11	-0.0013	0.03	-0.01	0.094	-0.00042	0.07
Tailings Ponds	11	0.00047	0.03	0.00019	0.0083	0.0017	0.077	0.0036	0.031	0.025	0.18	0.0083	0.055
Misc. Facilities	28	0.000352	0.185	-0.0011	0.0059	0.011	0.046	0.01	0.029	0.022	0.039	0.0075	0.074
Sediment (mg/kg):	**68**												
Streams	38	0.22	9.4	1.8	11	4.9	6500	12	97	16	95	20	270
Background Streams	16	0.34	2.2	1.8	9.1	49	3800	17	69	16	71	38	150
Waste Dump Seeps	5	7.1	240	5.7	130	72	5800	36	630	55	780	140	2100
French Drains	2	2.9	76	7.6	13	700	6000	58	240	62	120	220	930
Stock Ponds	7	1.2	69	6.4	130	80	740	40	330	77	1000	130	1800
Soil (mg/kg):	**65**												
Waste Dumps	45	2.3	210	4.9	91	86	5500	740	3900	60	640	200	1800
Waste Dump Seeps	5	0.69	330	7.4	110	77	2400	380	4000	66	520	130	2100
Background	15	0.61	16	4.9	28	510	4300	310	1100	43	150	110	450
Vegetation (mg/kg):	**65**												
Waste Dumps	45	0.19	84	0.093	8.4	12	120	0.92	18	-0.71	9	19	140
Waste Dump Seeps	5	0.18	48	0.39	1.2	11	94	1.2	10	-1.3	0.41	24	100
Background	15	-0.015	0.78	0.1	2.1	27	92	0.52	2	-0.89	1.2	19	43
Groundwater (mg/l):	**35**												
Private Wells	2	0.00038	0.00087	0.0004	0.0026	0.0032	0.0061	-0.0033	0.0071	0.00081	0.016	0.040	0.042
Stock Wells	6	-0.000018	0.0083	-0.001	0.0032	-0.00042	0.012	-0.0034	0.014	-0.0056	0.024	0.10	1.3
Mine Wells	27	0.000006	0.033	-0.0022	0.0085	-0.0002	0.3	-0.0073	0.18	-0.011	0.025	-0.0015	1.1

Notes:

[1]Number of samples reported in the MW documents (MW 1998a, MW 1999b, MW 2000) for 1997, 1998, and 1999. Does not include quality control samples.

[2]The range of analytical results are reported directly from the MW documents (MW 1998a, MW 1999b, MW 2000).

The 1997 water quality survey was intended to be a preliminary investigation that would lay the foundation for subsequent regional investigations. A total of 70 surface water locations were sampled, including 37 stream locations and 33 mine facilities. Background water samples were collected at 6 stream locations. All water samples were collected in September and the analytical suite consisted of total and dissolved selenium and total dissolved solids.

The results of the 1997 survey are documented in the Fall 1997 Interim Surface Water Survey Report (MW 1998a). The results showed that surface water samples collected from, or near, mine facilities contained elevated concentrations of selenium. Of the 70 sample (samples vs. locations, reference the phone conversation) locations, MW stated that 35 exceeded the EPA chronic aquatic cold-water standard of 0.005 mg/l; 17 exceeded the upper range of veterinary advisory levels for livestock drinking water (0.05 mg/l); and 2 exceeded the lower range known to cause chronic selenosis in mammals (0.5 mg/l). The highest selenium concentration (1.55 mg/l) was in a sample collected from a waste rock dump seep.

TtEMI is unaware of the existence of an EPA "chronic aquatic cold-water standard" for selenium that is an enforceable limit. The assumption is made that the level of 0.005 mg/L referred to in the MW report (MW 1998a) is actually the National Ambient Water Quality Criteria Freshwater Continuous Criterion Concentration (NAWQC CCC) for total recoverable selenium from 40 CFR 131.36. The MW COPEC screening for surface water did not use site-specific values for hardness to adjust the reference values, where needed. The assumptions used to derive the hardness adjusted screening values were not presented in the report.

1998 Regional Investigation: In 1998, the media representation was increased to include groundwater, stream sediments, soils, vegetation, and trout fillets. The frequency of stream sampling was also increased to include the spring runoff (May), as well as the September low-flow event. Similarly, the analytical suite was expanded to include a broad range of parameters, including six target elements:

- Selenium
- Cadmium
- Manganese
- Nickel
- Vanadium
- Zinc

According to MW (1999b), the objectives of the 1998 investigation were to:

- Characterize the extent and magnitude of selenium and other target element releases from phosphate mine waste rock in a broad range of environmental media.
- Characterize the threat to human health, livestock, and aquatic and mammalian wildlife from the releases of selenium and other target elements from waste rock.
- Initiate a Management Study to develop and identify BMPs for mitigating potential releases of target elements.

Surface water samples were collected from 57 stream locations and 21 mine facilities. Sediment samples were collected at 54 of the stream locations and 14 of the mine facilities. Trout were collected at 3 of the stream sampling locations. Groundwater was collected from 18 wells, including 1 private well, 3 stock wells, and 14 mine wells. Soil and vegetation samples were collected from 9 waste dumps, 5 waste dump seeps, and 3 background locations. The 9 waste dump sample locations were distributed among 5 of the 14 mines, while the 5 seeps were at 3 of the mines. The background locations for surface water, soils and vegetation were selected in areas with natural exposures or outcrops of the Phosphoria Formation.

The surface water sample results showed that 12 of the stream surface water samples and 15 of the mine facility surface water samples exceeded the NAWQC CCC for selenium of 0.005 mg/l. The waste dump seeps and french drains typically had the highest concentrations of selenium. Only two of the samples exceeded the NAWQC CCC for cadmium; both were from mining facilities. According to MW (1999b), the other target elements do not appear to be a concern. Groundwater sample results from two of the mine wells (non-potable water source) exceeded the maximum contaminant levels (MCL) for cadmium (0.005 mg/l) and nickel (0.1 mg/l). All other groundwater results were below the MCLs for the other target elements.

In general, the sediment, soil, and vegetation sample analysis results indicate elevated levels of the target elements at sample locations associated with mining facilities. The trout fillet results indicated that the selenium levels in fish tissue were higher where NAWQC CCC for selenium was exceeded than in streams where the selenium levels were below the criterion; however, the results were based on a relatively small sample population.

The data collected in 1998 were used in the preliminary ecological and human health risk assessments and are documented in the 1998 Regional Investigation Report (MW 1999b). The preliminary assessments

were intended to be refined based on new data gathered during future investigations. The preliminary risk assessments are discussed in more detail in Sections 3 and 4 of this report.

1999 Interim Investigation: In 1999, additional investigations were conducted to collect time critical data and implement special studies on selected biotic components in the Resource Area. Surface water was the primary environmental media sampled outside of the special studies and the list of target elements was reduced to selenium and cadmium. According to MW (2000), the objectives of the 1999 interim investigation were to:

- Characterize selenium and cadmium concentrations in surface water at select stream locations.
- Characterize selenium and cadmium concentrations in bird eggs.
- Characterize the sensitivity of native cutthroat trout to elevated concentrations of selenium.

Surface water samples were collected at 12 stream locations in 1999. Of the 12 stream locations, only 8 locations had been previously sampled in 1998. All 12 locations were sampled in May and 2 of the 12 locations sampled monthly through September. No additional sampling was conducted at background stream or soil-vegetation locations during the 1999 season. Existing municipal groundwater compliance data were compiled from Soda Springs and Fort Hall; otherwise, no groundwater samples were collected.

The surface water results showed that 10 of the 12 samples collected in May exceeded the EPA criterion for selenium of 0.005 mg/l. Only one exceedance was noted in the subsequent samples collected at the 2 stations monitored through September. The seasonal decrease in selenium concentrations with time is consistent with the surface water data collected in 1998. The compliance monitoring data for municipal water supply sources in Soda Springs showed historic selenium and cadmium concentrations well below EPA MCLs. No data were available for selenium and cadmium in the Fort Hall municipal water supply sources from 1990 through 1999.

Four special studies were initiated in 1999 to provide information on selected biotic components in the Resource Area:

1) Bird egg investigation
2) Cutthroat trout investigation
3) Elk tissue investigation
4) Cattle tissue investigation

The bird egg investigation is a two-year study being conducted by Dr. John T. Ratti, an ornithologist from the University of Idaho (U of I), to assess the target trace element concentrations in eggs across various trophic groups. In 1999, 215 eggs were collected from 27 bird species in four habitats, including seleniferous and non-seleniferous environments. Eggs were collected from 20 species in mining areas (seleniferous environments) and from 7 species in non-mining areas that were assumed to be non-seleniferous. The eggs were analyzed for selenium and cadmium concentrations. Preliminary data indicated that 7 of the 20 species (15 of 117 eggs) collected from the mining areas had selenium concentrations greater than 10 mg/kg (dry). This study is on-going and will be valuable in future risk assessment efforts.

The cutthroat trout investigation is also a two-year study and is being conducted by Dr. Ronald W. Hardy and Dr. Madison S. Powell at the U of I Aquaculture Research Institute at the Hagerman Fish Culture Experiment Station. The study consists of three components: (1) an egg viability study to determine if selenium concentrations are causing birth defects; (2) a feeding trial to determine if dietary selenium impacts growth rates, survivorship, or subsequent breeding success; and (3) a genetic analysis to evaluate whether test results might be skewed by survivorship bias (MW 2000). The preliminary results of the three studies are discussed in Section 3 of this report.

The elk investigation was a cooperative effort between the IMA Selenium Committee and the IDFG to assess selenium and cadmium concentrations in elk liver and skeletal muscle. The elk tissue samples were also analyzed for copper, iron, lead, manganese, molybdenum, and zinc. Approximately 229 elk were sampled resulting in 323 elk tissue samples, of which 251 samples were analyzed. The results indicated a correlation between the level of selenium and proximity of the kill location to a phosphate mine. The study found that the elk killed near phosphate mines typically had higher tissue selenium concentrations; however, tissue cadmium concentrations did not appear to be correlated. The elk study results are discussed in more detail in Section 3 of this report.

The cattle tissue study was an expansion of an existing cattle grazing study at the Henry Mine by Monsanto. According to MW's 2000 study, the objectives were to:

- Determine whether selenium levels in beef tissues from steers exposed to pastures affected by phosphate mining are elevated.
- Characterize levels of selenium in skeletal muscle and other soft tissues to reduce uncertainties in the PHHRA.

- Estimate the rate of depuration of selenium from beef tissue to reduce uncertainties quantified in the PHHRA.

A secondary objective of the study was to use the data to extrapolate the health effects to other wildlife grazing on affected pastures. The study compared selenium levels in 15 steers that grazed during the summer for a 9-week period on three seleniferous pastures and 5 steers randomly selected from native, undisturbed, non-seleniferous pastures. All 20 steers were pastured for one month on a non-seleniferous pasture before being transferred to a feedlot where they were monitored for four months. Liver and skeletal muscle tissue biopsy samples were collected three times and whole blood and serum was sampled every two weeks. The sample results showed that muscle selenium levels were higher in the steers grazed on the reclaimed lands than those grazed on the non-seleniferous pastures. This study contains important information on the selenium levels in beef grazed on reclaimed lands in the project area and should prove valuable for future risk assessment activities.

Results of the environmental media sampled in 1999 and discussions of the four special studies are presented in the 1999-2000 Interim Investigation Data Report (MW 2000).

2.2 SAMPLING METHODS

The sampling protocols presented in the 1997 Interim Surface Water Survey Report (MW 1998a) and the 1998 and 1999 regional sampling and analysis plans (MW 1998b and 1999a) for surface water, sediment, and groundwater are generally consistent with standard practices applied in environmental investigations. The methods were designed to promote the collection of representative samples and reduce the likelihood of cross contamination.

The mechanics of the soil sampling methods employed by MW are generally acceptable with adequate precautions to avoid cross contamination. The samples were collected from the upper 2-inches of soil which is acceptable for describing the surface conditions, but may be inadequate for relating soil-constituent levels to plant uptake. The soil sampling objectives need further clarification to determine the adequacy of the sampling protocol.

The mechanics of the vegetation sampling are generally considered acceptable. However, MW's Standard Operating Procedure (SOP) for plant sampling provides only general guidance rather than specific information on the methods used in 1998 investigation. The vegetation samples apparently represented total aboveground biomass (current and previous years growth) rooted in the sample

quadrants. Total aboveground biomass samples may underestimate selenium levels in the vegetation relative to the levels that might be found in the current year's growth. Specific information on the species that were collected may improve the interpretation of the results.

Fish tissue samples were collected from three locations where a viable human fishery was believed to exist to provide an initial assessment of selenium levels in fish that might be consumed by humans. This sampling may be appropriate for assessing human health issues, but may not be reflective of the ecological condition in low order streams. The analysis of fish fillets rather than whole fish may limit the application of the data to selected receptors.

2.3 ANALYTICAL METHODS

The analytical methods used to characterize the major environmental media (surface water, groundwater, soil, and sediment) are listed in Table 2-3. The analyses were performed using generally accepted methods prescribed by the EPA and other standard sources. The primary exception to this conclusion is the analysis of selenium, which was performed using methods employed at the U of I (Tracy and Moller 1990, Anderson and Issacs 1993, Anderson and Issacs 1995). The method employs a nitric-hydrochloric-perchloric acid (HNO_3-HCl-$HClO_4$) digestion of the environmental media to release selenium into solution. HCl and sodium borohydride are used sequentially to reduce the dissolved selenate to hydrogen selenide gas that is measured by hydride-generation, inductively coupled plasma atomic emission spectrometry (HG-ICP-AES).

The digestion procedure used by the U of I for plant and animal tissues is well founded and is preferable to the EPA Method 3050 digestion (HNO_3-HCl). Wet digestion procedures (strong acid digestion) of biological media (plant and animal tissue) are preferred over dry-ashing procedures for constituents like selenium that are susceptible to high temperature volatilization (Jones and Steyn 1973). The use of a mixed acid digestion that includes $HClO_4$ is necessary to release selenium from complex organic compounds and this practice should be continued.

Table 2-3. Major Analytical Methods Used in the Selenium Project Investigation

Parameter	Surface Water	Ground Water	Sediment	Soil	Vegetation
Cadmium	200.7	200.7	3050/6010	3050/6000	ICP
Manganese	200.7	200.7	3050/6010	3050/6000	ICP
Nickel	200.7	200.7	3050/6010	3050/6000	ICP
Selenium	ICP-HG	ICP-HG	ICP-HG	ICP-HG	ICP-HG
Vanadium	200.7	200.7	3050/6010	3050/6000	ICP
Zinc	200.7	200.7	3050/6010	3050/6000	ICP
Iron	200.7	200.7	3050/6010	3050/6000	ICP
Calcium	200.7	200.7	3050/6010	3050/6000	--
Magnesium	200.7	200.7	3050/6010	3050/6000	--
Sodium	200.7	200.7	3050/6010	3050/6000	--
Potassium	200.7	200.7	3050/6010	3050/6000	--
Sulfate	300.0	300.0	0.08 M $Ca(H_2PO_4)_2$	0.08 M $Ca(H_2PO_4)_2$	--
Chloride	300.0	300.0	--	--	--
Alkalinity	310.1	310.1	--	--	--
Hardness	Calculated	-	--	--	--
Ammonium–N	--	--	--	2 M KCl	--
Nitrate–N	--	--	--	2 M KCl	--
Phosphorus	--	--	--	0.5 M $NaHCO_3$	--
pH	--	--	--	USDA # 60-21a	--
CEC	--	--	USDA # 60-19	USDA # 60-19	--
Organic Carbon	--	--	USDA # 60-24	USDA # 60-24	--
Particle Size Dist.	--	--	ASA # 9 15-4.2.2	ASA # 9 15-4.2.2	--
Water Content	--	--	--	ASTM D2216-90	--

Notes:
AES = Atomic emission spectrometry
ASA = American Society of Agronomy
ASTM = American Society of Testing and Materials
CEC = Cation exchange capacity
ICP = Inductively coupled plasma
HG = Hydride generation
M = Molar
MCAWW = "Methods for Chemical Analysis of Water and Wastes." EPA 1983.
N = Nitrogen
SW-846 = "Test Methods for Evaluating Solid Waste." EPA 1996.
USDA = U.S. Department of Agriculture

EPA MCAWW Method 200.7 – Inductively Coupled Plasma
U of I Method – Inductively Coupled Plasma using Hydride Generation
EPA MCAWW Method 300.0 – Ion Chromatography
EPA MCAWW Method 310.1 – Titrimetric Alkalinity
EPA SW-846 Method 3050B – Acid Digestion of Sediments, Sludges, and Soils
EPA SW-846 Method 6010B – Inductively Coupled Plasma-Atomic Emission Spectrometry
Sulfate titration with 0.08 M calcium phosphate [$Ca(H_2PO_4)_2$]
Ammonia and nitrate titration with 2 M potassium chloride (KCl)
Phosphorus titration with 0.5 M sodium bicarbonate ($NaHCO_3$)
USDA SOP # 90 – Soil Salinity Laboratory
ASA Method #9 – Methods of Soil Analysis
ASTM Method D2216 – Water Content

Kubota and Cary (1982) recommend the HNO_3-HCl-$HClO_4$ digestion for soil-selenium in agricultural soils. The use of the HNO_3-HCl-$HClO_4$ is probably adequate for selenium analysis of the soils and rocks associated with the Phosphoria Formation since selenium is generally not a structural component in silicate minerals. However, the recovery of selenium and other constituents from soils may be improved by the use of a digestion procedure that includes hydrofluoric acid (HF) (e.g., HNO_3-HCl-HF-$HClO_4$), which has the capacity to completely dissolve silicate minerals, biogenic opal, and secondary silica precipitates. The USGS generally employed a 4-acid digestion (HNO_3-HCl-HF-$HClO_4$) to obtain total elemental composition in samples analyzed as part of their Phosphoria Formation investigations.

The EPA Method 3050 digestion used for metals other than selenium is consistent with EPA guidance, but may not provide an accurate depiction of the elemental composition of constituents associated with recalcitrant organic compounds, silicate minerals or opaline silica. Based on a review of the raw laboratory data, the inefficiency of the EPA Method 3050 digestion was evident in poor recoveries for some of the analytes in the Montana Soil standard reference material. The differences in sample pretreatment should be noted when comparing total metals analyses from different sources (i.e., U of I versus USGS).

2.4 QUALITY CONTROL AND DATA VALIDATION

Data validation is an assessment (independent from the reporting laboratory) of analytical data that characterizes potential limitations of the data relative to specific quality control (QC) criteria. The purpose is to provide an objective appraisal of individual data points, so that interpretations made using the data can be categorized with respect to scientific validity. The EPA provides guidelines for validating laboratory data that are used in environmental investigations (EPA 1994).

The data validation process generally considers all the functional elements used to create the sample results, including review of documentation from the time a sample is collected in the field until the final

results are calculated and reported. Documentation includes, but is not limited to, field notes, chain-of-custody records, laboratory sample receipt records, sample preparation logbooks, standard preparation logbooks, sample analysis run (including all raw data from the instrument), QC sample preparation and analysis records, and calculations.

The individual sample results are qualified based on the comparison of QC results with a set of project-specific QC criteria or general regulatory guidelines. QC results include instrument sensitivity (detection limits), instrument calibration, calibration verification, instrument blank analysis, method blank analysis, and all other method-required QC samples. Data with analytical limitations are marked with qualifiers defined in validation guidance. It is important to note that data may be qualified based on analytical uncertainty but remain valid. However, when serious analytical limitations are identified, data points may be rejected (determined to be invalid). Once the data are validated, they can collectively be used to determine whether project QC objectives of precision, accuracy, representativeness, comparability, and completeness are met.

Data evaluation is a follow-up to data validation and may be conducted by different reviewers. Data evaluation determines the usability of data by comparing all valid data points against the project's data quality objectives (DQO) established before sampling began. Data evaluation may also include (1) comparing results to screening levels or action levels, (2) conducting risk calculations for sensitive receptors, and (3) inputting results into modeling programs. However, data evaluation cannot be effectively undertaken without complete validation to determine whether data are valid.

2.4.1 MW Data Validation Procedure

MW developed and implemented an alternative process for data validation rather than using the EPA methods specified in SOP-NW-18.1 (MW 1998b) and SOP-18.1 (MW 1999a) for the Selenium Project. MW (2000) indicated that they used the Association of Official Analytical Chemists (AOAC) data validation process based on the work of Mandel and Linnig (1957), Linnig et al. (1954), and Wernimont (1985). Those papers discuss theoretical considerations associated with the use of statistical methods to evaluate constant and relative type errors in the development of laboratory calibrations curves, rather than a comprehensive validation process. Thus, the data validation method applied by MW was independently developed for the Selenium Project and does not include all aspects of the proper data validation process provided in EPA guidance (EPA 1994).

MW modified the uncensored (raw) laboratory data from the U of I prior to reporting and subsequent statistical analyses. The modifications involved the subtraction of the mean laboratory blank value from the sample results and the subsequent division by a slope factor developed from the results of the check standards (Equation 1). The laboratory-adjusted values were further modified by subtraction of the field equipment rinse blank results and dividing by the percent recovery for the matrix spikes (Equation 2). The equations are listed below and Section 3.4.2 in the 1999 Interim Investigation Data Report (MW 2000) provides a more complete description.

$$X_{LA} = (X_L - b_L)/ m_L \qquad \textbf{Equation 1}$$

$$X_{FLA} = (X_{LA} - b_F)/ m_F \qquad \textbf{Equation 2}$$

Where:

X_{LA} = laboratory adjusted value for a constituent
X_L = uncensored lab value for a constituent
b_L = mean laboratory method blank value for a constituent
m_L = slope of measured to known values for check sample and stand reference materials
X_{FLA} = field adjusted value for a constituent
b_F = mean field equipment rinse blank value for a constituent
m_F = mean percent recovery for matrix spike

The intent of the mathematical operations performed by MW was to improve the quality of the data under the assumption that constant and proportional errors were present in the raw data. The value of the laboratory adjustments (Equation 1) is questionable given the high quality of the laboratory data. The blank correction factors used by MW were, with few exceptions, below the estimated detection limit (EDL) developed by the laboratory. The EDL reported in the raw data is equivalent to an instrument detection limit (IDL). IDLs are typically determined using the following process:

1) Measure the instrument signal produced during the analysis of 7 to 10 laboratory water blank samples;
2) Calculate the standard deviation (SD); and
3) Multiply the resulting SD by 3.

Thus, the IDL is considered to represent the population of instrument noise under the assumption that the noise is random and normally distributed. Mandel and Linnig (1957) and Linnig et al. (1954) discuss both practical (chemical) and statistical tests for determining whether a blank correction of the analytical process is justified. Neither form of justification was provided in the MW reports. However, because the

method blanks in the majority of analyses are below the IDL, it is difficult to conclude from a practical perspective that the blanks represent a constant error of significant magnitude to justify correction of the environmental samples.

The relationship among the check standard and standard calibration curve slopes needs further clarification to determine if the m_L term is an appropriate correction for the data as applied in Equation 1. Modern laboratories commonly use matrix-matched standards to develop instrument calibration curves. Specifically, the concentration and quality of acid (matrix) in the standard calibration samples is similar to that in the environmental samples. In these situations, the influence of the matrix should already be accounted for in the slope calculations used to develop the standard calibration curve and subsequent results for the environmental samples. This process amounts to a slope correction to account for relative type errors as discussed by Mandel and Linnig (1957). Applying the slope correction a second time as in Equation 1 is redundant.

The field adjustments (Equation 2) need further justification to resolve conceptual concerns. The primary concerns are compound errors associated with the laboratory blank, uncertainties related to the initial composition of the rinse water, and extrapolation of the slope from the matrix recovery to samples outside the range of calibration. The field blanks (b_F) consist of the data from the field equipment rinse samples that represent rinse water collected after field sampling equipment is decontaminated. Distilled water obtained from local commercial sources was used to rinse the equipment. The following equation can be used to describe the major sources of error associated with this factor:

$$b_F = b_L + R_c + E_c \qquad \textbf{Equation 3}$$

Where:

b_F = field blank concentration
b_L = mean laboratory method blank value for a constituent
R_c = contaminants in the source rinse water
E_c = contaminants on the equipment after cleaning and rinsing

The errors associated with the laboratory blank (e.g., instrument noise, process interference, and contamination) are included in the b_F term (Equation 3). Thus, any errors associated with b_L are compounded in the calculation of X_{FLA} since they were previously subtracted in Equation 1. The degree of compounding will depend on the magnitude of the slope factor (m_L).

The validity of the field adjustment of the raw data is further confounded by the uncertainties associated with the initial composition of the source water. Because distilled water, rather than reagent grade deionized water, was used in the rinse process, the source water may contain trace levels of contaminants that are unrelated to the sampling process. Analysis of the source-rinse water was not available to determine if the distilled water is a potential source of contaminants. Nonetheless, it seems unlikely that the concentration of a contaminant in the rinse water would be fully represented in an environmental sample regardless of the source of contamination. If the contaminant source was the rinse water used to decontaminate sampling equipment, a correction factor would need to be developed to quantify the volume of rinse water that is actually contained in the samples.

2.4.2 Spot Validation of Selenium Project Data

TtEMI conducted a partial validation of a fraction (5 to 10 percent) of the surface water and soil data collected in the Selenium Project area. The validation that TtEMI performed is considered partial since not all the information that is typically evaluated was reviewed (e.g., initial instrument calibrations, chain-of-custody forms, lab notebooks). Data quality was evaluated for 8 water, 6 soil, and 2 sediment samples out of a total of 218 water and 133 sediment/soil samples collected in 1997 and 1998. Samples with results above the EDL for the major constituents were selected for review. The validation was conducted on results for these samples contained in an electronic file supplied by MW through the IDEQ. The results of the data validation are provided in Appendix A.

The conclusion reached in the partial validation is that the overall quality of the data package was acceptable. Minor problems were noted with calibrations, blanks, matrix spikes, laboratory control samples, and spiked reference materials based on the samples that were selected. However, because the validation was selective, it did not fully represent the quality of the entire data set. For instance, the partial validation indicated that the recoveries for some constituents were low suggesting that the sample results may be biased low. A more complete evaluation of the data was performed to determine if the conclusions of the partial validation were correct for the data set as a whole. The comprehensive evaluation is discussed in the following section.

2.4.3 Comprehensive Evaluation of the Lab Data

The fractional validation (5 to 10 percent) was complemented by a more comprehensive evaluation of the QC parameters in the raw laboratory data supplied by MW. This evaluation included a review of the following QC data for all analytical runs:

- Check Standards
- Blanks
- Matrix Spikes and Matrix Duplicates
- Laboratory Control Samples
- Standard Reference Material

Check Standards: Check standards were not consistently reported for all constituents in the earlier data sets (i.e., May 1998 water data). However, check standards were reported more consistently in the subsequent data sets. For the data set as a whole, the recoveries of check standards for the target analytes were generally within QC guidance limits of 85 to 115 percent. Good recoveries for check samples indicate that the instruments maintained calibration throughout the analytical run.

Blanks: The method blanks were generally below the EDL with the exception of some of the soil analyses (i.e., cadmium, calcium, selenium, sodium, and vanadium). The soil-blanks did not significantly exceed the EDL and would likely have fallen within the method detection limit (MDL), had it been developed. Thus, the blank results suggest that laboratory contamination was minimal.

Matrix Spikes: Matrix spike recoveries for the target analytes were, with few exceptions, within the QC guidance limits of 75 to 125 percent. All matrix duplicate relative percent differences were within acceptable QC limits of ≤ 20 percent for water samples and ≤ 35 percent for soil and sediment samples.

Laboratory Control Samples: Blank spikes were not consistently reported in the early analyses for all analytes, but subsequent data sets contained this information. Where reported, laboratory control sample (blank spike) recoveries for the target analytes were almost always within the QC guidance of 80 to 120 percent. These data indicate that matrix interference was generally minimal and within reasonable analytical bounds.

Standard Reference Materials: Internally and externally developed standards were reported as standard reference materials (SRM) to assess the accuracy of the analyses. The internally developed standards (e.g., soil south and house water reference) were developed by the U of I and should probably be considered laboratory control samples, rather than standard reference materials. Nonetheless, the recoveries were almost always within acceptable limits indicating good precision and possibly high accuracy.

The externally developed or commercial standards (e.g., Montana Soil 2710, Buffalo River Sediment, APG 7870) are conventional SRMs that were prepared and analyzed by outside sources to establish known values. The recoveries for the external standards were generally good with the exception of some of the soil and sediment analyses where the reported values deviated significantly from the known values. In these cases, both positive and negative deviations were noted depending on the element. Because the analytical methods used in the source lab that developed the SRM may vary from those used in the reporting lab, it is not uncommon for SRM recoveries to deviate from the true values. The low recoveries could be related to potential differences in pretreatment (two- versus four-acid digestion) or instrumentation (see Section 2.3).

Sensitivity: The issue of reporting limits (IDL, EDL, and MDL) needs to be clarified and defined relative to the potential water quality and toxicological criteria. Method detection limits can be lowered for some analytes and media by using different methods or instrumentation. These methods or instrumentation must be specified prior to analysis. The uncertainties related to detection limits for some constituents (metals other than selenium) and media (primarily water) represent the primary weakness of the Selenium Project data.

Overall Assessment: The laboratory data are considered to be high quality based on a comprehensive review of the QC information in the raw data package, analytical methods, and discussions with the current U of I laboratory staff. Only minor and isolated problems were noted with calibrations, blanks, matrix spikes, laboratory control samples, and standard reference materials. No apparent and consistent bias was detected in the analysis. The primary limitation of the data is related to uncertainties associated with detection limits relative to potential water quality guidelines. This concern is mainly restricted to surface and groundwater analyses for some of the target analytes, other than selenium.

2.5 STATISTICAL ANALYSIS

From a mechanistic perspective, the statistical analyses generally appear to have been performed correctly and the level of detail that was provided in discussing various statistical procedures demonstrates that the authors have a good understanding of statistical concepts. However, it is difficult to fully evaluate the statistical approach and analytical protocols given uncertainties associated with the experimental design and questions concerning both the reliability of the data (i.e., method detection limit) and the selection and application of the specific statistical tests. In some instances, statistical tests were used when the underlying assumptions for application of the tests were either not fully met or not verified. Moreover,

the DQOs were not explicitly outlined, so it was not always possible to evaluate if the data collection and analysis were adequate for supporting the human health and ecological risk assessments. Thus, there are outstanding questions concerning the selection of specific statistical tests and, more generally, whether both the quantity and quality of data collected were adequate to meet the DQOs for this project. Additional discussion of each of these issues is provided in the following sections.

2.5.1 Experimental Design

The specific objectives of each component of the sampling design (e.g., chemical characterization of soil, water, and biota at both site and background locations) needs to be explicitly stated in order to assess if adequate data were collected and if appropriate statistical procedures were applied to the data. For example, it is unclear whether sampling soil and vegetation from nine waste dumps at five mines was intended to make inferences about the entire population of waste dumps at all mines in the Resource Area, conditions at the individual dumps actually sampled, or the relationship between soil-selenium concentrations and plant uptake. In the case of the soil-vegetation sites, the sampling depth (upper 2 inches) was not sufficient to adequately characterize soil-plant uptake relationships. If the intent was to estimate the range or average elemental concentrations in the waste rock dumps, samples should probably have been collected at more than 9 waste dumps and from more than 5 of the 14 mines.

The sampling design employed (e.g., simple random, two-stage, stratified random, judgmental) should be explicitly stated to allow reviewers to determine if appropriate statistical tests were applied. The 3 background-soil and 9 waste dump locations were represented as simple random samples composed of 15 and 45 samples, respectively. The statistical independence of samples collected at each site is questionable (e.g., samples from individual rock dump, dump seep, and background sites appear to be subsamples from a single randomly selected quadrate within each of these locations) and the subsequent statistical analyses may be afflicted by problems associated with pseudoreplication (Hurlburt 1984). Because sample size figures prominently in tests of significance, conclusions associated with these sites need to be reevaluated. In other cases, the sampling designs may have been appropriate, but the total number of samples collected was inadequate to support the statistical tests that were conducted.

2.5.2 Distribution Testing

The probability density function (e.g., normal, lognormal, etc.) that best fits a particular data set must be determined prior to selecting the most appropriate statistical test. MW assumed that the environmental samples for the target analytes were represented by a lognormal distribution, but did not confirm this assumption by reporting the results of goodness-of-fit tests. Although not initially recognized, some of

the environmental data that were assumed to follow a lognormal distribution were later found to not be lognormally distributed based on goodness-of-fit testing (Personal Communication William Wright, 12/18/2000 and calculations performed as part of this review). Incorrect assumptions concerning the distribution of the data could have introduced bias into the analyses that were subsequently conducted (Gilbert 1987). Thus, it may be appropriate to reevaluate conclusions where statistical tests based on lognormal distributions were applied to non-lognormal data.

Any reevaluation of the data distributions should also consider the effects of sample size and detection frequency on goodness-of-fit and other statistical tests. In some instances, where the sample size was small, it may be useful to consider alternative approaches, such as resampling statistics, for estimating population parameters and conducting tests of hypotheses. There is abundant literature on specialized techniques that can be used for treating data below the detection limit for different intended uses (i.e., estimating population moments versus hypothesis tests).

2.5.3 Quantitative Reliability of Data and Statistical Testing

As discussed previously, the laboratory data is considered to be of high quality within the limitations of the methods and instrumentation that were used. It is unclear whether the method that MW used to avoid censoring the raw laboratory data affects the estimation of moments of populations or any subsequent tests of hypotheses. To have high confidence in the conclusions and statistical analyses presented in the preliminary risk assessment, it would be necessary to reanalyze the entire data set using more conventional methods for data validation and statistical testing. There are, as previously stated, concerns about the types of statistical tests that were applied to data sets with high proportions of below detection limit data. This concern is relevant regardless of the method of validation.

MW reported and statistically analyzed data from the environmental samples below both the IDL provided by the laboratory and the upper tolerance bound (UTB) values calculated by MW. The below detection limit data were used to calculate UTBs for the comparison of background and area-wide environmental populations. Gilbert (1987) and other sources support the use of raw lab results for data reported below detection limits. However, the use of these data must be qualified with respect to the types of statistical tests that can be performed based on the sample size and proportion of data above the detection limit. The concerns relative to below detection limit values are likely to be most prevalent in the surface and groundwater data since these substrates tend to be represented by low levels of constituents.

The comments in this section should not be viewed as a condemnation of the statistical analyses performed in the Selenium Project as a whole. The examples that are presented merely represent situations that require further clarification or possibly validation using alternative statistical approaches. Because many factors (e.g., detection limits, sample sizes, etc.) are systemic and interrelated in complex ways, it is difficult to quantify the impacts on the present conclusions of the study without performing a thorough reanalysis of all the data. Ultimately, these factors may not affect the conclusions that should be drawn, but they do introduce additional uncertainties into the study that confound interpretation of the data.

Finally, it is important to point out that environmental data sets present special challenges for data analysts and statisticians, but care should be taken to assure that efforts to apply state-of-the-art statistical procedures should not overshadow the importance of having a sound experimental design and the rigorous application of a DQO process. It is TtEMI's position that the primary focus of any reevaluation of the Selenium Project data should be first on providing clear and explicit statements concerning the DQOs for each of the study components, and second, on assuring that the level of statistical analysis applied is appropriately matched to the stated DQOs.

3.0 ECOLOGICAL RISK ASSESSMENT

Risk-related evaluations were submitted in three major documents produced for the Selenium Project (MW 1998b, 1999b, and 2000). The evaluations were preliminary in nature and focused on different objectives. The primary emphases of the risk evaluations in the individual reports were as follows:

- **1998 Sampling and Analysis Plan (1998b)**. MW used existing surface water data from two streams collected by FS and FMC as the basis for screening the contaminants of potential concern (COPC) for human health and contaminants of potential ecological concern (COPEC).

- **1998 Regional Investigation Report (1999b)**. MW evaluated the potential risk associated with COPECs and COPCs. This evaluation used a hazard quotient (HQ) approach for assessing risks to ecological receptors. Deterministic and probabilistic risk evaluations were conducted for human health.

- **1999 Interim Investigation Data Report (2000)**. MW presented a series of specialized studies that were undertaken to clarify the potential risk to human and ecological receptors.

3.1 EVALUATION OF EXISTING AREA-WIDE ECOLOGICAL RISK ASSESSMENTS

The Selenium Project reports are considered to be preliminary or screening-level Ecological Risk Assessment (ERA). In a screening-level ERA, conservative assumptions about exposure and adverse ecological effects are used in lieu of site-specific information that is not available or cannot be collected in a timely manner. This approach is designed to ensure that ecological risks are not underestimated. Because of the conservative nature of the assessment, potential risk identified in the screening-level ERA should not be interpreted to imply that a risk actually exists. Screening-level ERAs are used to determine either that COPECs pose a negligible risk to potential ecological receptors or that further evaluation should be conducted.

The MW reports were reviewed in the context of screening-level ERAs. TtEMI's review was conducted to evaluate the methods, data and input parameters, and the validity of the conclusions. To facilitate the review of the MW reports, the following comments were also considered to identify issues of concern.

- Response to risk assessments comments from Dr. Karl Ford (IMA 4/24/00)
- Response to SAIC comments on the Preliminary Human Health Risk Assessment, Draft 1998 Regional Investigation Report
- Comments on Preliminary Risk Assessment from Karl Ford
- Comments on the 1998 Draft Regional Investigation Report

- Comments on the 1998 Draft Regional Investigation Report
- Responses to comments on the 1998 Draft Regional Investigation Report (MW 1999b)
- Comments on cases ENV99-01P and ENV99-03P

TtEMI's comments are presented in the following sections by topic, rather than by specific report.

3.1.1 Contaminant of Potential Ecological Concern Screening

The goal of COPEC screening is to eliminate constituents that pose no apparent risk (EPA 1997a). As discussed previously, the screening process is conservatively biased to ensure that constituents that pose a potential risk are not eliminated at the screening stage. The initial screening of COPECs performed by MW was based on surface water data from Maybe and Dry Valley Creeks collected by the FS and FMC (MW 1998b). The surface water samples were analyzed for 16 inorganic constituents:

- Aluminum
- Antimony
- Arsenic III
- Arsenic V
- Barium
- Cadmium
- Chromium
- Copper
- Lead
- Manganese
- Molybdenum
- Nickel
- Selenium
- Uranium
- Vanadium
- Zinc

The surface water data were screened based on potential risks to aquatic and terrestrial receptors to focus the investigation on those contaminants that posed the greatest risk. Significant issues associated with the COPEC screening include the acceptability of the data set, derivation of numeric criteria for aquatic organisms, and the method used to screen constituents for terrestrial receptors.

3.1.1.1 Acceptability of Data Used for Screening COPECs

The data used for initial evaluation of COPECs consisted of a limited data set of surface water samples. No information is available concerning the number of samples collected, sample collection dates or methods, analytical methods used, detection limits, or laboratory quality assurance (QA). Based on those facts, the data used to screen COPECs is not believed to be acceptable for the following reasons.

- A large percentage of the analytical results were reported as below detection limit. Without information on methods and QA, the usability of the data for risk assessment cannot be evaluated. Variations in methods, detection limits, or problems with analyses could result in detection limits that are above acceptable screening criteria.

- Water quality data indicate that there is a strong seasonal variation in contaminant levels in streams downgradient of the mines (MW 1999b and 2000). The highest values are generally

associated with spring runoff. If the samples used in the preliminary COPEC screen were collected during late summer or fall the results may underestimate the concentration of contaminants in the water.

- The spatial distribution of samples (two streams) does not provide a representative sample of the potential water quality conditions that may exist throughout the Resource Area. A larger sample set representative of all watersheds and mine drainage areas is necessary to adequately screen COPECs.

3.1.1.2 Screening Criteria for Aquatic Receptors

The COPEC screening for aquatic receptors consisted of comparing the maximum detected concentrations to numeric toxicity criterion. Several sources of aquatic screening criteria were used, including National Ambient Water Quality Criteria (NAWQC), EPA lowest chronic values, U.S. Department of Energy surface water preliminary remediation goals (PRG), EPA tier II secondary chronic values, and Oak Ridge National Laboratory (ORNL) aquatic population EC20 values. The NAWQCs were used as the primary screening criteria. However, if a constituent was not listed in the NAWQCs, one of the other sources was used to establish the screening criterion.

Several issues are associated with the selection of screening criteria for COPECs for aquatic receptors.

- Several of the NAWQCs for metals are hardness dependent. However, no information was presented to document assumptions for hardness used in the assessment. In cases where hardness data are not available, the most conservative screening criteria should be used. Application of the hardness needs to be clarified for those constituents that are hardness dependent.

- Although a NAWQC was available for selenium, a less conservative value was selected based on the criterion maximum concentration for the Great Lakes system. The Great Lakes System criterion requires knowledge of the selenium speciation, which was not included in the report.

- In general, the rationale for the selection of the screening criterion was not well documented and justification for selecting less conservative criteria was not provided.

3.1.1.3 Screening for Terrestrial Receptors

The method for screening COPECs for avian and mammalian terrestrial receptors was based on toxicological benchmarks for selected receptors species. Surface water screening criteria were developed based on no observed adverse effects levels (NOAEL) for avian and mammalian test species. The NOAEL values were allometrically converted to account for differences in body weight between the test species and the selected receptor species. The resulting calculations generated a surface water concentration value that was deemed to be protective for terrestrial receptors.

This method is inappropriate for screening COPECs because it only accounts for exposure through the drinking water pathway and ignores indirect ingestion through the food chain. Excluding indirect ingestion may result in the elimination of a number of detected constituents that may pose a risk for which further evaluation is necessary. For the terrestrial receptors selected, ingestion of food, contaminated soil, or sediment contributes a larger percentage of the overall dose than ingestion of surface water (Taylor and others 1992). This oversight is particularly noteworthy for herbivorous and omnivorous receptors that consume plant materials that bioaccumulate metals to relatively high levels.

3.1.1.4 1998 COPEC Screening

The initial COPEC screening process resulted in the selection of cadmium, manganese, nickel, selenium, vanadium, and zinc for further evaluation (MW 1998b). In the 1998 Regional Investigation Report these six COPECs were reevaluated based on data collected in 1998 (MW 1999b). This phase of screening resulted in the elimination the COPECs identified in the initial screening, except for cadmium and selenium. Results of the 1998 screening must be qualified by uncertainties associated with the issues of sample size, statistical assumptions and data validation (see Section 2).

3.1.1.5 Conclusions Concerning COPEC Screening

Based on the issues discussed concerning the suitability of the data, selection of aquatic screening criteria, and methods used to establish terrestrial screening criteria, the results of the COPEC screening are considered inconclusive. Additional information and reassessment is needed to conclusively eliminate or focus the study on the appropriate COPECs for this region.

3.1.2 Ecotoxicological Assessment of COPECs

COPECs can induce a variety of effects that depend on the constituent, species, trophic level of the species, and other environmental factors. To conduct an ERA, it is necessary to understand the mechanisms of toxicity associated with each of the COPECs and likely categories of receptors that could be affected. In the absence of toxicity information, significant uncertainty may exist with respect to the selection of assessment and measurement endpoints. For example, a primary consumer may be inappropriately selected to evaluate a bioaccumulative chemical when the greatest risk is to higher trophic level receptors. The assessment may indicate that the chemical presents limited or no risk when significant risks are posed to receptors that were not evaluated.

Ecotoxicological information was not available in the 1998 Regional Investigation Report (MW 1999b). This information would have improved our understanding of the rationale for the selection of assessment and measurement endpoints.

3.1.3 Evaluation of the Ecological CSM

The ecological CSM is a key element of an ERA. Sufficient detail should be presented in the CSM to identify complete exposure pathways and the relationship of assessment endpoints to measurement endpoints (EPA 1997a).

The ecological CSM presented in the 1998 Regional Investigation Report is based on a block diagram that emphasizes physical transfer mechanisms and routes (MW 1999b). This is a commonly used type of CSM that follows EPA guidance for remedial investigations. The following issues are noted concerning the existing ecological CSM.

- Contaminant movement to and through groundwater was not considered in the ecological CSM. This pathway should be considered and included on the diagram, even if the pathway is considered to be incomplete.
- All pathways in the ecological CSM were depicted as being unidirectional. This depiction does not account for contaminants in sediment reentering the water column as dissolved constituents or being deposited as soil during flood events.
- In arid areas, almost all species utilize the available aquatic habitats. The ecological CSM did not recognize that terrestrial organisms may be exposed to riparian or aquatic vegetation and sediments.
- Entire groups of organisms, such as terrestrial invertebrates and upper trophic-level carnivores, were not identified in the CSM.
- Feeding habits and food chain pathways are important exposure routes for many contaminants. The ecological CSM does not clearly convey these pathways. In some cases, groups of organisms such as aquatic invertebrates or terrestrial plants are identified. In other cases, specific species are identified. To evaluate potential assessment endpoints, the receptors should be grouped into feeding guilds.
- Organizing the ecological CSM by media may obscure the cumulative exposure for each receptor or group. Some organisms or groups appear in as many as four blocks. It would be clearer to organize the CSM by groups of potentially affected receptors.

Overall, the ecological CSM is sufficient to convey a basic understanding of most of the potential exposure pathways. However, this generalized ecological CSM does not provide sufficient information to support an area-wide ERA.

3.1.4 Development of Assessment and Measurement Endpoints

Unlike human health risk assessment (HHRA), which evaluates only one species, the ERA involves multiple species with different degrees of exposure and toxicological responses. For the purpose of an ERA, investigations should focus on endpoints most likely to be affected, given the fate and transport mechanisms of the contaminants involved, ecotoxicological properties of the contaminants, habitats at the site, and potential ecological receptors (EPA 1997a). The following sections discuss assessment and measurement endpoints and evaluate the endpoints selected in the 1998 Regional Investigation Report (MW 1999b).

3.1.4.1 Assessment Endpoints

EPA defines an assessment endpoint as an "explicit expression of an environmental value to be protected" (EPA 1997a). Useful assessment endpoints define both the valuable ecological entities at the site and a characteristic of the entity to protect, such as reproductive success or production per unit area. Ecological resources may be considered valuable when their absence would significantly impair ecosystem function; when they provide critical resources, such as habitat or fisheries; and when humans perceive them as valuable, such as endangered species.

MW selected the following assessment endpoints to evaluate risk to ecological receptors:

- Protection of the growth and survival of aquatic/riparian organisms (e.g. fish, waterfowl, shore birds, marsh-dwelling passerines, omnivorous mammals, and herbivorous mammals)
- Protection of the growth and survival of large terrestrial herbivores

Additional assessment endpoints may be needed to evaluate terrestrial avian and mammalian carnivores. Without a consensus COPEC list, adequate ecotoxicological information for each of the COPECs, and a detailed ecological CSM, it is difficult to evaluate the adequacy of the assessment endpoints. Nonetheless, these broad assessment endpoints should be refined to provide additional focus to the ERA.

3.1.4.2 Measurement Endpoints

Assessment endpoints are usually not amenable to direct measurement. Instead, measurement endpoints that are related to assessment endpoints must be developed. A measurement endpoint is defined by the EPA as "a measurable ecological characteristic that is related to the valued characteristic chosen as the assessment endpoint and is a measure of biological effects (e.g., mortality, reproduction, growth)" (EPA 1997a). Measurement endpoints can include measures of exposure or effect. They are frequently numerical expressions of observations that can be compared statistically to a reference site or scientific study to detect adverse responses to a site-specific COPEC. Each measurement endpoint should correlate directly with a corresponding assessment endpoint and be based on accepted mechanisms of toxicity. Occasionally, multiple measurement endpoints may be necessary to properly evaluate a single assessment endpoint.

MW selected receptor-specific hazard indices (HI), as their measurement endpoints for terrestrial and riparian receptors. These HIs were calculated by summing the HQs. The receptors selected for calculation of HIs were cutthroat trout, red-winged blackbird, common snipe, mallard, muskrat, moose, sheep, horses, and cattle. The following issues are associated with the measurement endpoints selected by MW:

- HIs or HQs are not typically presented as measurement endpoints. An HQ is a numerical calculation that presents the relative potential for a specific adverse effect to occur. This adverse effect can vary and may include chick deformities, mortality, loss of balance, liver damage, or other types of effects. The HQ is calculated by dividing the daily dose of a specific COPEC received by a specific receptor by a toxicity reference value (TRV), typically a NOAEL that is derived from the literature. Therefore, the measurement endpoint should be specific to the receptor and the type of effect. For example, if the most conservative TRV was based on reproductive effects in avian species, a measurement endpoint might be stated as potential reproductive impacts to the common snipe.

- Only cadmium and selenium were considered in selecting endpoints. Additional COPECs may need to be evaluated. These additional COPECs may affect other species or have different mechanisms of toxic effect. Therefore, without a consensus list of COPECs, endpoints cannot be established without significant uncertainties.

Significant concerns exist with the development of the measurement endpoints. Without a consensus COPEC list, adequate toxicological information for each of the COPECs and a detailed ecological CSM, it is difficult to fully evaluate the adequacy of the measurement endpoints.

3.1.5 Exposure Assessment

MW conducted an exposure assessment for terrestrial and riparian receptors. In the exposure assessment of a screening-level ERA, EPA recommends that in the absence of site- or species-specific data, conservative assumptions should be used. These assumptions include concentrations of COPECs in various media, ingestion rates, type of food, body weights, site use factors (SUF), and exposure durations. EPA guidance (EPA 1997a) provides the following conservative assumptions for use in screening-level exposure assessments:

Area Use Factors -- All species should be considered to live and feed within the site at all times.

Bioavailability -- All COPECs should be assumed to be 100 percent bioavailable for all trophic levels and species.

Life Stage -- The most sensitive life stage for each species should be assumed to be exposed to COPECs.

Body Weight and Food Ingestion -- The lowest body weight indicated should be used in conjunction with the highest reported or calculated ingestion rate.

Dietary Composition -- The diet should be assumed to consist 100 percent of the most contaminated food item for the animal species.

The assumptions for each parameter used by MW are discussed in the following sections.

3.1.5.1 Exposure Point Concentrations and Biotransfer Coefficients

MW selected an upper bounding estimate for an exposure concentration based on the 95 percent upper confidence limit (95 UCL) of the data set, or in cases where the 95 UCL exceeded the maximum, the maximum detected value was used. Because of sample size limitations and high variability in the data, this resulted in the maximum detected values being used in most cases. Insufficient information was presented in the report to independently calculate 95 UCL values to verify that the appropriate exposure point concentration was used in each case. However, the general approach used is conservative and appropriate for a screening-level ERA.

Biotransfer coefficients are used to develop concentrations in various biological media for which no analytical data is available. Starting with an abiotic or biotic media concentration derived from laboratory analyses, biotransfer coefficients are multiplied by the starting concentration to estimate the concentration that may be present in higher trophic level organisms. The biotransfer factors used by MW appear to be appropriate for a screening-level ERA.

3.1.5.2 Body Weights

The selection of assumed body weights for each receptor is one of the more important assumptions in the screening-level ERA. For most receptors, food ingestion rates, abiotic rates, and allometrically converted receptor-specific TRV use body weight as a major input. Therefore, in a screening-level ERA, conservative or minimum reported body weights should be used to ensure that all potential risks are identified.

MW used average body weights for all receptors in their assessment, which is acceptable for a baseline ERA. However, because of the limited data set and numerous assumptions, using average body weights in a screening-level ERA may result in underestimating the potential risk associated with the COPECs.

3.1.5.3 Food Ingestion Rates

Food ingestion rates may be available from the literature or derived based on calculations in EPA guidance (EPA 1993). Food ingestion rates were calculated for each receptor based on average body weights (MW 1999b). However, according to EPA guidance (EPA 1997a), the screening-level exposure assessment should be based on conservative ingestion rates. Since the food ingestion rates were calculated from body weights, the maximum reported body weight for each receptor should have been used to calculate food ingestion rates. Therefore, using average body weights to calculate food ingestion rates may have resulted in underestimating the potential risk associated with the COPECs.

3.1.5.4 Abiotic Ingestion Rates

Water, soil, and sediment ingestion rates may be obtained from the literature or estimated using EPA guidance (EPA 1993). Water, soil, and sediment ingestion rates were calculated for each receptor based on average body weights (MW 1999b). Because the water, soil, and sediment ingestion rates were calculated using average, rather than maximum body weights, the analysis is considered to be non-conservative based on EPA guidance for screening level assessments (EPA 1997a).

3.1.5.5 Skin Surface Area, Contaminant-Specific Dermal Absorption Factors, and Soil Adherence Factors

Skin surface area, contaminant-specific dermal absorption factors, and soil adherence factors are all directly related to the dermal exposure pathway. While this pathway is normally evaluated in HHRAs, very little information is available to evaluate this pathway for ecological receptors. For most receptors, the dermal exposure pathway provides a small percentage of the overall dose. Because of the limited

information on the pathway and the minor contribution to the overall dose, this pathway is normally disregarded for most ecological receptors.

MW (1999b) calculated the skin, feet, and muzzle or beak areas based on equations provided in EPA guidance. The values used for contaminant-specific dermal adsorption and soil adherence were taken from EPA HHRA guidance and are not typically applied to ecological receptors.

3.1.5.6 Site Utilization Factor

The SUF for a specific receptor is a relative percentage based on the size of the contaminated area in relation to the home range of the receptor. This value is used to estimate the percentage of the dose the receptor receives based on the assumption that equal time is spent in all areas of the home range. For many receptors, the SUF is one of the most important parameters in determining the overall dose. Therefore, the SUF is normally assumed to be 100 percent for a screening-level ERA.

MW developed SUFs for each receptor based on data presented in the National Audubon Society's *Field Guide to North American Birds (1977)* and *Field Guide to North American Mammals (1996)*. These references generally do not provide sufficient information to calculate a defensible SUF and no additional justification was provided in the risk assessment report. EPA Wildlife Exposures Handbook (EPA 1993) presents home range data on a large number of avian and mammalian receptors. The data presented by EPA suggest that home range can vary significantly based on a variety of factors. Therefore, the basis for the home range value (maximum, mean, or minimum reported) should be presented for evaluation.

MW used SUFs for all receptors in their assessment to calculate a dose, which is an acceptable practice in a baseline ERA. However, because of the limited data set and numerous assumptions for other parameters, all SUFs should be assumed to be 100 percent. Using lower SUFs may result in underestimating the potential risk associated with the COPECs.

3.1.5.7 Exposure Duration

The exposure duration (ED) attempts to quantify the portion of the year that the animals actually use a contaminated area. This is primarily applicable to migratory or hibernating species. EPA guidance (EPA 1997a) recommends that for screening-level ERAs, a value of 100 percent be used for the ED.

MW assumed an ED of 50 percent for migratory birds, 100 percent for muskrat and moose, 16.7 percent for sheep, and 33.3 percent for horses and cattle to calculate the corresponding doses in their assessment.

This is acceptable in a baseline ERA; however, the rationale for these assumptions was not documented and needs further verification.

3.1.6 Toxicity Reference Values

TRVs are typically values that represent NOAELs determined from laboratory studies. The literature-based NOAELs are related to an adverse effect that is a specific adverse physiological impact to a specific receptor. NOAELs can be developed for reproductive, developmental, behavioral, neurological, or other impacts. TRVs are based on the most sensitive, ecologically significant impact identified from the literature for similar species (e.g., avian to avian and mammal to mammal).

In most cases, the NOAEL values identified in the literature are based on species that are not being evaluated in the risk assessment. Those values are converted based on differences in body weight between the measurement endpoint species and the species used in the study. Those allometrically converted NOAELs are then used as a species specific TRVs for evaluating the potential impacts from exposure to a specific COPEC.

MW obtained all of the NOAELs for terrestrial receptors that were used in the screening-level assessment from *Toxicological Benchmarks for Wildlife: 1996 Revision* (Sample and others 1996). Those NOAELs were allometrically converted for each receptor under consideration to create receptor specific TRVs for each COPEC. The following issues are associated with the TRVs used by MW:

- The NOAELs used were all based on reproductive effects. No consideration was given to other potential adverse effects and the TRVs may not represent the most sensitive effect and may underestimate the potential risk to ecological receptors.

- The studies from which the NOAELs were derived may not represent the most conservative studies. EPA Region 10 does not have published NOAELs for evaluating the appropriateness of the values used in the MW reports; however, the NOAELs used by MW were compared to NOAELs approved by EPA Region 9 for use in Superfund risk assessments. In all cases, the NOAELs used by MW were higher than the NOAELs approved by EPA Region 9.

- MW did not conduct specific analyses to determine the form of selenium present in the samples. The form of selenium strongly influences the toxicity of selenium to various receptors. Therefore, the lack of selenium speciation data introduces uncertainty into the assessment.

The methodology used by MW to develop receptor specific TRVs is generally acceptable. However, based on the issues discussed in this section, the TRVs used in the assessments may not have been sufficiently conservative for a screening level assessment.

3.1.7 Risk Calculations

The method used by MW in performing the risk calculations is commonly used and is acceptable.

3.1.8 Special Ecological Studies

Several special biological studies were presented to support the evaluation of data in the risk assessment. The study species included cutthroat trout (*Oncorhynchus clarki*), birds, domestic cattle, and elk. These studies can be used to supplement a risk assessment in a weight-of-evidence approach and were reviewed to determine how they supported the area-wide risk assessments and the uncertainty associated with each study. Each receptor study is discussed in the following sections.

3.1.8.1 Cutthroat Trout Studies

The study "Review of Selenium Exposure on Cutthroat Trout (*Oncorhynchus clarki*) " conducted by Ronald W. Hardy, and Madison S. Powell, Hagerman Fish Culture Experiment Station, Hagerman, Idaho, was evaluated to determine its ability to support risk conclusions. There were three parts to the study:

- Egg viability study to assess if dietary selenium concentrations are causing birth defects.
- Feeding trial to assess if dietary selenium impacts growth rates, survivorship, or subsequent breeding success.
- Genetic analysis to evaluate whether test results might be skewed by survivorship bias.

The study protocol is provided in Appendix B of the 1999 Interim Investigation Data Report (MW 2000) and the review comments are discussed below.

<u>Egg-Viability Study</u>

Some of the results of this study as reported by MW (2000) were as follows:

- The Blackfoot River fish eggs had higher selenium concentrations than did Henry's Lake eggs.
- The percentage of deformed fry was similar between fish and was an order below the percentage, described by Lemly (1993) as "being the upper range of background for fish not exposed to elevated levels of selenium."

- There was no discernable difference in the rate of birth defects.
- All selenium levels in fish eggs were below the suggested level of 10 mg/kg (dry) for indication of reproductive failure in fish (Lemly 1993) as stated in MW (2000).
- The tabulated egg concentration data was not correlated to the birth defects rate data.
- The observations suggested that either exposures to elevated selenium concentration in the water-column were insufficient to cause toxic accumulation in fish eggs or that cutthroat trout may not accumulate selenium as readily as do other fish species.

These data provide an estimate of selenium concentrations in fish tissue in an important fish species in the Resource Area. Useful information for evaluative purposes would be the selenium levels in the abiotic media where the fish were collected along with tissue levels in adult fish. Lemly (1996) did issue a toxic effects threshold for reproductive failure of 10 mg/kg (dry weight) for ovaries and fish eggs. However, Lemly (1998) also states "excess dietary selenium (>3 μg/g) causes elevated concentrations of selenium to be deposited in developing eggs, particularly the yolk." With knowledge of the tissue and abiotic media selenium concentrations, additional uncertainty associated with those data may be explained. The data may be available, but was not reported along with the results.

Feeding Trial

Results of the feeding trial provide useful data to compare against the reported selenium levels in fish tissue that can potentially cause toxicity. Some uncertainty will result from a lack of data indicating the selenium concentrations in sediments or water of the respective lakes at the time the trout were collected. With that data, the baseline selenium concentration in the fish can be verified before feeding trials were initiated. Again, the data may be available but were not presented in MW's report.

Genetic Analysis of Blackfoot River Cutthroat Trout

There were three objectives identified for this study (MW 2000):

- Determine the taxonomic status of cutthroat trout collected from the Blackfoot River and Henry's Lake Hatchery in 1999.
- Determine if cutthroat trout collected from Henry's Lake that are being used in selenium diet experiments are genetically different from those collected from the Blackfoot River.
- Determine if the cutthroat trout from the Blackfoot River watershed lack genetic variation compared to cutthroat trout populations from adjacent areas.

MW (2000) concluded that there was no evidence to indicate that the population of Yellowstone cutthroat in the Blackfoot River has less genetic diversity than observed in Yellowstone cutthroat trout populations that live in non-seleniferous habitats; however, no data were presented to support this assumption.

3.1.8.2 Bird Egg Studies

The study "Analysis of Selenium and Cadmium Levels in the Eggs of Selected Avian Species" developed by John T. Ratti, Research Professor, Department of Fish and Wildlife Resources, U of I, was evaluated to determine its ability to support risk conclusions. The study was initiated in the spring of 1999 and data from the first sampling field study were published in the 1999 Interim Investigation Report (MW 2000). The objectives of this study were to determine:

- If selenium and cadmium in watersheds associated with mining activity are present in avian tissues (eggs).
- If present, are selenium and cadmium levels significantly higher than those from background (i.e., control) areas in the immediate region not disturbed by phosphate mining.

Selenium in the bird egg, rather than in the parent bird, causes developmental abnormalities and death of avian embryos (Heinz 1996). Thus, selenium levels in the egg provide the most sensitive measure of evaluating toxicity hazards to birds. These results provide another data point, even if estimated, that can be used on a weight-of-evidence approach to evaluate risk. However, there are some uncertainties associated with the studies:

- What portion of the each bird's home range overlaps the areas affected by mining activities.
- The data appear to address only omnivorous birds and in only one or two of the habitat types of interest. The results of the first year of data for birds collected in control areas, only two species of birds, American robin and yellow-headed blackbird were consistently found in all habitat types. The diets of these birds indicate that they are omnivorous (Ehrlich and others 1988). Second to those two species was the brown-headed cowbird and song sparrow that were found in three of the four habitats. Those two species are also omnivorous, even though song sparrows may be considered as herbivorous in some areas of the U.S. (Ehrlich and others 1988). All other species reported were found in only one or two of the habitats of interest. For bird eggs collected in mining areas, only four species were found with eggs in all habitat types: American robin, brown-headed cowbird, red-winged blackbird, and song sparrow. Second in quantity of habitats where eggs were found was the mallard. All of these species are omnivorous (Ehrlich and others 1988) with the exception of the song sparrow.

There are some additional uncertainties associated with the anticipated data for the 2000 field study:

- Five bird species were targeted for the 2000 field study. One of these species, the American coot, was only found in two of the four habitats in the control area, and in only one habitat of the mining area. Therefore, its inclusion may again limit the data for habitats of interest.

- Only two of the bird species (red-winged blackbird and yellow-headed blackbird) selected for sampling in the 2000 field study were found to have selenium levels in eggs above the 10 mg/kg threshold. In addition, of the seven birds with selenium levels in eggs greater than 10 mg/kg in the 1999 study, the song sparrow, was found in all of the mining area habitats and in three of the four control area habitats, but was not listed as a species to be sampled in 2000. Therefore, these data may not be as applicable to all habitats and feeding types as originally planned.

- Data was provided on selenium concentrations in various streams in the area of study. However, there is no correlation of the stream data with nest locations where eggs were collected. Therefore, it is unclear if the areas where nests were found were actually impacted by selenium from the mine sites.

3.1.8.3 Beef Depuration Studies

The Beef Depuration Study conducted by the SeWG and the U of I, Rangeland and Management Department, and the U of I Beef Center was evaluated to determine its ability to support risk conclusions. The primary objectives of this study were to (MW 2000):

- Ascertain if selenium levels in beef tissue collected from steers exposed, under presumed worst case conditions, to pastures affected by runoff from phosphate mining areas are elevated and, if elevated, to what degree.

- Characterize levels of selenium in skeletal muscle and other soft tissues, such as liver, heart, and kidney, to reduce uncertainties associated with the PHHRA.

- Estimate the rate of depuration of selenium from beef tissue in order to reduce uncertainties associated with the PHHRA.

A secondary objective was to use this information to evaluate the potential health effects to the steer themselves, and to extrapolate this information to other grazing cattle and wildlife. There is some uncertainty associated with the results of this study as indicated below:

- The study did not indicate the selenium levels in the soils and the forage where the steers were pastured for the nine-week grazing period or the one-month pasturing on lowland pasture (non-seleniferous). This information would be useful to better understand the relationship between the selenium concentrations in steer tissues and diet. The data may be available, but was not published with the results.

- Extrapolation of health effects to cattle and other grazing wildlife must be made with care to account for differences in digestive systems. Cattle are classified as ruminants, which include deer, antelope, sheep, and goats (Vaughan 1978). Ruminants have multiple compartmented stomachs and their digestive specialization is called polygastric. Horses and other wildlife, not classified as ruminants, have stomachs that are monogastric. Both obtain their nourishment from vegetation that involves the breakdown of cellulose. In the polygastric animal, microorganisms that live in the rumen cause fermentation by breaking down cellulose. In monogastric animals, the fermentation process occurs in the large intestine or hindgut. While the cellulose is being broken-down by the microorganisms, these same microorganisms also process the selenium that eventually is made available to the ruminant or monogastric animal.

  The monogastric stomach is less efficient than that of the ruminant, where food requires more time in the alimentary tract (Vaughan 1978). The emphasis in the ruminant is on highly efficient digestion (food remains in the gut for 70 to 100 hours) and on more selective feeding, but not on high rates of food intake, whereas, the monogastric animal has less efficient digestion (food remains in the gut for 30 to 45 hours) but eats greater quantities of food. If food is in short supply, the ruminant will probably survive after the monogastric animal has died. The ruminant digests and absorbs large quantities of dead microorganisms for their protein and energy source. Because there is less time for food to reside in the alimentary tract the monogastric animal does not benefit as much as the ruminant from the protein source afforded by the microorganisms. Because all cattle are ruminants, including steers, bulls, and cows, there should be no inherent differences in the way the animals are exposed to and absorb selenium.

This study compared the steer muscle tissue concentrations to an Australian standard for human consumption of beef skeletal muscle. For comparison, health advisories for domestic livestock in the U.S. recommend limited consumption by healthy adults and no consumption by children or pregnant women when tissue levels of selenium equal or exceed 2 mg/kg (wet weight) (Skorupa 1998). A complete ban on human consumption is recommended when selenium is equal to or greater than 5 mg/kg (wet weight).

Based on the results presented in MW (2000), it is apparent that cattle feeding on seleniferous pastures can accumulate tissue concentrations of selenium that exceed acceptable levels for consumption by humans. The selenium is slowly depurated from the tissue when the selenium is removed from the food source. However, even after an extended depuration period, a small portion of the test animals had selenium concentrations that were in excess of safe concentrations for consumption by humans.

MW (2000) stated that the muscle concentrations observed in the cattle after depuration were considered non-toxic to cattle based on a reference to Puls, 1994. For comparison, Skorupa (1998) indicates that overt toxicity thresholds for domestic livestock range from 3 to 5 mg/kg (dry weight).

3.1.8.4 Elk Study

The Elk Study was evaluated to determine its ability to support risk conclusions. Objectives of this study were to:

- Determine levels of selenium and cadmium in liver and skeletal muscle of elk.
- Determine if levels of selenium and cadmium are elevated in elk tissue as a result of increased exposures attributable to phosphate mining.
- Quantify any threat posed to human health.

This is a very valuable study in that 323 elk tissue samples were analyzed. This data is very useful in a risk assessment, because it provides a good estimate of the tissue concentrations of selenium and other metals in a food item often consumed by humans.

The only other element identified in the study as being a potential rick to elk was molybdenum. The issue of molybdenosis in grazing animals and wildlife was recognized in the 1999 Interim Investigation Report (MW 2000). Molybdenosis is a copper-deficiency disease that is caused by depression of the physiological availability of copper as a result of high molybdenum concentrations (Eisler 1989). Potential problems with molybdenosis can be ascertained by comparing molybdenum concentrations to concentrations of copper and sulfate (Eisler 1989, Sefchick-Edwards 1998). Molybdenum concentrations in animal tissue provide little indication of the dietary molybdenum status and are of little value for diagnosing molybdenum toxicity unless the sulfate, protein, and copper status of the diet are also known (Eisler 1989). As a guideline, a copper to molybdenum ratio of less than 2:1 will result in a copper deficiency, whereas a ratio of greater than 10:1 increases the risk of developing copper toxicosis, particularly in sheep (Sefchick-Edwards 1998). Sefchick-Edwards (1998) indicates that in monogastric animals, sulfate protects against molybdenum toxicity, but in ruminant (polygastric) animals, sulfate enhances toxicity. Thus, the extrapolation of molybdenum data from one class of animal to another must be made with consideration of basic differences in physiology. Finally, the issue of molybdenosis needs further investigation to evaluate if inter-element (copper, sulfate, selenium) antagonism or synergism is occurring. Access to complete databases for all metals analyzed in the elk study would improve the review of this issue.

4.0 HUMAN HEALTH RISK ASSESSMENT

This section provides a review of the area-wide PHHRA prepared for the Resource Area. The PHHRA was presented in Section 5.1 of the 1998 Regional Investigation Report (MW 1999b). Risks were estimated using both deterministic and probabilistic methods. Some of the more important aspects of the PHHRA are discussed in this section.

Several investigations were implemented to fill data gaps recognized in the PHHRA (MW 1999b, 2000). Those investigations included (1) collection and analysis of skeletal muscle and liver samples from elk and (2) a study of the depuration of trace elements in beef cattle. The elk skeletal muscle samples were intended in part to replace the reliance on extrapolation from beef cattle. The liver samples addressed one type of organ meat that receptors may ingest. Finally, the depuration study allows the risk assessment to be refined in order to include a dynamic component to the concentration of trace elements in beef tissue. The IMA also conducted a preliminary assessment of the potential for acute effects in humans from the consumption of contaminated elk tissue. The results of these studies may be important for future risk assessment activities.

4.1 IDENTIFICATION OF COPCS

As described earlier, six target elements were selected as Selenium Project COPECs using a risk-based screening process that focused on ecological risk. The six constituents identified as COPECs are: selenium, cadmium, manganese, nickel, vanadium, and zinc. For the purposes of the preliminary risk assessment, human health COPCs were identified by comparing the maximum concentrations of each of the six COPECs in surface water and soil and comparing them against EPA Region 9 PRGs (EPA 1999b). The results of this comparison showed that only selenium and cadmium concentrations in surface water exceeded EPA Region 9 “tap water” PRGs; the exceedances for selenium were much greater than for cadmium. Also, the maximum soil concentrations of all six ecological COPCs were less than EPA Region 9 industrial soil PRGs. Based on these results, the PHHRA focused exclusively on selenium. The basic deficiencies that were discussed relative to the ecological risk assessment COPECs apply to the human health COPCs (see Section 3.1.1).

4.2 EXPOSURE ASSESSMENT

The objectives of the exposure assessment phase of a risk assessment are to define sources of exposure, exposure pathways, and receptors, and to estimate the magnitude, duration, and frequency of exposure to

site contaminants for each receptor. Those issues are discussed below as they relate to the interpretation of the PHHRA.

A fundamental understanding of the nature and extent of contaminants and fate and transport processes is generally considered important for defining exposure pathways. The primary dispersion mechanisms, including surface runoff, erosion, and leaching were broadly recognized on an area-wide basis. However, the number, type, and arrangement of sources and mechanisms of release at individual mine sites was not well characterized and more detailed information may be needed to justify the elimination of selected exposure pathways.

A complete exposure pathway ties together sources, mechanisms of release, exposure media, and receptors. The CSM developed for the screening-level ERA identified the first three of these elements from a broad ecological perspective, but did not explicitly recognize human receptors. The PHHRA identified two primary human exposure pathways outside of the CSM. The exposure pathways for human health included:

- A recreational fisherman fishing downstream of phosphate mines and consuming his catch
- A receptor consuming beef grazed on phosphate mine waste rock dumps

These exposure pathways considered adult receptors only and may not represent the receptor groups in the area. Because at least some risk was identified in association with the deterministic risk assessment, the revised area-wide risk assessment may need to consider at least adult and child receptors from three primary receptor groups including (1) the general public, (2) local Native American community, and (3) subsistence receptor. The missing exposure pathways that might be important for the Native American and subsistence receptors involve ingestion of plant material, wild game, and organ meats.

Potential exposure to COPCs in soil, sediment, and surface water were either eliminated or not considered in the PHHRA. Exposure through these pathways is expected to be complete. Based on a review of the available data, it is unlikely that exposure to COPCs in soil (through ingestion, direct contact, and inhalation of fugitive dusts) represent significant exposure pathways. In most cases, exposure pathways related to these media are likely to represent a very small portion of total receptor exposure when compared to other exposure routes. Nonetheless, indirect exposure pathways may generate potentially significant exposures and the final area-wide HHRA may need to consider these additional exposure pathways as part of an expanded CSM.

4.2.1 Exposure Quantification

The primary purpose of the exposure quantification step in the HHRA process is to calculate the amounts of each COPC to which human receptors are potentially exposed. To this end, the exposure assessment revolves around three steps: (1) determination of medium-specific concentrations of each COPC that receptors may be exposed at specified exposure points (these COPC-specific concentrations are referred to as exposure point concentrations [EPC]), (2) identification and documentation of the magnitude and frequency of medium-specific potential exposure for each receptor based on a review of actual and potential receptor-specific activity patterns (the result of this step is the identification of exposure parameter values), and (3) the calculation of COPC-, medium-, and receptor-specific exposures (this step merges the results of the first two steps).

Calculation of medium-specific EPCs is influenced by a variety of factors. However, three factors play especially important roles. Those factors are (1) the areal distribution of medium-specific data, (2) the statistical evaluation and manipulation of the medium-specific data (for example, determination of the distribution of medium-specific data sets and the treatment of analytical results reported as nondetected), and (3) the equations used to calculate EPCs.

Much of the available analytical data were based on medium-specific samples that were located based primarily, if not exclusively in some instances, on ecological and not human health considerations. Therefore, locations of maximum and most likely human exposure may not have been sampled. To the extent that human health considerations were involved in the selection of medium-specific sampling points, the health of the general population, and not potentially exposed subpopulations, was the primary consideration. As a result, receptor-specific activity patterns incorporating cultural, religious, and lifestyle considerations, were not adequately considered. For example, the PHHRA does not consider various ceremonial, religious, medicinal and other uses of plants by Native American tribes.

Because the analyses of the skeletal muscle from the cattle pastured at the Henry Mine were not available, the EPC for selenium in beef cattle was predicted based on locally derived blood concentrations and an externally derived coefficient (MW 1999b). This approach seems reasonable for the PHHRA, but should be improved by using skeletal muscle data from the cattle pastured on a Henry Mine reclaimed waste dump and the elk study.

Similarly, the EPC for selenium in fish fillets was identified as the maximum selenium concentration measured in fillet samples from three locations on the East Mill Creek and the Blackfoot River. Because

of the potential for widely varying concentrations of COPCs in surface waters and, therefore, fish tissue within the Resource Area, fish tissue COPCs for use in an area-wide HHRA will be recalculated as data become available.

The methods used in the PHHRA to quantify exposures through ingestion of beef and fish are consistent with relevant risk assessment guidance (EPA 1989). In addition, the potential exposure to selenium through ingestion of dietary supplements was correctly incorporated in the PHHRA. To the extent that receptors ingest supplements containing any additional COPCs that might be identified as part of a revised area-wide HHRA, this supplementary ingestion will need to be considered as part of the exposure quantification.

4.2.2 Toxicity Assessment

As recommended by the EPA Risk Assessment Guidance for Superfund (RAGS), the toxicity assessment typically consists of a description of the models used to develop noncarcinogenic and carcinogenic toxicity factors (EPA 1989). For noncarcinogens, the toxicity factor used to characterize noncarcinogenic hazards posed by particular exposures is called the reference dose (RfD). For carcinogens, the slope factor is the toxicity factor used to characterize the carcinogenic risks posed by particular exposures.

The six PHHRA COPCs identified in the 1998 PHHRA are all considered to be noncarcinogens through the exposure routes that were evaluated. The 1998 PHHRA correctly identified the oral RfD for selenium from EPA's Integrated Risk Information System (IRIS) (EPA 1999b). Hazards were not calculated for any other constituents, based on the results of the original COPC screening process. MW (1999b) recognized that additional risk calculations might be required in the future if cadmium levels of sufficient magnitude are identified in subsequent sampling events.

EPA's RAGS recommends discussion of the overall toxicity, including a summary of the exposure route-specific dose response for each COPC. These discussions are typically referred to as toxicity profiles. Toxicity profiles are important for documenting the toxicity values selected for each COPC and COPC-specific target organs (sometimes referred to as endpoints). The PHHRA included a toxicity profile for selenium (MW 1999b). Toxicity profiles should be included in a revised area-wide HHRA for all medium-specific COPCs.

4.2.3 Risk Characterization and Uncertainty Assessment

The risk characterization step of an HHRA merges the results of the exposure assessment and toxicity assessment phases. The PHHRA characterized risks only for potential exposure to selenium. Selenium is not considered to be a potential human carcinogen and, therefore, only noncarcinogenic hazards associated with potential exposure to selenium were characterized in the PHHRA. The deterministic procedure calculated a total hazard index of 1.7, which only marginally exceeds the threshold hazard index of 1.0.

The procedure for calculating noncarcinogenic hazards was satisfactory with one exception. The report states, "none of the other five target trace elements (cadmium, manganese, nickel, vanadium, and zinc) has the same toxicological endpoint as does selenium" (MW 1999b). Therefore, there was no need to consider potential cumulative impacts of exposure to metals other than selenium. However, both manganese and selenium affect the human nervous system and the final area-wide HHRA will need to consider potential cumulative impacts of selenium and any additional elements that might be identified as COPCs.

Finally, the PHHRA included risk interpretation and risk summary sections. The uncertainty assessment was reasonably detailed and well documented.

4.3 PROBABILISTIC RISK ASSESSMENT PROCEDURE

The PHHRA included a probabilistic risk assessment (PRA) as documented in Attachments H-1 through H-3 of the 1998 Regional Investigation Report (MW 1999b). The PRA, included as part of the PHHRA, is based on the same exposure pathways considered in the deterministic risk assessment using the same spreadsheet model. Therefore, the discussion of revisions to the CSM, exposure pathways, receptors, and exposure routes associated with the deterministic assessment apply to the PRA.

The PRA followed some, but not all, of EPA's principles and recommendations for conducting PRAs. In general, if a PRA were to be included in a revised area-wide HHRA, the PRA would need to follow and refer to relevant EPA and other guidance for preparing PRAs. However, it is important to note that EPA does not recommend use of a PRA under all circumstances (EPA 1997b). The deterministic PHHRA procedure calculated a total hazard index of 1.7. This level does not typically justify further analysis using probabilistic methods. The need for and utility of preparing a revised PRA should be reconsidered after review and analysis of the deterministic noncarcinogenic hazard and carcinogenic risk (as necessary) estimates prepared as part of a revised area-wide HHRA.

4.4 IDENTIFICATION OF PROBABILITY DENSITY FUNCTIONS

In general, the basis for input parameter-specific values and distributions used in the PRA were not well documented and were sometimes based on limited data. For example, the basis for each Probability Density Function (PDF) assumed in the PRA is identified, but the documentation consisted primarily of a numeric or statistical description of the PDF with general reference to a guidance document. Without additional text describing the basis for the PDF selected, in many cases it is not possible to determine the applicability of the selected PDF.

In other cases, such as the identification of the mean concentration of selenium in fish tissue fillets, the PDF is based on a data set with sample size limitations. Also, the development of the PDF for this variable was further adjusted based on the assumption that 95 percent of the fishing pressure on the two streams was occurring on the Blackfoot River, with the remainder on East Mill Creek. However, because fish may be caught in other streams, the PDFs used to represent the mean concentration of selenium in fish tissue are based on an insufficient amount of data from an area-wide perspective.

4.5 RISK CHARACTERIZATION

The PRA was performed using acceptable software (Crystal Ball) and the same spreadsheet model used in the deterministic risk assessment. The PDF for the hazard associated with on-site exposure to selenium through ingestion of beef, fish, and dietary supplements was adequately presented. The results are discussed in comparison to the hazard calculated in the deterministic assessment as recommended by EPA guidance (EPA 1997c). However, the discussion of the contribution to the total hazard from various sources of selenium ingestion was poorly documented.

4.6 UNCERTAINTY ASSESSMENT

Consideration of the results of the PRA as part of the overall uncertainty assessment of the PHHRA and comparison of the deterministic and probabilistic results were adequate and consistent with EPA guidance. However, the sensitivity analysis conducted to evaluate the relative contribution of various parameters to the incremental and overall uncertainty associated with the PRA results would benefit from more discussion and further documentation. Statements made in the text regarding the contribution of sources of selenium ingestion to the total dose and the contribution of individual parameters to the uncertainty associated with the results of the PRA could not be readily verified.

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APPENDIX A

DATA QUALITY EVALUATION REPORT

DATA QUALITY EVALUATION REPORT

Site Name: Review of Selenium Studies

Client: Idaho Department of Environmental Quality

Data Evaluator: Nancy McDonald, Tetra Tech EM Inc.

Report Date: January 17, 2001

1.0 INTRODUCTION

Data quality was evaluated on the analytical data for 8 water, 6 soil, and 2 sediment samples out of a total of 218 water and 133 sediment/soil samples collected in 1997 and 1998. Samples evaluated are summarized in Table A-1. Samples with detected results (above the reporting limits) were specifically selected for review. Results for these samples were bolded in the electronic file supplied by Montgomery Watson through Idaho Department of Environmental Quality. The data file included raw instrument data. The samples were analyzed for metals (cadmium, calcium, iron, magnesium, manganese, nickel, potassium, selenium, sodium, vanadium, and zinc) and wet parameters such as alkalinity, ammonia, cation exchange capacity, chloride, filterable residue, nitrate, organic carbon, pH, phosphorus, and sulfate.

Table A-1. Summary of Samples Evaluated

Sample Media	Sample Identification	Sample Dataset
Water	091697SW08-0-U	September 1997
	092297SW-49-0-U	September 1997
	051198SWSP11-0-U	May 1998
	051298SWST044-2-U	May 1998
	050298SWST001-4-U	May 1998
	090998GW01-0-U	September 1998
	091298SWST044-MS	September 1998
	091398SWST019-0-U	September 1998
Soil	21SSWD74-1-MS-C5	July 1998
	23SSBB1-1-0-C5	July 1998
	23SSBB1-5-0-C5	July 1998
	25SSWD75-3-0-C5	July 1998
	25SSBB3-3-3-C7	July 1998
	27SSWD034-1-3-C5	July 1998
Sediment	091298SEST022-MS-C	September 1998
	091098SESP24-MS-C	September 1998

Data were evaluated in general accordance with the Contract Laboratory Program National Functional Guidelines for Inorganic Data Review, dated February 1994. Data evaluation was based on the following

parameters:

- Calibrations
- Blanks
- Matrix Spikes (MS) and Matrix Duplicates
- Laboratory Control Samples (LCS)
- Spiked Reference Material

The following data qualifiers are used in this data quality evaluation report. The definitions are consistent with the Contract Laboratory Program National Functional Guidelines for Inorganic Data Review, dated February 1994:

- **No qualifier.** Indicates that the data are acceptable both qualitatively and quantitatively
- **U.** Indicates that the compound was analyzed for but not detected above the concentration listed; the concentration listed is the sample reporting limit
- **J.** Indicates an estimated concentration; the result is considered to be qualitatively acceptable, but quantitatively unreliable
- **UJ.** Indicates an estimated quantitation limit; the compound was analyzed for, but was considered to be nondetected

2.0 DATA COMPLETENESS

The analytical data was presented in a Microsoft Excel file without dates and times of analysis. Quality control (QC) samples were presented by dataset; therefore, qualifications based on QC results were applied to all samples evaluated within the dataset. In addition, holding times were not evaluated (dates of sample collection and analysis were not included in the electronic data file). Because of the long holding time for metals (6 months), the holding time is generally not exceeded. No qualifications are warranted for these irregularities.

3.0 CALIBRATIONS

Initial calibrations were not presented in the data reviewed. No data qualifications were performed based on the lack of initial calibration data. Results for check standards were not consistently reported in the datasets. Recoveries of check standards for the target analytes selenium and sulfate were outside QC limits of 85 to 115 percent. Selenium recoveries of 66 and 75 percent in May 1998 water data and 130 percent in September 1998 sediment data were outside QC limits. The sulfate recovery of 159 percent in May 1998 water data was also above QC limits. Results for these target analytes in associated samples were flagged “J” or “UJ”, as appropriate, to indicate that they are estimated.

4.0 BLANKS

Low-level concentrations of the target analytes ammonia, calcium, cadmium, chloride, iron, magnesium, nickel, phosphorus, selenium, sulfate, vanadium, and zinc were detected in laboratory blanks. Sample results less than five times the blank concentrations were flagged “U” and considered laboratory contamination. The target analytes cadmium, calcium, iron, magnesium, manganese, nickel, potassium, sodium, and zinc were detected in equipment blanks. Sample results less than five times the equipment blank concentrations were

flagged "U" and considered nondetected.

5.0 MATRIX SPIKES AND MATRIX DUPLICATES

MS recoveries for the target analytes cadmium and zinc in May 1998 water data; cadmium, nickel, and sulfate in July 1998 soil data; potassium in September 1998 sediment data; and cadmium, vanadium, and zinc in September 1998 water data were biased low and outside QC limits of 75 to 125 percent. Low MS recoveries may indicate that sample results are biased low. Results for these target analytes in associated samples were flagged "J" or "UJ", as appropriate, to indicate that they are estimated. MS recoveries for the target analytes selenium in May 1998 water data and potassium and sodium in September 1998 sediment data were biased high and outside QC limits of 75 to 125 percent. High MS recoveries may indicate that sample results are biased high. Results for these target analytes in associated samples were flagged "J" to indicate that they are estimated. In several cases, concentrations in the unspiked samples were greater than four times the spiking concentrations. Therefore, the above QC limits did not apply and no qualifications were performed.

All matrix duplicate relative percent differences were within QC limits of $\leq$ 20 percent for water samples and $\leq$ 35 percent for soil and sediment samples.

6.0 LABORATORY CONTROL SAMPLES

LCS (blank spike) recoveries for the target analytes nickel in May 1998 water data and vanadium and zinc in September 1998 water data were biased low and outside QC limits of 80 to 120 percent. Results for these target analytes in associated samples were flagged "J" or "UJ", as appropriate, to indicate that they are estimated. LCS recoveries for calcium and phosphorus in July 1998 soil data and cadmium, calcium, nickel, selenium, and sodium in September 1998 sediment data were outside QC limits of 80 to 120 percent. Results for these target analytes in associated samples were flagged "J" to indicate that they are estimated.

7.0 STANDARD REFERENCE MATERIAL

Recoveries for the target analytes alkalinity in May 1998 water data and cadmium, calcium, iron, manganese, potassium, selenium, sodium, vanadium, and zinc in September 1998 sediment data were biased low and outside QC guidelines of 75 to 125 percent. Results for these target analytes in associated samples were flagged "J" or "UJ", as appropriate, to indicate that they are estimated. Although QC limits for standard reference material are not specified in functional guidelines, the validator applied limits recommended for matrix spikes. Recoveries for the target analytes cadmium in July 1998 soil data and cadmium, organic carbon, and selenium in September 1998 sediment data were biased high and outside QC guidelines of 75 to 125 percent. Results for these target analytes in associated samples were flagged "J" to indicate that they are estimated.

8.0 OVERALL ASSESSMENT OF DATA

The overall quality of this data package was acceptable based on the data reviewed. Minor problems were noted with calibrations, blanks, matrix spikes, laboratory control samples, and standard reference materials. Raw instrument data less than the reporting limits were reported in the electronic data file. Results less than the reporting limits were considered unreliable (instrument detection limits were not reported). Therefore, these results were flagged "U" and raised to the appropriate reporting limits to indicate that they are considered nondetected. All evaluated sample results were bolded in the Microsoft Excel file and can be used, as qualified, for any purpose.

APPENDIX B

SELENIUM IN THE ENVIRONMENT

SELENIUM IN THE ENVIRONMENT

INTRODUCTION

Selenium is ubiquitous in the environment occurring at trace concentrations in almost all media (soil, air, water, rocks, plants and animals). Humans and other animals require selenium for normal growth and reproduction (Levander, 1986). The essentiality of selenium in plants has not been conclusively demonstrated, although it may be essential in primary selenium accumulator species (Ganje, 1966: Emerick and DeMarco, 1991). The intent of this appendix is to provide a summary of selenium chemistry and toxicology.

Chemistry

Selenium behaves much like sulfur and occurs most extensively in the Earth's crust by substituting for sulfur in various sulfur compounds and minerals. In nature, selenium has three common oxidation states referred to as selenide (-2), selenite (+4), and selenate (+6). Selenide substituting in sulfide minerals represents the most common geologic form. Metal selenides range from sparingly soluble when associated with alkaline earth metals (e.g., Na and Ca) to relatively insoluble when associated with Cu and Pb. Selenium has six stable isotopes with ^{78}Se and ^{80}Se being the most prominent. The two radioactive isotopes, ^{75}Se (120.4 days) and ^{79}Se (1 x 10^4 years) have divergent half-lives that may be useful for understanding uptake and partitioning in plants. Soluble selenates typically occur in oxidizing environments and under anoxic conditions may be slowly reduced to selenites and eventually to selenide and elemental selenium. Selenium forms a number of biologically mediated organic compounds including seleno amino acids and derivative proteins, methyl selenides, methyl selenic esters, methyl selones and methylselenonium ions (Herring, 1991).

Occurrence in Environmental Media

Selenium is widely distributed in nature and is especially abundant with sulfide minerals of metals, such as, iron, lead, and copper. The normal concentration in soils range from 0.1 to 5 mg/kg and plants from 0.0001 to 2 mg/kg (Bowen, 1979). Average concentrations of selenium in other media are presented in Table B-1.

Table B-1. Selenium concentrations in various environmental media.

Medium	Average Concentration ppm	Reference
Earth's crust	0.05	Elmsley (1989)
Seawater, near surface	0.15×10^{-7} to 0.46×10^{-7}	Elmsley (1989)
Seawater, deep	1.65×10^{-7} to 1.8×10^{-7}	Elmsley (1989)
Freshwater	4×10^{-4}	Rose et al. (1979)
Limestones	0.88	Rose et al. (1979)
Sandstones	0.05	Rose et al. (1979)
Shales	0.6	Rose et al. (1979)
Black Shales (Wyoming)	20	Rosenfeld and Beath (1964)
Igneous rocks	0.13 to 0.14	Rose et al. (1979)
Soils	0.1 to 5	Bowen (1979)
Freshwater algae	0.1 to 1.5	Skorupa (1998)
Terrestrial plants	0.0001 to 2.0	Bowen (1979)
Aquatic invertebrates	0.4 to 4.5	Skorupa (1998)
Terrestrial invertebrates	0.1 to 2.5	Skorupa (1998)
Fish (whole)	1.0 to 4.0	Skorupa (1998)
Fish (liver)	2.0 to 8.0	Skorupa (1998)
Reptile/Amphibian (whole)	1.0 to 3.0	Skorupa (1998)
Reptile/Amphibian (liver)	2.9 to 3.6	Skorupa (1998)
Birds (whole)	< 2.0	Skorupa (1998)
Birds (muscle)	1.0 to 3.0	Skorupa (1998)
Birds (eggs)	< 5.0	Skorupa (1998)
Birds (liver)	< 10.0	Skorupa (1998)
Birds (feathers)	1.0 to 4.0	Skorupa (1998)
Birds (whole blood)	0.1 to 0.4	Skorupa (1998)
Mammals (whole)	< 1.0 to 4.0	Skorupa (1998)
Mammals (muscle)	< 1.0	Skorupa (1998)
Mammals (liver)	1.0 to 10.0	Skorupa (1998)
Mammals (hair)	< 1.0 to 3.0	Skorupa (1998)
Mammals (milk)	< 0.05	Skorupa (1998)
Mammals (whole blood)	0.1 to 0.5	Skorupa (1998)

SELENIUM IN SOILS

Selenium occurs in soils as native selenium, metal selenides, weakly soluble oxyanions, adsorbed ions, and organoselenium compounds. In soils, selenium chemistry is complicated because it can concurrently exist in more than one oxidation state. Solution pH and redox potential are the primary determinants of the selenium oxidation state, although the microbial mediation of the selenium redox reactions limits simple predictions in soil systems (Guo et al., 1998).

The solubility of selenium in soils is determined primarily by its oxidation state and mineral form, while adsorption processes control its mobility (Elrashidi et al., 1987; Brown, 1991). Selenite is predicted under mildly oxidized conditions and selenate is the major species expected under high redox potentials. Selenides and elemental Se are predicted to occur at low redox potentials. Metal selenides (e.g., PbSe, CuSe, and $FeSe_2$) or elemental Se solid phases are very insoluble and control the solution concentrations under reduced conditions where they are the stable forms. In well-oxidized soils, adsorption, rather than dissolution-precipitation, controls the solution concentration of selenite and selenate (Elrashidi et al, 1987). Selenite and selenate adsorption is pH dependant with maximum adsorption occurring under acid conditions (Neal et al., 1987; Neal and Sposito, 1989). Selenate is less strongly adsorbed than selenite and many of the other soil solutions anions (Ryden et al., 1987). Thus, Se mobility and availability are expected to be highest in well-drained, alkaline soils, since the redox potential favors selenide mineral dissolution and the stability of mobile selenate species.

A number of organoselenium compounds occur in soils (Abrams et al., 1990) and mine-related waste rock (Sharmasarkar and Vance, 1995). Organoselenium in soils results from plant organic matter cycling and microbial transformation of inorganic selenium and may include immobile, soluble, and volatile compounds. The formation of volatile selenium compounds (e.g., dimethylselenide) by microorganisms has important implications for selenium cycling in soils and aquatic sediments (Doran and Alexander, 1977; Gao and Tanji, 1995; Zhang and Frankenberger, 2000). Because volatilization losses may be significant, microbial volatilization has been recognized as a potential remediation measure for selenium-affected soils and wetlands (Frankenberger and Losi, 1995). Volatilization of selenium is affected by the availability of carbon sources, microbial activity, temperature, soil-water regime, soil texture, aeration, and concentration and form of water-soluble selenium (Zieve and Peterson, 1981; Zhang and Moore, 1997; Frankenberger and Losi, 1995; Zhang and Frankenberger, 1999).

PLANT UPTAKE AND ASSIMILATION OF SELENIUM

Plants are the primary pathway for selenium exposure to animals, although some uptake occurs through the direct ingestion of soils and water. Plant uptake of selenium depends on the fundamental properties of selenium and the soil environments impact on redox chemistry. Mineral solubility, reaction kinetics, redox potential, sorption/desorption reactions, microbial activity, mineralization of organic matter, and volatilization control the availability and mobility of selenium in the reclaimed environments. It is well known that water content, redox conditions, electrical conductivity, and microbial activity change seasonally and with depth in soils. Thus, the spatial and temporal dynamics of the physicochemcial condition in soils complicate the interpretation of soil-Se/plant uptake relationships.

Selenosis in native vegetation is undocumented, but toxicities in selected crop plants are known to occur (Ganje, 1966; Carlson et al., 1989; Mayland et al., 1989). Some plants can absorb large amounts of selenium with no apparent detrimental affects. Plants that tolerate high levels of Se are classified as primary or secondary accumulators species (Table 2). Primary Se accumulators are apparently restricted to seleniferous soils, whereas, secondary Se accumulators occur on both seleniferous and nonseleniferous soils. Selenium concentrations in primary accumulators may range from 1,000 to 10,000 mg/kg on a dry weight basis (DW), while the concentration in secondary accumulators may range up to 1,000 mg/kg DW (Emerick and De Marco, 1991). The tissue-Se levels of nonaccumulator species growing on seleniferous soils generally do not exceed 25 to 50 mg/kg DW.

Table B-2. Genera of recognized primary and secondary selenium accumulator species in the western United States (adapted from Emerick and DeMarco, 1991).

Primary Accumulators		Secondary Accumulators	
Genus	Common Name	Genus	Common Name
Aplopappus	Goldenweed	*Aster*	Aster
Astragalus	Locoweed	*Astragalus*	Locoweed
Haplopappus	Goldenweed	*Atriplex*	Saltbush
Machaeranthera	Aster	*Castilleja*	Paintbrush
Oonopsis	Goldenweed	*Comandra*	Toadflax
Stanleya	Primrose	*Grayia*	Hopsage
Xylorhiza	Aster	*Grindelia*	Gumweed
		Guterrezia	Snakeweed
		Haplopappus	Goldenweed
		Machaeranthera	Aster
		Mentzelia	Blazing star

Mikkelson et al., (1989) and Mayland et al., (1991) reviewed the factors affecting plant uptake of selenium and indicated that plant uptake increased as soil pH, redox potential, and clay content increased. A comprehensive study of selenium plant uptake in reclaimed mine lands in Wyoming found that the selenium content in plants was influenced by percent clay, total organic carbon, extractable soil Se, electrical conductivity, sulfate, geomorphic position, and the age of the reclaimed site (Spackman et al., 1995). The authors of the Wyoming study were unable to develop a definitive relationship between plant uptake and extractable soil Se because of the complex dynamics of the soil-Se/vegetation system (Spackman et al., 1995).

Plants absorb selenate, selenite, and organo-selenium, but seem to preferentially absorb selenate and organoselenium. Increasing boron, chloride, and sulfate concentrations usually depress Se uptake. The antagonistic effects of sulfate on plant uptake of Se have been noted by a number of researchers (Epstein, 1955; Gissel-Nielsen, 1973; Smith and Watkinson, 1984; Wan et al., 1988). The reduction in Se uptake associated with sulfate is probably the result of specific-ion competition (Epstein, 1955). Based on this mechanism, gypsum soil amendments have been used to mitigate Se uptake in seleniferous soils (Wan et al., 1988). By extension, the naturally high levels of sulfate that are normally associated with sulfide-containing waste rock would be expected to mitigate Se uptake. The uptake of selenate is affected to a greater degree than selenite by competing anions (Mayland et al., 1991).

For obvious reasons phosphorous/selenium interactions are important in the phosphate mining regions of southeastern Idaho. Unfortunately, the interactions of phosphate and selenium are complex and not completely understood (Mayland et al., 1991). However, limited information suggests that high amounts of phosphorous may reduce selenium uptake (Singh and Singh, 1979). Similarly, the effect of soil organic matter content on Se uptake is not clear and it appears to either enhance or depress Se uptake by plants.

Selenium absorbed as selenate is translocated directly to the plant tops as selenate, while the selenite form is rapidly metabolized in the roots and transported to the tops in the xylem-sap (Brown and Shrift, 1982). Selenate absorption by plants is an active process with selenate accumulating in root tissues at levels higher than those in the corresponding soil solution. In contrast, selenite absorption is considered passive and root concentrations seldom exceed the soil solution concentrations.

Once absorbed, selenate is reduced to selenite and selenide before incorporation into organoselenium compounds. Adverse biochemical reactions may occur at the cellular level as a result of the Se/S

substitutions in the proteins of plants (accumulator and nonaccumulator species) and animals. Selenium accumulator plants metabolize selenium differently than nonaccumulator species (Brown and Shrift, 1982). Selenium accumulators have the ability to sequester Se in non-protein amino acids (e.g., Se-methylselenocysteine and selenocystathionine) rather than allowing the selenium to substitute for sulfur in proteins. Nonaccumlator plants incorporate about 10 to 15 percent of the selenium in protein (as selenomethionine), while accumulator species tend to have a lower proportion of the selenium in proteins. Selenomethionine is the likely precursor to volatile selenium compounds (Banuelos et al., 1995).

Selenium concentrations in plant vary structurally, as well as, temporally (Ohlendorf, 1989). The leaves of plants generally contain higher selenium levels than seeds reflecting the association of selenium in proteins. Aged vegetation (straw) tends to lower concentrations than actively growing plants. Spackman et al., (1995) found pronounced changes in vegetation selenium concentrations from year to year on the same sites. They attributed the difference to annual variations in weather and soil water conditions.

Concerns exist that accumulator plants may cycle selenium from deep soil layers to the surface as plant detritus thereby increasing the bioavailability of selenium to terrestrial biota (Irwin et al., 1997). Munn (1995) found elevated levels of selenium in surface soil layers in a seleniferous area of Wyoming, but determined that increased Se concentrations resulted from erosion and sedimentation rather than bioconcentration. He speculated that volatilization of selenium may account for the apparent lack of Se accumulation associated with the mineralization of plant detritus.

Aquatic plants, like algae, accumulate selenium from the water sources (Lemly and Smith, 1991). Uptake by algae and other aquatic plants is important because they represent a potential dietary pathway for other organisms, as well as, a mechanism for the removal and sequestration of water borne selenium. Selenium is translocated to the sediment when aquatic plants die and the sediment acts as both a source and sink for selenium. The fate of the selenium in aquatic systems is complicated by the complex interaction of the biogeochemical reactions between sediment, biota, and water. Growth retardation of aquatic plants has been associated with elevated selenium levels in the water column (Irwin et al., 1985; Skorupa, 1998).

SELENIUM IN GROUNDWATER

The extent that selenium is present in groundwater depends on a number of factors, including the depth to groundwater (thickness of the unsaturated zone), character of the vadose zone, geochemical conditions in the aquifer, and reaction path kinetics (Ahlrichs and Hossner, 1987; Naftz and Rice, 1989; Reddy et al.,

1995). Under alkaline oxidizing conditions selenate is directly transported to groundwater. Selenite is more strongly attenuated by adsorption mechanisms than selenate, and thus, is predicted to be less mobile under acidic and less oxic conditions. Deeper groundwater tends to be less oxic and selenite and selenides are likely to be dominant. Under strongly reduced conditions, relatively insoluble metal selenides are likely to predominate resulting in low selenium concentrations in groundwater. Evidence of the reductive accumulation of selenium as metal selenides in groundwater systems can be found in uranium roll front deposits (Howard, 1977). Dreher and Finkelman (1992) reported decreases in the concentration of soluble selenium species in groundwater associated with coal mining over a ten-year period following the cessation of mining. The decreased selenium concentrations in groundwater were attributed to microbial reduction and adsorption. Irrigation with selenium containing waters and evapoconcentration may result in high selenium levels in soils associated with shallow groundwater (Fuji and Deverel, 1989).

SELENIUM IN ANIMALS

The occurrence and concentration of selenium in the environment may favor or adversely affect the growth, survival, and reproduction of terrestrial and aquatic organisms. Selenium is essential for proper nutrition of humans and other animals (Levander, 1986). Selenium deficiencies in livestock and poultry may result in a long list of ailments (Egan, 1966; Shapiro, 1973; Combs and Combs, 1986). Deficiencies in humans are rare, but have been recognized in isolated areas with extremely low soil-Se levels and in instances of extreme malnutrition (Chen et al., 1980; Majaj and Hopkins, 1966). Animal requirements are reported to range from 0.05 to 0.1 mg/kg diet (Mayland et al., 1989), with up to 0.3 mg/kg diet required as feed supplements for maximum productivity of poultry and livestock (CAST, 1994).

Selenium toxicity in animals is well documented and depends on a number of factors including, environmental concentration and form of selenium, animal species, age, sex, dietary compliments, and health. Reproductive toxicity is one of the most sensitive endpoints for vertebrates. In general, toxicity symptoms may occur at dietary-Se levels ranging from 3.0 to 20.0 mg/kg for chronic exposure and from 400-800 mg/kg for acute exposure (Mayland et al., 1989; James et al., 1991). Selenium toxicity in humans is rare, but has been reported from China, where the inhabitants diet was restricted solely to food grown on highly seleniferous soils (Levander, 1986). Additional instances of human toxicity were associated with the consumption of unregulated selenium food supplements. Combs and Combs (1986) suggest that elevated levels of dietary selenium may function to reduce the incidence of cancer and cardiovascular disease. Interestingly, both selenium deficiency and toxicity appear to cause similar health

affects in humans (e.g., reproductive depression, anemia, weight loss, and immune dysfunction) Skorupa et al., 1996).

Animals absorb selenate, selenite, and some organoselenium compounds more readily than selenides and elemental selenium (Ohlendorf, 1989). About 75 percent of absorbed selenium is fairly rapidly excreted, while the remainder is incorporated into blood and tissue proteins that are gradually eliminated over time. Selenium from plant sources tends to be more readily absorbed by animals than selenium from animal sources (i.e., meat and fish). Thus, animal may absorb 80 to 100 percent of the selenium from plant sources as opposed to 20 to 50 percent of the selenium contained in meat and fish (Ohlendorf, 1989).

Bioaccumulation and Biomagnification

Bioconcentration is the process whereby organisms assimilate and retain a constituent at levels that are higher than the environmental media to which it is exposed. Bioconcentration of selenium by aquatic and terrestrial plants was discussed earlier. Selenite and selenate, the most common forms of selenium in natural waters and soil solutions, are converted to organoselenium compounds by plants, animals, and microorganisms. The primary and secondary accumulators have the capacity to significantly bioaccumulate selenium, but these plants are generally considered to be unpalatable and are not consumed freely. Lower bioaccumulation factors for nonaccumulator species are offset by the higher degree of palatability and increased potential for consumption. In aquatic systems, bioconcentration factors for algae have been reported to range from 100 to 2600 (Ohlendorf, 1989). Bioconcentration factors estimated for uptake of selenium as selenomethionine at initial concentrations of 1 μg/L were approximately 16,000 for algae and 200,000 for daphnids (Irwin et al., 1997). Notably, bioconcentration of selenium by marine organisms partially accounts for the elevated levels of selenium in the Phosphoria Formation (Piper, 1999).

Biomagnification refers to the successive increase in the concentration of a constituent with increases in the trophic level of a food chain. Efficient absorption and slow elimination of a constituent result in biomagnification. Biomagnification of selenium in the lower trophic levels of aquatic food chains has been demonstrated, but occurrence of biomagnification in terrestrial food chains is controversial (Ohlendorf, 1989). Biomagnification factors for lower level consumers in aquatic systems are generally on the order of 2 to 6 times the concentrations in the primary producers. Thus, fish and lower invertebrates may bioconcentrate selenium 200 to 6000 times the original concentration in the water

column (Lemly and Smith, 1991). The low rates of absorption of selenium from animal protein sources may affect the potential for biomagnification in terrestrial food chains.

Invertebrates

Terrestrial and aquatic invertebrates are important food sources for birds, fish, and small mammals. Selenium-induced alterations of invertebrate populations could indirectly impact invertebrate predator populations. However, there is no field evidence to support the contention that fish and other wildlife populations are adversely affected by selenium-induced alterations of invertebrate populations. Thus, the direct ecological effects of consuming selenium-containing invertebrates are considered more important than indirect effects of changes in the prey population structure (Skorupa 1998).

In non-seleniferous environments, freshwater invertebrates typically contain less than 4 mg Se/kg, and terrestrial arthropods contain less than 1 mg Se/kg (Ohlendorf, 1989). Skorupa (1998) indicates that background selenium concentrations in aquatic invertebrates range from 0.4 to 4.5 mg Se/kg and are typically less than 2.0 mg Se/kg, while terrestrial invertebrates ranged from less than 0.1 to 2.5 mg Se/kg and are typically less than 1.5 mg Se/kg. Helmke et al., (1979) reported selenium concentrations in earthworms of 15 to 22 mg/kg DW in control and sewage sludge treated soils, respectively.

Selenium toxicity data for terrestrial invertebrates is generally lacking, although some information exists for aquatic invertebrates (Ohlendorf, 1989; Skorupa 1998). Acute toxicity of aquatic invertebrates associated with waterborne selenium may occur at concentrations ranging from 70 to 760 :g/l. Lowest thresholds for chronic toxicity are reported to occur at concentrations of 25 to 100 µg/L for inorganic selenium and less than 0.5 µg/L for waterborne selenomethionine (Skorupa, 1998).

Amphibians and Reptiles

Toxicology research on reptiles and amphibians is generally lacking. Nonetheless, reptiles apparently do not biomagnify metals commensurate with their trophic level and mortality from metal intoxication is undocumented (Linder and Grillitsch 2000). Based on a review of the literature, Skorupa (1998) suggests that whole-body background concentrations for selenium range from 0.7 to 3.0 mg/kg (typically less than 2.0 mg/kg) in amphibians and reptiles. Normal background concentrations of selenium in amphibian and reptile eggs typically range from 1 to 3 mg/kg.

Ohlendorf (1989) reported increased levels of selenium in bullfrog (45.0 mg/kg) and gopher snake (11.1 mg/kg) livers in seleniferous environments around Kesterson Reservoir when compared to bullfrogs (6.22 mg/kg) and snakes (2.05 mg/kg) in non-seleniferous areas. Manifestations of toxicity were not confirmed in these species, but the selenium levels were high enough to justify concerns relative to these animals and their predators. Toxicity test data revealed that African clawed frog (*Xenopus laevis*) larvae are sensitive to greater than 1,000-µg/L waterborne selenite (Linder and Grillitsch 2000). The LC50 (median lethal concentration) for waterborne selenite for the eggs and larvae of the narrow mouthed toad was 90 µg/L (Linder and Grillitsch 2000).

Fish

A nationwide study in the United States found that the average selenium concentration in fish was about 0.5 mg Se/kg on a whole-body, wet-weight basis (Ohlendorf, 1989). Whole-body selenium levels in fish from seleniferous environments may be 5 to 20 times higher the average national background level (Lemly and Smith, 1991). Specific organs (e.g., spleen, liver, and kidneys) generally contain somewhat higher concentrations of selenium than skeletal muscle tissue (Ohlendorf, 1989; Lemly and Smith, 1991).

Acute and chronic toxicity associated with selenium have been recognized in fish. Irwin et al., (1997) cite acute (96-hour LC50) values for teleost fish as ranging from 620 to 66,000 :g /L. For 96-hour exposures, LC50 values ranged from 16.9 mg /L for Coho salmon to 38.0 mg /L for Silver salmon and from 46.6 to 96.8 mg/L for Chinook salmon. Reproductive failure and mortality associated with chronic food chain bioconcentration may potentially occur in fish at relatively low selenium concentrations in water (< 2 to 5 :g/l), sediment (> 4 mg/kg), and food (> 5 mg/kg) (Lemly and Smith, 1991).

Skorupa (1998) suggests that measuring selenium levels in gravid ovaries may be the best way to assess the risks associated with exposure of fish to selenium. He indicated that the lowest concentration of selenium in fish gonads and eggs resulting in total reproductive failure is 25 to 30 mg/kg, and that 7 to 13 mg/kg in gonad or egg tissue may result in reproductive impairment in sensitive species such as, perch and bluegill. The experimental LOAEL (lowest observed adverse effect level) for reproductive impairment by way of lethal larval dietary exposure to salmon, bluegill, and razorback suckers is 3 to 8 mg/kg as food-chain selenium or selenomethionine (Skorupa 1998).

Birds

Selenium concentrations in the livers, kidneys, and eggs of birds are related to dietary concentrations (Ohlendorf, 1989). Dry weight selenium concentrations in wild birds from fresh water, non-seleniferous environments vary for the livers (4 to10 mg/kg), kidneys (4 to 8 mg/kg), and eggs (1 to 3 mg/kg). Ohlendorf (1989) indicates that the eggs and organs of marine and estuarine birds tend to have somewhat higher selenium levels, although he doesn't indicate whether the differences are environmentally or physiologically related.

Excessive selenium uptake by birds can cause growth reductions, decreases in the number and size of eggs, reduced hatchability, anemia, and embryo deformation (Eisler, 1985). In birds, the developing embryo is highly susceptible to excess selenium levels and the hatchability of eggs is the most sensitive measure of selenium toxicity (Ohlendorf, 1989). Thus, selenium levels in bird eggs are considered the best predictor of potential reproductive impairment (Skorupa, 1998). Reduced hatchability, survival, and duckling weight in mallards was observed with dietary selenium levels of greater than 10 mg/kg as selenomethionine (Heinze et al., 1990). These researcher noted differences in the manifestations of toxicity associated with selenium delivered as sodium selenite and selenomethionine. In addition, less of the organoselenium form was needed to produce measurable symptoms. Similar, but slightly lower levels of dietary selenium (6 to 9 mg./kg) produced reduced hatchability in chickens (Ohlendorf, 1989).

Possibly because seeds tend to have lower selenium concentrations than other plant parts, waterfowl feeding on zooplankton and/or algae are considered more sensitive to selenium contamination than species whose diet is composed of a larger proportion of seeds (Irwin et al., 1997). Thus, mallards, cinnamon teal, and pintails may be at less risk than gadwells and northern shovelers, which consume relatively more algae and zooplankton.

Livestock and Mammalian Wildlife

Because selenium is an essential element for animals, deficiency and toxicity relationships are fairly well understood for livestock and laboratory animals, although the toxicokinetics are still not fully understood (O'Toole and Raisbeck, 1998). Unfortunately, less is known about selenosis and background selenium levels in terrestrial mammals. Nonetheless, Ohlendorf (1989) indicated that selenium concentration in the livers of terrestrial herbivores usually average less than 2 mg/kg DW, while river otters (2.1 mg/kg wet weight), raccoons (2.8 mg/kg wet weight), and moles (2.6 mg/kg) contained slightly more selenium. Deer

mice (*Peromyscus maniculatis*) livers were reported to contain 1.4 mg Se/kg prior to mining and 1.9 mg Se/kg in reclaimed areas on coalmines in the Powder River Basin of Wyoming (Raisbeck et al., 1995). White-tailed deer from Michigan averaged 0.16 mg Se/kg (Ullrey et al., 1981).

Acute and chronic intoxication are recognized in livestock (James et al., 1989). Acute selenosis may occur when livestock are forced to eat highly seleniferous feed (400 to 800 mg Se/kg). Acute poisoning in cattle, horse and swine is manifest in abnormal posture, unsteady gait, diarrhea, abdominal pain, increased pulse and respiratory rate, prostration, and death. Distinct symptoms are less apparent in sheep and they simply suffer depression and death (James et al., 1991). Raisbeck et al., (1996) indicate that this form of selenosis can be clinically induced but is unlikely to occur in range animals for two reasons. First the amount of selenium needed to achieve selenium intoxication would require the consumption of unreasonably large quantities of unpalatable primary accumulator plants, and second, accessory toxins in the primary accumulators (e.g., swainsonine in two-grooved milkvetch) would override consideration of selenium toxicity.

Selenium levels of 4-5 mg/kg body-weight are required for manifestations of chronic toxicity symptoms (Mayland et al., 1989). Traditionally, chronic selenosis has been differentiated into alkali disease and blind staggers, based on the type of vegetation consumed and duration of exposure. Alkali disease is indicated when livestock (cattle, swine, and horses) ingest feed composed of non-accumulators plants containing 5 to 40 mg Se/kg for a period of weeks or months. Alkali disease can be clinically induced with inorganic selenium compounds and in documented as occurring under range conditions. In cattle, horses, and swine it is characterized by dullness, lack of vitality, emaciation, rough hair, loss of coat, and lameness. Sheep show some of these symptoms, but do not display hoof lesions or loss of wool (Mayland et al., 1989; James et al., 1991).

Blind staggers was associated with the consumption of selenium accumulator plant by over periods of days or weeks, however, the symptoms cannot be induced by Se-salts, and the disease may be caused by factors other than selenium toxicity (Lavender, 1986; James et al., 1991; Mayland, 1995;Raisbeck et al., 1996;). Mayland (1995) and Raisbeck et al., (1996) indicate that the condition referred to as blind staggers is probably polioencephalomalcia (PEM), which may be caused by excess sulfur consumption, rather than selenium intoxication.

Skorupa (1998) published interpretative guidance for selenium in mammals. Background levels (reported as dry weight) are reported as ranging from less than 1 to 4 mg/kg (typically less than 2 mg/kg) for whole

body; less than 1 mg/kg for muscle; 1 to 10 mg/kg in the liver of mammals in an aquatic environment; 0.1 to 0.5 mg/L for blood; and less than 1 to 3 mg/L for hair. Reproductive depression has been reported when the selenium concentration in hair is greater than 10 mg/kg DW. The overt toxicity threshold for dietary selenium exposure in domestic livestock is 3 to 5 mg/kg (Skorupa 1998), although Raisbeck et al., (1996) consider this level to be conservative for range animals.

TERRESTRIAL AND AQUATIC GUIDELINES FOR SELENIUM

This section presents guidelines that have been developed for selenium in terrestrial and aquatic environments by government agencies in the United States and elsewhere.

Soil Guidelines

The Office of Surface Mining recommends total selenium concentrations of less than 0.8 mg/kg and extractable (water or AB-DTPA) concentrations of less than 0.15 mg/l in root zone of western coalmines. These values have been increased on mine based on the demonstration of no effect on grazing animals. There is some limited information on guidelines for selenium levels in soils. Similar levels are applied in other western states as part of the coalmine regulatory program.

Maximum allowable concentrations of selenium in selected European countries ranged from 3 mg/kg in London to 10 mg/kg in Stuttgart, Germany (Irwin et al., 1997). Quebec considers 1 mg Se/kg as background; 3 mg Se/kg as moderately contaminated soils; and 10 mg Se/kg as a threshold that requires immediate cleanup (Beyer, 1990). The Ontario Ministry of Agriculture and Food for recommended a selenium limit of 1.6 mg/kg for soils treated with sewage sludge. Ontario considers 1.6 mg Se/kg as the maximum level for redevelopment as agriculture and 5 mg Se/kg as the maximum for residential or park land (Beyer, 1990). The soil cleanup value for selenium recommended by the New Jersey Department of Environmental Protection was 4 mg/kg DW (Beyer 1990). The Canadian Council of Ministers of the Environment (CCME) developed soil-selenium remediation levels for agricultural (2 mg/kg), residential/parkland (3 mg/kg), and commercial/industrial (10 mg/kg) land uses (CCME 1991).

Aquatic Guidelines

The following freshwater ambient water quality criteria have been proposed for total selenium (Skorupa 1998):

- Acute: 20.0 µg/L for 1-hour average
- Chronic: 5.0 for 4-hour average
- Drinking water maximum concentration level - 50 µg/L

Oak Ridge National Laboratory developed ecological risk assessment freshwater benchmarks for selenium (in µg/L) (Sample et al., 1996)

- National Ambient Water Quality Criterion - Acute: 20
- National Ambient Water Quality Criterion - Chronic: 5
- Secondary acute value - no information
- Secondary chronic value: no information
- Lowest chronic value - fish: 88.32
- Lowest chronic value - daphnids: 91.65
- Lowest chronic value - aquatic plants: 100
- Lowest chronic value - all organisms: 8.32
- Lowest test Effective Concentration 20 (EC 20) - fish: 40
- Lowest test EC20 - daphnids: 25
- Sensitive species test EC20: 2.6

In 1989, the U.S. Fish and Wildlife Service evaluated selenium toxicity research and recommended the following total recoverable selenium concentrations as target levels for cleanup of affected areas associated with the Kesterson Reservoir and the San Luis Drain Projects (Irwin and others 1997):

- Water - 2 ppb
- Sediment - 4 ppm DW
- Food for warm water fishes - 5 ppm DW.
- Food for waterfowl - 3 ppm DW

The CCME proposed an interim assessment criterion of 1 µg/L for selenium in water (CCME, 1991). In addition, they developed remediation criteria for freshwater aquatic life (1 µg/L), irrigation (20 to 50 µg/L), livestock water (50 µg/L), and drinking water (10 µg/L).

Wildlife Benchmarks

Skorupa (1998) summarized biotic effects of selenium in water, sediment, diet, water bird eggs, and fish (Table 3). Table 4 presents toxicity effect thresholds for plants, invertebrates, fish, amphibians and reptiles, birds, and mammals based on a review of selenium toxicity by Skorupa (1998).

Table B-3. Summary of comprehensive biotic effects of selenium[1]

Medium	No Effect[2]	Level of Concern[3]	Toxicity Threshold[4]
Water (total recoverable selenium - µg/L)[5]	<1.0	1.0 to 2.0	> 2.0
Sediment (mg/kg DW)	< 1.0	1.0 to 4.0	> 4.0
Diet (mg/kg/day DW)	< 2.0	2.0 to 3.0	> 3.0
Water bird eggs (mg/kg DW)	< 3.0	3.0 to 6.0	> 6.0
Fish, whole-body (mg/kg DW):			
Warm-water species	< 3.0	3.0 to 4.0	> 4.0
Cold-water species	< 2.0	2.0 to 4.0	> 4.0

µg/L Micrograms per liter
mg/kg Milligrams per kilogram

1 Adapted from Skorupa (1998)
2 Concentrations that are lower than this value produce no discernable adverse effects on fish or wildlife.
3 Concentrations of selenium in this range rarely produce discernable adverse effects.
4 Selenium concentrations above this value appear to produce adverse effects on some fish and wildlife.
5 Total recoverable selenium is equivalent to unfiltered water samples.

Table B-4. Summary of effect of thresholds for various organisms[1]

Interpretive Guidance	Effective Concentration Threshold (mg/kg unless otherwise denoted)
Plants	
Experimental LOAEL for sublethal effects (growth) in algal tissue	Plant Selenium Concentration 4.0
Experimental LOAEL for sublethal effects (growth) in macrophyte tissue (lettuce)	Plant Selenium Concentration 250
Experimental LOAEL for lethal effects in macrophyte (lettuce) tissue	Plant Selenium Concentration 800
Toxicity test LOAEL for sublethal effects on green algae	Waterborne Selenium Exposure (µg/L) 10.0 to 300 selenate 75 selenite
Toxicity test LOAEL for sublethal effects on blue-green algae	Waterborne Selenium Exposure (µg/L) 100 selenomethionine 3,000 selenate 3,000 selenite
Toxicity test LOAEL for sublethal effects on macrophyte (lettuce)	Waterborne Selenium Exposure (µg/L) 200 selenate 3,000 selenite
Invertebrates	
Experimental LOAEL for sublethal effects (growth), midge larvae and amphipod tissue concentrations	Invertebrate Selenium Concentration 2.5 to 15.0
Experimental LOAEL for sublethal effects (respiration rate) in crayfish	Invertebrate Selenium Concentration 30 (hepato-pancreas)
Experimental LOAEL fro reproductive effects, amphipod tissue concentration	Invertebrate Selenium Concentration 32
Experimental LOAEL for sublethal effects (growth) in midge larvae	Dietary Selenium Exposure 2.1
Experimental NOAEL for acute toxicity in amphipods	Dietary Selenium Exposure 300
No clear community level effects on benthic macro-invertebrates, outdoor macrocosm studies	Waterborne Selenium Exposure (µg/L) 25 inorganic mixture
Altered protozoan species diversity	Waterborne Selenium Exposure (µg/L) 20 to 160 (selenite)
Toxicity test LOAEL's for acute toxicity, in midge larvae amphipods	Waterborne Selenium Exposure (µg/L) 4.0 (selenomethionine) 200 (selenite) 500 (selenate)
Toxicity test LOAEL for sublethal (growth) effects on protozoans	Waterborne Selenium Exposure (µg/L) 3.0 (selenite)
Toxicity test LOAEL's for chronic toxicity in midge larvae and amphipods	Waterborne Selenium Exposure (µg/L) < 0.5 (?) (Selenomethionine) 25 to 100 (selenite) 25 to 100 (selenate)
Experimental LOAEL for drinking water toxicity in house flies	Waterborne Selenium Exposure (µg/L) 4,000 (selenite)
FISH	
Lowest validated concentration in edible tissue (trout fillet) warranting human health advisory	Fish Selenium Concentration 2.0

Table B-4. Summary of effect of thresholds for various organisms[1] (Continued)

Interpretive Guidance	Effective Concentration Threshold (mg/kg unless otherwise denoted)
Outdoor macrocosm LOAEL for reproductive impairment (bluegill)	Fish Selenium Concentration 16 to 18 (gonad and egg tissue)
Estimated true threshold range (≈ IC10) for reproductive impairment in sensitive species (perch, bluegill)	Fish Selenium Concentration 7.0 to 13.0 (gonad and egg tissue)
Experimental LOAEL for total reproductive failure (bluegill)	Fish Selenium Concentration 15 to 20 (whole body, parental)
Estimated true threshold range (≈ IC10) for reproductive impairment in sensitive species (perch, bluegill, salmon)	Fish Selenium Concentration 4.0 to 6.0 (whole body, parental or offspring)
Complete reproductive failure (IC10) in sensitive species (bluegill)	Dietary Selenium Exposure 30 to 35 (food chain selenium or selenomethionine)
Estimated true threshold range (≈ IC10) for reproductive failure in sensitive species (bluegill), parental exposure only	Dietary Selenium Exposure 10 (food chain selenium or selenomethionine)
Experimental LOAEL's for reproductive impairment via lethal larval dietary exposure (salmon, bluegill, razorback suckers)	Dietary Selenium Exposure 3.0 to 8.0 (food chain selenium or selenomethionine)
Health advisories recommend limited fish consumption by healthy adults and no consumption by children and pregnant women	Edible Tissue Selenium 2.0 (wet weight)
Complete ban on human consumption of fish recommended	Edible Tissue Selenium 5.0 (wet weight)
Amphibians and Reptiles	
Presumptive reproductive impairment threshold	Biomass Selenium Concentration ≥ 10 (eggs)
Presumptive adverse effects threshold on a whole body basis (10 x normal)	Biomass Selenium Concentration ≥ 20 (whole body)
Lowest toxicity test LC50 for amphibian eggs and larvae	Waterborne Selenium Exposure (µg/L) 90
Birds	
Embryo teratogenesis threshold (≈ IC10), wild ducks (sensitive taxon)	Bird Selenium Concentration 23 (in ovo)
Embryo viability (≈ egg hatchability) threshold, captive mallards	Bird Selenium Concentration 10 (in ovo)
Embryo teratogenesis threshold (≈ IC10), American avocets (tolerant taxon)	Bird Selenium Concentration 74 (in ovo)
Embryo viability (= egg hatchability) threshold, American avocets	Bird Selenium Concentration 61 to 80 (in ovo)
Hepatic threshold for juvenile and adult toxicity	Bird Selenium Concentration 30 (liver)
Muscle threshold for juvenile and adult toxicity	Bird Selenium Concentration ≈ 20 (breast muscle)
Provisional feather threshold warranting further study	Bird Selenium Concentration 5.0 (breast feathers)
Provisional blood threshold warranting further study	Bird Selenium Concentration 1.0 (whole blood) (wet weight)
Reproductive impairment threshold	Bird Selenium Concentration 3.0 to 8.0
Toxicity threshold for nonbreeding birds exposed to winter stress	Bird Selenium Concentration 10 to 15
Health advisories recommend limited consumption by healthy adults and no consumption by children and pregnant women	Edible Tissue Selenium 2.0 (wet weight)
Complete ban on human consumption recommended	Edible Tissue Selenium 5.0 (wet weight)

Table B-4. Summary of effect of thresholds for various organisms[1](Continued)

Interpretive Guidance	Effective Concentration Threshold (mg/kg unless otherwise denoted)
Mammals	
Reproductive depression threshold hair	Mammal Selenium Concentration (dry weight) > 10
Overt equine selenosis threshold, blood	Mammal Selenium Concentration (dry weight) 1.0 mg/L
Human chronic selenosis threshold, blood	Mammal Selenium Concentration (dry weight) 3.0 mg/L
Acute lethal toxicity LOAEL, sea lions, blood	Mammal Selenium Concentration (dry weight) 5.0 mg/L
Veterinary toxicological handbook threshold, domestic livestock, liver	Mammal Selenium Concentration (dry weight) 45 to 60
Sublethal effects threshold, lifetime exposure of rats	Dietary Selenium Exposure (dry weight) 1.4
Chronic selenosis threshold, humans	Dietary Selenium Exposure (dry weight) 1.9
Reduced longevity threshold, lifetime exposure, rats	Dietary Selenium Exposure (dry weight) 3.0
LOAEL for reproductive selenosis, in rats	Dietary Selenium Exposure (dry weight) 3.0
Overt toxicity thresholds, domestic livestock	Dietary Selenium Exposure (dry weight) 3.0 to 5.0
Sublethal effects LOAEL, dogs	Dietary Selenium Exposure (dry weight) 7.0
Health advisories recommend limited consumption by healthy adults and no consumption by children or pregnant women	Edible Tissue Selenium (wet weight) ≥ 2.0
Complete fan on human consumption recommended	Edible Tissue Selenium (wet weight) ≥ 5.0

IC10 Threshold of reproductive failure
LC50 Lethal concentration fifty
LOAEL Lowest observed adverse effect level
µg/L Micrograms per liter
Mg/kg Milligrams per kilogram
Mg/L Milligrams per liter
NOAEL No observed adverse effect level

[1] Adapted from Skorupa (1998)

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