ABSTRACT

PRELIMINARY ECOLOGICAL RISK ASSESSMENT TO ASSESS THE IMPLICATIONS OF REPLACING CHROMIUM PLATING WITH TANTALUM COATINGS

by
Erik Jonathan Weiss

An ecological risk assessment process requires a modeling tool that can adapt to changing environmental conditions. Computer simulation tools are a useful means to develop an ecological risk assessment, because if properly used they can provide an organized framework to evaluate multiple data sources, complex problems and hypotheses. An evaluation was completed of the University of Tennessee CHEMS-1 model that ranks and scores contaminant toxicity and exposure potential. Tantalum posed less of a hazard than hexavalent chromium to the terrestrial and aquatic animals. Although, results indicated that the vanadium compounds, in particular vanadium pentoxide, presented the greatest hazard, with hexavalent chromium following. A significant limitation of this model is that only two animals are used to assess ecosystem toxicity. Furthermore, due to multiple toxicity data and therefore uncertainty, many hazard values overlapped. Overall, the model is qualitative and cursory at best, and is not recommended as a tool for ecological risk assessment.

In the RESRAD-ECORISK model, a transport model is linked to the ecological risk model for soil contamination. This model is limited to five receptors: American robin, mallard, white-tailed deer, white-footed mouse, and the eastern cottontail. (A code problem currently being addressed by the developers prevented risk assessment of the mallard.) Risks are categorized into four groups ranging from potential to an extreme

adverse risk. The code also includes a sensitivity analysis. Applying this model revealed risks posed to receptors were found to be greatest for the American robin, where all metals resulted in extreme adverse effect risk characterization. While extreme risks were found for the eastern cottontail and white-footed mouse from exposure to vanadium, moderately high risks were observed from exposure to Cr(VI). On the other hand, the White-tailed deer received the least amount of risk from these contaminants, where all risk resulted as "potential". Based on vanadium and chromium (VI) surrogates, tantalum and molybdenum, respectively, contaminated soil presented a limited risk to the deer, while tantalum contaminated soil posed a greater risk to the rabbit and mouse than molybdenum contamination.

The third model, the Columbia River Comprehensive Impact Assessment (CRCIA), included the most comprehensive ecological habitat of the models evaluated. Risk in this model is divided into two categories; a site requires further assessment when a potential risk exists, which was the case for terrestrial and aquatic plants when exposed to any contaminants. Overall risks posed by the metals followed the order of Cr > V > Ta > Mo. Only three (of the twenty) terrestrial animals were at risk; the muskrat and raccoon were at potential risk from vanadium and tantalum, and the American coot was at risk from hexavalent chromium. Therefore, because of the multiple receptors at potential risk, CRCIA protocol would deem further assessment of the contaminated site applying stochastic risk assessment methods.

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by
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Thesis is dedicated to
my beloved family and Lauren my fiancé

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CHAPTER 1

INTRODUCTION

1.1 Objective

As part of the Department of Defense "Sustainable Green Manufacturing" initiative, a preliminary ecological risk assessment was undertaken to assess the implications of replacing chromium plating with tantalum coatings in artillery gun barrels. To achieve this, a comprehensive assessment of the life-cycle processing of tantalum was required. This life-cycle analysis included an evaluation of mining, refining, and recycling methods; an overview of world supply, market conditions, and uses; and, thermodynamic data. A preliminary, ecological risk assessment was conducted using three models that integrated data from multiple sources to determine contaminant impact to the ecology. This research includes a critical review and application of these models, a compilation of toxicity data required, and estimation methods used to evaluate ecological risk. The modeling provides a general ranking of chromium versus tantalum, an ecological assessment using a soil exposure code, and application of an integrated ecological risk model.

1.2 Tantalum Background Information

1.2.1 History

Tantalum is not found in its metallic state as a pure metal in the environment and is commonly found in conjunction with another element referred to as niobium. In 1801, Charles Hatchett an English chemist, tested a columbite ore that was part of a collection presented to the British Museum (Miller, 1959). The black stone was believed to have originated from Connecticut approximately a century earlier from John Winthrop, the first governor of Connecticut (Winter,1997). Hatchett's analysis determined that there was a new element present, which he referred to as columbium, named after America. However, Hatchett was not successful at isolating the free element. Shortly after, in 1802 the Swedish chemist Anders Gustaf Ekeberg, was able to isolate an acidic metallic oxide from columbium (Miller, 1959). This he termed tantalum because of its tantalizing behavior in attempts to dissolve it in acids. Further research indicated that columbite was a composite of two closely related metals (Miller, 1959).

In the early 1800's the chemist H. Rose analyzed a columbite sample obtained from Bavaria. His research led him to discover that columbite was composed of tantalum and another acidic element. He named the new acidic element niobium, after Niobe, the mythical daughter of Tantalus. After much debate it was determined that Hatchett's columbium was the same as Rose's niobium and at the Fifteenth International Union of Chemistry Congress at Amsterdam the metal was given the official name of niobium (Miller, 1959).

In 1824, J.J. Berzilius successfully produced for the first time an unrefined tantalum metal. Although the experiment was a success, no precautions were taken to avoid atmospheric contamination and as a result the tantalum was highly contaminated with oxide (Miller, 1959). In 1865, the chemist J.C.G. DE Marignac discovered that it was possible to separate tantalum from niobum because of their difference in relative solubilities as fluorides of potassium. The discovery of potassium fluorotantalate and potassium oxyfluoronibate resulted in the first pure compounds of the two elements (Miller, 1959).

A significant turning point in the purification of tantalum occurred in 1905, when Dr. W. von Bolton was successful in producing a pure tantalum metal by heating the lower oxides of tantalum to very high temperatures. The pure metal that was formed was ductile enough to be used for fabrication. He then suggested that this metal be used as an alternative filament in incandescent bulbs. This replaced carbon filament from 1905-1911 until which time tungsten became the preferred filament metal (Miller, 1959).

1.2.2 Physical Characteristics and Properties

Tantalum is similar in color and luster to that of platinum but is a darker silvery-gray; it is highly corrosion resistant to most commercial combinations of acids at standard temperature and pressure (Chen et al., 1996; Kroschwitz et al., 1997). Tantalum will dissolve in fluorine, hydrofluoric acid, sulfur trioxide (including fuming sulfuric acid), concentrated strong alkalis, and certain molten salts. However, it is resistant to attack by the following liquid metals as long as there is no oxygen present: Li (<1000°C), Na, K and NaK (<1000°C), ThMg (<850°C), U (<1400°C), Zn (<450°C), Pb (<850°C), Bi< (500°C), and Hg (<600°C). The corrosion resistance of tantalum can be compared to the corrosion resistance of glass, but tantalum withstands to even greater temperatures (Kroschwitz et al., 1997 and REMBAR, 1997). Presented in Table 1 are typical physical and mechanical properties of tantalum (Kroschwitz et. al.,1997).

Table 1 Physical Properties and Mechanical Properties of Tantalum

Property	**Value**
atomic number	73
atomic weight	180.9479
atomic volume, cm^3/mol	10.9
atomic radius, pm	147
Crystal Structure Lattice Type	body-centered cubic
Lattice Constant at 20°C, nm	0.33026
Density (at 20°C),g/cm^3	16.62
Melting Point, °C	2996
Boiling Point, °C	5427 ±100
Enthalpy of Fusion, J/mol^a	31,400
Enthalpy of Vaporization, J/mol^a	75.3 X 10^5
Heat Capacity at 20℃, J/(kg.K)^a, T from 25 to 2000°C	$24.2 + 3.0T + 0.2 \times 10^{-6} T^2$
Coefficient of linear thermal expansion, °C^{-1} at 20°C	6.5 X 10^{-6}
for T = 20-500°C	$L_0(1+ (6.59\ T + 0.0008\ T^2) \times 10^6$
Thermal Conductivity, J/(cm.℃)^a	
at 20°C	0.540
at 568°C	0.680
at 828°C	0.720
Electrical Resistivity (μΩ cm)	
at 20°	13.5
at 1500°C	71
Temperature Coefficient Of Electrical Resistivity (at 0-100°C)°C^{-1}	0.00382
Thermionic Work Function,eV	4.12
Magnetic Susceptibility (cgs)	0.93 X 10^{-6}
Tensile Strength, Mpa^b	
at Room Temperature	241-483
at 1000°C	90-117
Young's Modulus, Gpa^b	
at Room Temperature	186
at 1000°C	152
Vapor Pressure, log $P_{kPa}{}^d$, *T* from 290 K-mp	$-40{,}800/T + 9.41$

Table 1(cont.) Physical Properties and Mechanical Properties of Tantalum

Ductile-to-brittle transition temp,°C	<-250
Working temp	Room
Recrystallization temp, °C	900-1200
Nuclear cross section for thermal neutrons, m^2/atom[c]	21.3 X 10^{-28}

[a] To convert J to cal, divide by 4.184, [b] To convert Pa to psi, divide by 6897, [c] To convert m^2 to barns, divide by 1.0 X 10^{-28}, [d] $\log P_{mmHg} = -40,800/T + 10.29$.

1.2.3 Occurrence

Tantalite is the primary source of the tantalum mineral and is usually found in conjunction with columbite. The mixture of columbite-tantalite, an iron-black to brownish columnar crystal like structure with a metallic to submetallic luster, is found as a by-product in the mining of tin (cassiterite), pegmatites associated with granite, and in the alluvium from the disintegration of granite (Miller, 1959).

The amount of tantalum obtained from mining relative to the amount of ore mined is usually only a fraction of a percent (Kroschwitz et. al.,1997). As a reference, the concentration of tantalum rarely exceeds 3-4 pounds per ton. Tantalum is also found with niobium, titanium, tin slags from smelting and recycled scrap, some rare earths, uranium, and thorium. Tantalite and columbite, are recognized to be the most important tantalum bearing minerals, $(FeMn)(Ta,Nb)_2O_6$ (Kroschwitz et. al.,1997). Tantalates and niobates of iron and manganese provide the basic composition of tantalum and variations in their concentrations and density can provide general insight as to how much tantalum is present in a particular compound and help in its identification. For example, when the amount of tantalum pentoxide, Ta_2O_5, exceeds the niobium pentoxide, Nb_2O_5, by mass it is referred to as the compound tantalite. Conversely, if the niobium content is greater than the tantalum content it is referred to as the compound columbite. Tantalum ore, contains 20-wt.% or more of Ta_2O_5 (Kroschwitz et. al.,1997). In addition, to being found with tantalite and columbite, tantalum can be also found in other minerals. The following table contains oxide minerals in which tantalum is known to occur (Kroschwitz et al., 1997 and Chen et al. 1996):

Table 2 Common Tantalum Containing Minerals

Mineral	Formula	TaO_5 content, wt.%	Nb_2O_5 content, wt.%
·**tantalite**	$(FeMn)(Ta,Nb)_2O_6$	42-84	1-40
·**columbite**	$(FeMn)(Ta,Nb)_2O_6$	1-40	40-75
Manganotantalite	$Mn(Ta,Nb)_2O_6$	40-82	-------
Tapiolite	$Fe(Ta,Nb)_2O_6$	40-85	-------
Skogbolite	$FeTa_2O_6$	86	-------
·**microlite**	$Ca_2(Ta,Nb)_2O_6(OH,F)$	60-70	5-10
simpsonite or calogerasite	$Al_2Ta_2O_8$ + CaO as an impurity	70-72	-------
thoreaulite	$SnTa_2O_7$ + CaO and Nb_2O_6 as impurities	60-75	-------
stibiotantalite	$(Sb,Bi)(Ta,Nb)O_4$	35-60	-------
yttrotantalite	$(FeCa)_2(Y,Er,Ce,U)_2(Ta,Nb)_4O_{15}\cdot 4H_20$	30-45	-------
tanteuxenite	$(Y,Er,Ce,U)(Ta,Nb)(Ti)O_6$	20-55	-------
·**wodginite**	$Mn_4(Sn>Ta,Ti,Fe)_4(Ta>Nb)_8O_{32}$	45-56	3-15
struverite	$(Ti,Ta,Nb,Fe)_2O_6$	7-13	9-14
euxenite	$(Y,Ca,Ce,U,Th)(Nb,Ta,Ti)_2O_6$	2-12	22-30
samarskite	$(Fe,Ca,U,Y,Ce)2(Nb,Ta)_2O_6$	15-30	40-55

·Traditional raw materials for the processing industry

The high melting point and refractory nature of tantalum limits the formation of many simple compounds. However, Moshier (1964) characterized the following compounds to further understand the properties of tantalum: aluminum tantalide, Al_3Ta; tantalum boride, TaB_2; tantalum carbide, TaC; tantalum pentachloride, $TaCl_5$; tantalum oxytrichloride, $TaOCl_3$; tantalum tribromide, $TaBr_3$; tantalum pentabromide, $TaBr_5$; tantalum pentaiodide, TaI_5; tantalum pentafluoride, TaF_5; potassium fluorotantalate, K_2TaF_7; tantalum hydride, TaH; tantalum nitride, TaN; tantalum oxides and tantalic acid include tantalum (II) oxide, Ta_2O_4; tantalum pentoxide Ta_2O_5; tantalic acid $HTaO_3 \cdot nH_20$ and tantalum sulfide, Ta_2S_4. Of all of the compounds, the most important one to industry is K_2TaF_7.

1.2.4 Sources, Availability, and Mining

Tantalum is found in conjunction with a variety of minerals but it is predominantly associated with tin. The association between tin and tantalum is so strong that it usually requires additional processing that conventional metallurgy techniques do not regularly use.

Upon the smelting of, cassiterite, the principal ore of tin, the slag is divided into two grades. High-grade slags contain greater than ten percent Ta_2O_5, while low-grade slags of tin have less than ten percent. The tantalum content is determined prior to processing, as the grade determines the number of steps required in the processing of the slag. High-grade ores can be directly processed. Low-grade ores must first go through a pyrometallurgical enrichment process to create a tantalum ferroalloy, a synthetic concentrate, suitable for extraction (Chen et al., 1996).

As of 1994, worldwide consumption of tantalum was approximately 2.2 million pounds, and increased to an estimated 2.8 million pounds in 1995 (Chen et al., 1996). Until 1988, Southeast Asia was a leading producer of tantalum because of its production of tantalum rich tin slags, but production decline in countries, such as Thailand and Malaysia, stimulated interest in tin from Brazilian, Indonesian, Chinese, and Peruvian ore deposits. This world market shift towards the newer deposits of tin has indirectly reduced the world supply of tantalum because the tantalum content of the tin slags of ore from the newly mined regions is significantly less or nonexistent. At present, it is cost prohibitive for the mining industry in the newer regions to target tantalum for further refining. The second source for tantalum production is natural deposits of alluvial tantalite/columbite. As these sources become depleted, tantalum will be mined from rock tantalite, which is the most expensive source of tantalum (Chen et al., 1996). Fortunately, mines in Australia, Canada, Kazakhstan, and Africa have provided significant quantities towards the world's supply of tantalum. In particular, the Tanco (Canada) and the Wodgina (Western Australia) pegmatites are known for their higher-grade ore bodies (Chen et al., 1996). Conversely, the Gwalia (Western Australia) and Kenticha (Ethiopia) deposits are known for higher tonnage volumes of tantalum but of a lower grade. Mozambique was a major source of tantalite but the unstableness of the government in the 1970's caused mining operations to provide limited output or stop entirely (Chen et al., 1996).

Tantalite is predominantly obtained as a by-product of the large-scale open pit mining of cassiterite. In addition, underground mining, and the occasional small mining enterprises of individuals with sluice box and shovel operations produce varied grades of tantilite ore from pegmatites and alluvial deposits. The Tanco mine, the largest underground mine worldwide for tantalum, contains rooms from 20 up to 40 meters in height, supported by 15 meter square pillars. Although the Tanco mine is automated, utilizing large-scale equipment, underground operation costs are considerably higher than open pit mining (Chen et al., 1996).

The United States has an estimated 1.4 million kilograms of tantalum resources in identified deposits throughout the country. However, due to its low grade and complex mineral structure it is not considered economically viable (Cunningham, 1995). For general comparison, the only domestic source of the chromium within the U.S. is from recycling; the U.S has no natural sources of chromite (Papp, 1997; Papp, 1998).

Commercial mining of tantalum in the U.S. was only done when shortages were caused by increased military demand during the Korean conflict but, no significant mining of tantalum ore has been done since 1959; some small-unreported quantities were produced in 1989-92 (Cunningham, 1995). The Mineral Commodity Summary, released in February 1997, by the U.S. Geological Survey identifies the following countries as important sources of tantalum for the U.S. from 1992-1995: Australia, 28%; Germany, 14% (majority of imports of unknown origin); Thailand, 11%; Brazil, 8%; and other, 39%. As a general reference two-thirds of the world production of chromite ore is from India, Kazakstan, and South Africa (Papp, 1997; Papp, 1998). The value of tantalum consumed by the U.S. in 1996 was estimated at about $140 million. On the other hand, average U.S. imports for 1997 of chromium ore and chromium containing products was 765,000 tons-gross estimated at about $450 million (Papp, 1997; Papp, 1998). In late November 1996, the price of tantalite ore ranged from $27-28.50 per pound of ore containing 60% tantalum pentoxide.

Industry has indicated the average selling prices for tantalum and chromium were as follows (Cunningham, 1995; Papp, 1997; Papp, 1998):

Table 3 Average Selling Prices and Price Quotations for Tantalum and Chromium

Product	Price
Ta Powder	\$100-\$180 (per pound)
Ta Wire	\$170-\$250 (per pound)
Ta Sheet	\$100-\$150 (per pound)
Ta_2O_5	\$40-\$90 (per pound)
TaC	\$45-\$60 (per pound)
Chromite Ore	\$73 (per metric ton)
High-carbon ferrochromium	\$0.48-\$0.49 (per pound)
Low-carbon ferrochromium	\$0.90-\$1.03 (per pound)
Electrolytic	\$4.15 (per pound)
Elchrome	\$5.57 (per pound)

The U.S. will not produce any tantalite ore in the near future and will continue to consume approximately over 500,000 kilograms yearly. In 1994 and 1995, the U.S. consumption of tantalum totaled 430,000 and 515,000 kilograms respectively. The predominant use (about 60%) was in the production of electronic components, primarily capacitors. Based upon current market trends it is estimated that by the year 2000, worldwide consumption of tantalum capacitors will reach 25 billion units. The production of so many capacitors is expected to require 794,000 kilograms of tantalum powder and 159,000 kilograms of tantalum wire (Cunningham, 1995). For reference and comparison the U.S. consumes about 12% of the worlds chromite ore production in the forms of ore, ferroalloys, metals, and chemicals.

The U.S. has uncommitted inventories in non-stockpile tantalum capacitor-grade powder, 454,000 kilograms in non-stockpile grade minerals, and 65,300 kilograms in tantalum metal ingots. The Department of Defense proposed to dispose of approximately 907 kilograms of tantalum carbide powder, 45,400 kilograms of tantalum minerals, and 9,070 kilograms of tantalum oxide in 1997 and 1998 (Cunningham, 1995).

CHAPTER 2

REFINING OF TANTALUM

2.1 Tantalum Ore

After mining, the tantalite-columbite ore, $(Fe,Mn)(Nb,Ta)_2O_6$, is sorted and separated from oversize material through screening methods. A series of crushing stages is used to liberate and reduce the raw ore to about 15-mm with minimal fines production. The ore is further reduced using rod mills and/or grate discharge ball mills (Chen et al., 1996). Subsequent to grinding, most concentrates require a further separation step to remove other minerals. Some of the following minerals commonly associated with the concentrate include but are not limited to, zircon, rutile, monazite, cassiterite, ilmenite, garnet, uranium and thorium minerals, sulfides, beryl, spodumene, tourmaline and aquamarines, and gold. Cleaning of the concentrate can be accomplished using wet or dry methods such as sizing, gravity concentration, flotation, leaching, magnetic and electrostatic separation. The majority of metals are currently processed by flotation, but gravity concentration is still preferred commercially for tantalum (Chen et al., 1996). Gravity concentration is selected because presently it can handle the wide size range of particles (Chen et al., 1996). To isolate the tantalum and niobium the ore concentrate is exposed to a combination of high-tension electrostatic and electromagnetic sources. The resulting ore contains a combined concentration of Ta_2O_5+Nb_2O_5 up to 70% as compared to unprocessed tantalum ore grades with contents of less than 0.1% Ta_2O_5 (Chen et al., 1996).

2.2 Tin Slag

During the smelting of cassiterite ore, which in its purest form contains 78.6 percent tin the ore is divided into two groups: the high-grade ore slag contains a Ta_2O_5 content of more than 10%, and the low-grade ore slag has a content of less than 10% (Chen et al., 1996 and Barry et al., 1983). The grade identification step helps industry reduce handling and processing because a high-grade slag can go directly to a tantalum extraction plant without further enrichment. Conversely, a low-grade slag with a content of 4% to 10% Ta_2O_5+Nb_2O_5 requires a pyrometallurgical enrichment process. The process creates a synthetic concentrate that can increase the Ta_2O_5 content by 20%. The pyrometallurgical process is an electrothermal reduction sequence of three processing steps. The slag, first mixed with additives such as Fe_2O_3, CaO, and C, is fed into a three-phase electrical arc furnace. Upon reaching a temperature of 1500°C, coke and charcoal are added to the high carbon ferroalloy, composition of 10-20% Ta_2O_5, 10-20% Nb_2O_5, 40-60% FeO and 5-10% TiO_2. The ferroalloy is then crushed and fed into a roasting process where it is oxidized into Ta_2O_5 and Nb_2O_5. The oxidized by-product of Ta_2O_5 and Nb_2O_5 is then processed in the furnace to remove impurities such as W, Sn, P and Fe in an alloy scrap. The resulting slag of Ta and Nb is sold or processed for extraction. Upon completion of the enrichment process the slag is suitable for extraction (Chen et al., 1996) Figure 1.

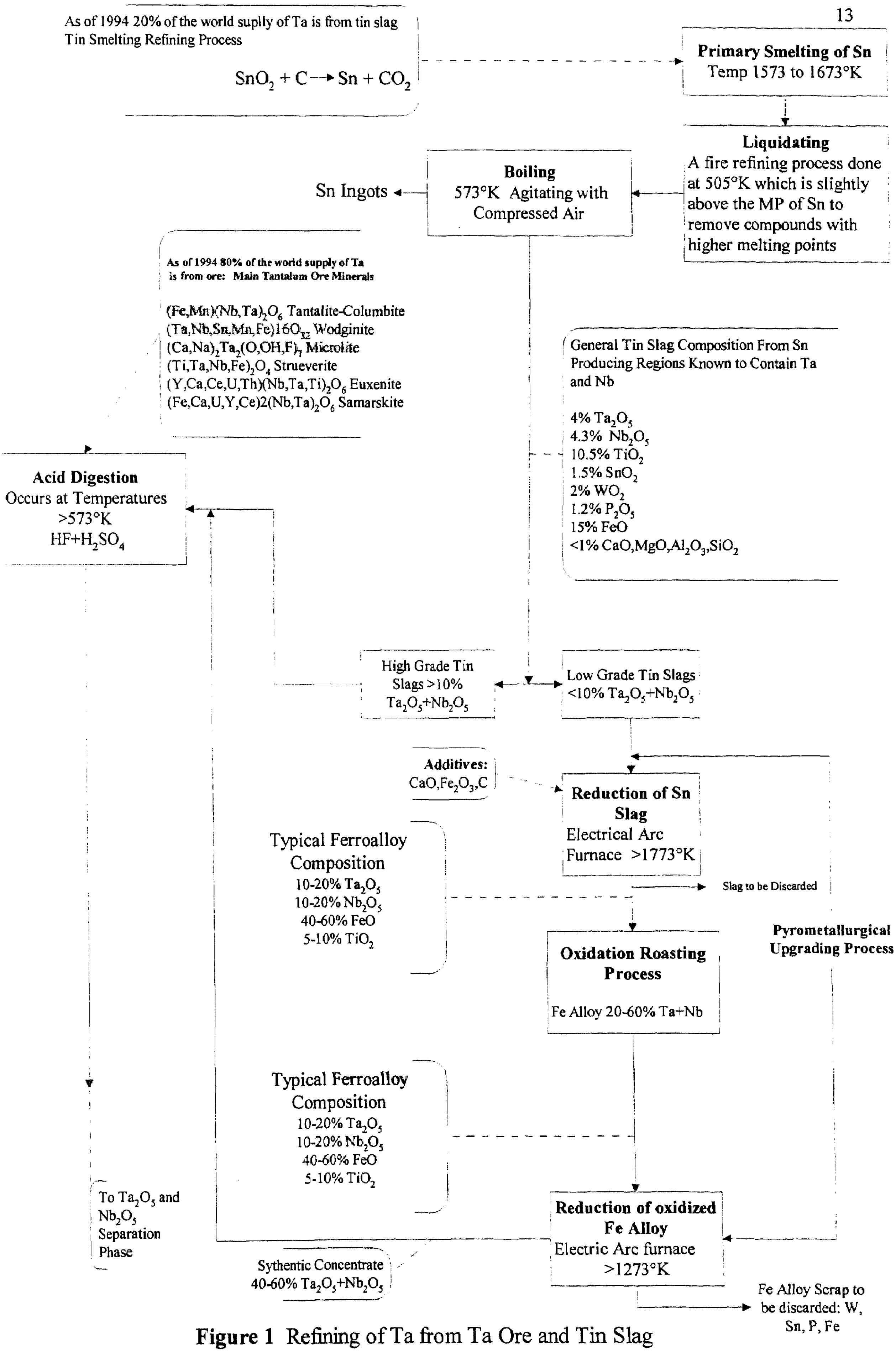


Figure 1 Refining of Ta from Ta Ore and Tin Slag

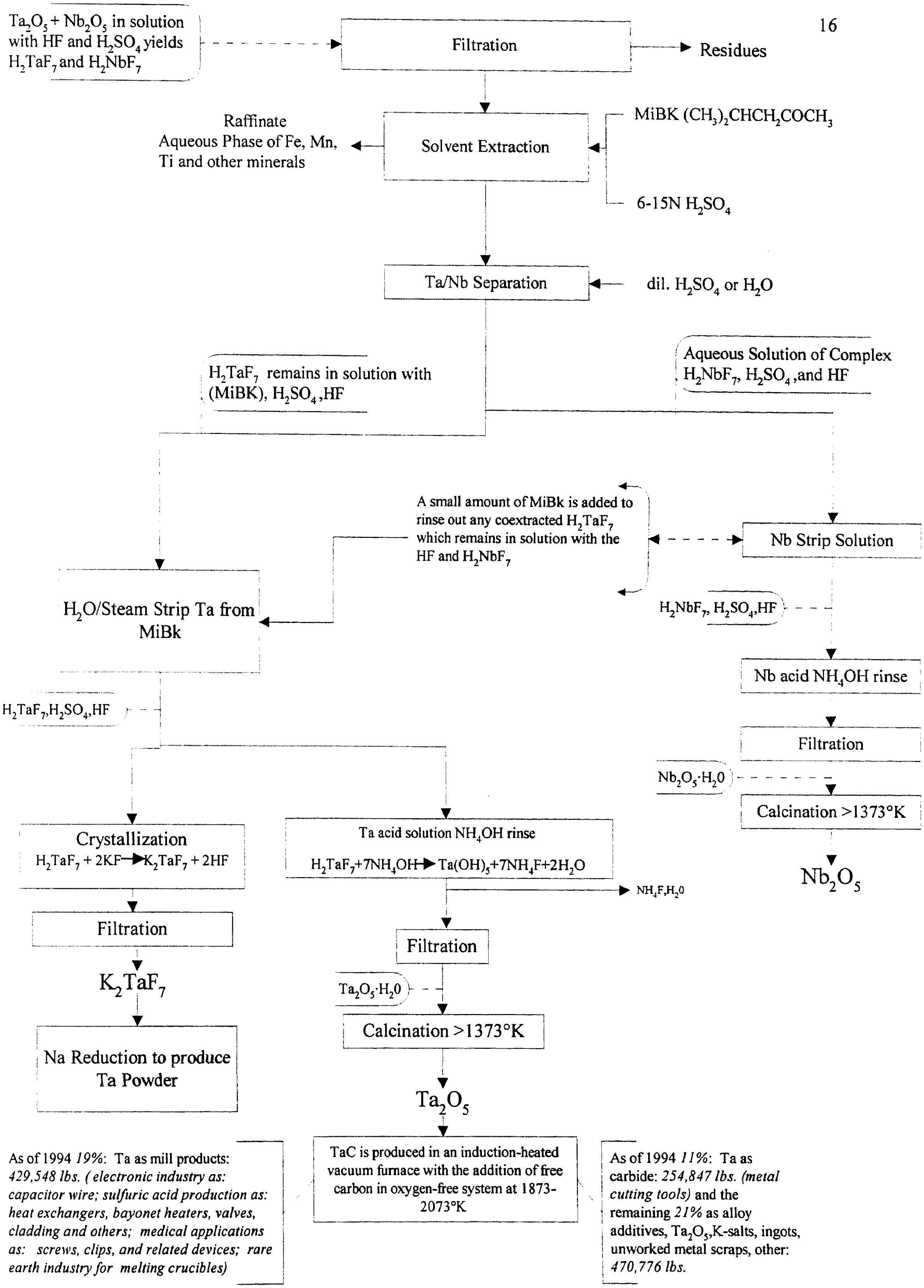
2.3 Separation and Extraction of Tantalum

Until 1957, extraction of tantalum metal from ore involved a combination of alkali fusion to decompose ore, acid treatment to remove impurities, and Marignac fractional crystallization to separate the tantalum from the niobium and purify the K_2TaF_7 end-product (Kroschwitz et. al.,1997). This extraction process was done commercially at Fansteel Metallurgical Corp. The process begins by fusing sodium hydroxide with pulverized ore to produce a crude sodium tantalate and niobiate. The raw ore is rinsed with water and steam to remove acidic components such as silica. The sodium tantalate and niobiate is then treated with hydrochloric acid to decompose the salts to earth acids and remove impurities such as iron, tin and manganese. The remaining material is then dissolved in a hot solution of hydrofluoric acid, where a potassium fluoride additive is introduced forming the salts K_2TaF_7 and K_2NbOF_3 (Miller, 1959). The resulting potassium tantalum fluoride, crystallizes as fine needles and is soluble in dilute hydrofluoric acid (HF). A dilute solution of HF with a minimum concentration of 0.5% is used to prevent hydrolysis of the salt to the insoluble basic fluoride. In addition, potassium niobium oxyfluoride also crystallizes as thin plates and is completely soluble in water even if hydrofluoric acid (HF) is not present. The solubility differences between K_2TaF_7 and K_2NbOF_5 allows the tantalum salt crystals to be separated from the platelets of niobium (Miller, 1959). This process developed by J.C. DE Marignac separated niobium and tantalum by the fractional crystallization of their potassium fluoride salts, employing conditions which produced the normal double fluoride of tantalum, K_2TaF_7, and the oxyfluoride of niobium, K_2NbOF_5 (Miller, 1959).

Current commercial tantalum refining relies on a hydrometallurgical process, commonly known as the fluoride or solvent extraction (Figure 2). This liquid-liquid extraction is based on the effect acidity has on the solubility of fluorides in methyl isobutyl ketone, (MIBK or $(CH_3)_2CHCH_2COCH_3$). Upon contact with the MIBK, the tantalum fluoride dissolves in the organic phase at a low acidity, the niobium fluoride dissolves in organic phase at a high acidity, and the other minerals remain in the aqueous raffinate (Kroschwitz et. al., 1997). Further separation of the tantalum and niobium fluorides is accomplished by converting them to hydrated oxides by precipitation with ammonia or to double fluoride crystals through the addition of potassium fluoride salts (Kroschwitz et. al., 1997).

The process first begins by digestion of tantalite-columbite ore, tin slag, or ferroalloy concentrate in a solution of HF and sulfuric acid (H_2SO_4) to create an aqueous medium for processing. The resulting reaction forms a complex of heptafluorides, H_2TaF_7 and H_2NbF_7, and precipitates of fluorides of alkaline earth and rare earth metals. The mixture is then filtered and the aqueous solution of Ta-Nb in HF is extracted through several columns with the organic solvent, MIBK. The addition of the organic component chemically attracts the complex fluorides of tantalum and niobium, with a raffinate of the aqueous phase of Fe, Mn, Ti, and other minerals.

The organic phase containing the complex fluorides of tantalum and niobium is washed with 6-15N H_2SO_4 and extracted with water or dilute H_2SO_4 (Chen et al., 1996). The aqueous phase acts as a solvent for the fluoroniobate and free hydrofluoric acid, while complex fluorotantalate remains dissolved in the organic phase. The aqueous



A small amount of MiBk is added to rinse out any coextracted H_2TaF_7 which remains in solution with the HF and H_2NbF_7

TaC is produced in an induction-heated vacuum furnace with the addition of free carbon in oxygen-free system at 1873-2073°K

As of 1994 *19%*: Ta as mill products: *429,548 lbs. (electronic industry as: capacitor wire; sulfuric acid production as: heat exchangers, bayonet heaters, valves, cladding and others; medical applications as: screws, clips, and related devices; rare earth industry for melting crucibles)*

As of 1994 *11%*: Ta as carbide: *254,847 lbs. (metal cutting tools)* and the remaining *21%* as alloy additives, Ta_2O_5,K-salts, ingots, unworked metal scraps, other: *470,776 lbs.*

Figure 2 Seperation and Extraction of Tantalum niobium solution is contacted with a small amount of MIBK to remove traces of coextracted tantalum. The organic phase that results is recycled through the tantalum-niobium extraction stage. Gaseous or aqueous NH_3 or NH_4OH is added to the acidic aqueous niobium solution to precipitate niobium oxide hydrate and is filtered with purified water, and calcined at high temperatures producing Nb_2O_5. Tantalum is stripped from the organic phase usually with a combination steam, water and dilute ammonium hydroxide. The resulting solution of tantalum oxide hydrate is precipitated by ammonia, filtered with purified water, and calcined at high temperature up to 1100°C resulting in tantalum pentoxide,Ta_2O_5. Potassium salts can also be added to produce crystals of potassium heptafluorotantalate when tantalum oxide hydrate is precipitated by ammonia to produce K_2TaF_7 (Chen et al., 1996).

2.3.1 Tantalum Powder

Most of the industrial tantalum powder in the world is currently obtained from the tantalum compound, K_2TaF_7, of which 90% is processed predominantly from the sodium reduction method (Chen et al., 1996).

$$K_2TaF_7 + 5Na = Ta + 2KF + 5NaF$$

K_2TaF_7 is preferred over other tantalum compounds because it is less complicated to extract from raw material and its natural nonhygroscopic character allows for easier processing. The sodium extraction process is based on modifications of the patented research by E.G. Heillier and G.L Martin (Chen et al., 1996)(Figure 3). The process is

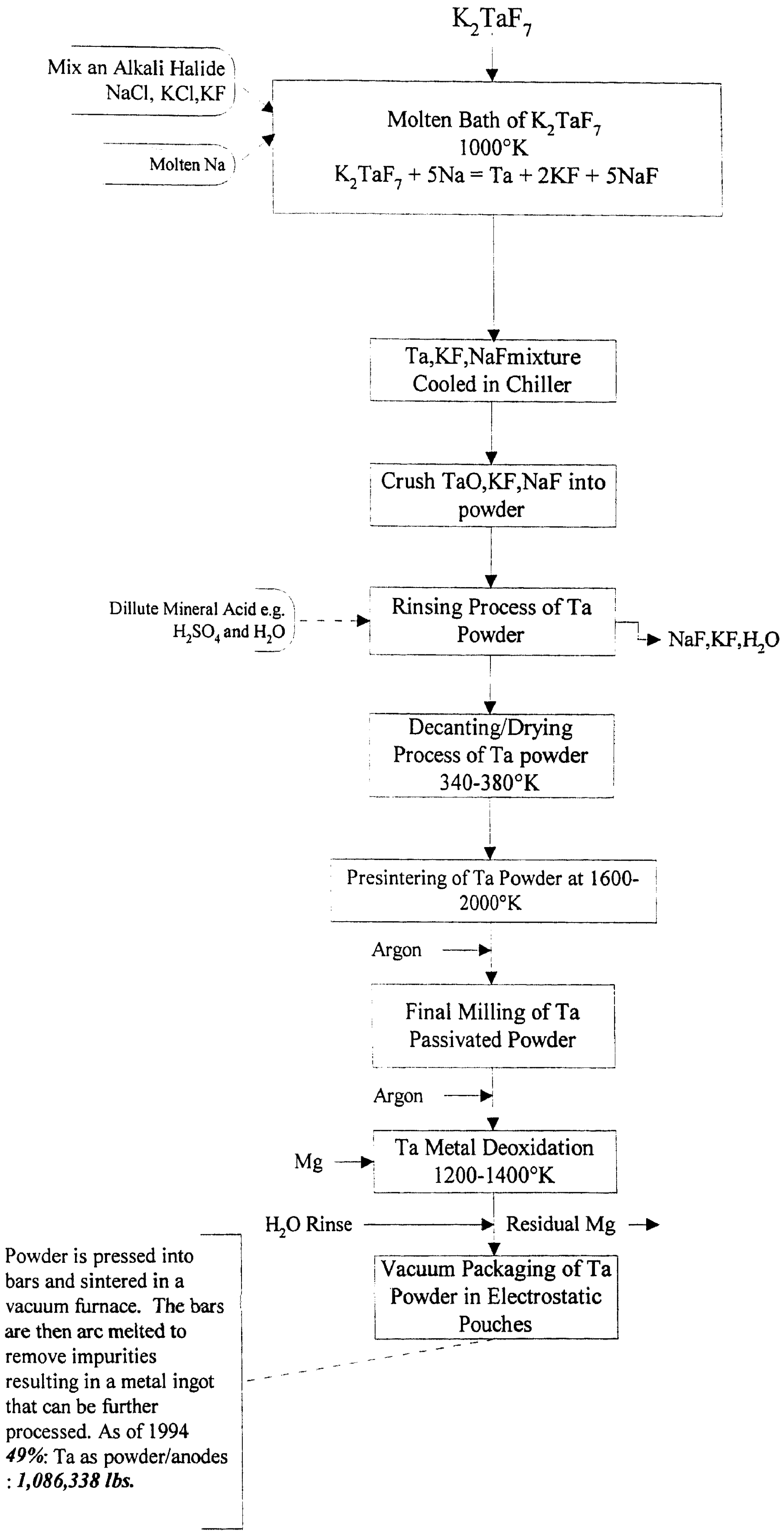


Figure 3: Refining of K_2TaF_7 with Na Reduction

initiated by creating a molten bath of K_2TaF_7 at 1000°K. When the operating temperature of the bath of K_2TaF_7 is reached, the reduction reaction is started by introducing molten sodium into the retort while the mixture is continuously agitated. Upon reaching the operating temperature an alkali halide such as NaCl, KCl, or KF is added to lower the melting point (Miller, 1959) and influence particle morphology. The amount of molten NaCl salt used affects the average particle size of the final tantalum powder product; the greater the diluent concentration the smaller the particle size. The flow rate of sodium is critical; it is regulated to balance the energy input by the furnace and the thermal energy from the reduction. Upon completion of the reaction the reactor is cooled with a chiller resulting in solid metal. The metal is removed and crushed to make it adequate for leaching in a dilute mineral acid solution. A final rinse with water is done to separate the tantalum powder from any of the residual salts; resulting in a primary powder. The primary powder is then decanted and dried at 340-380°K to evaporate off the excess moisture and prepare it for further processing (Chen et al., 1996).

The largest use of tantalum, over 60%, is in the manufacture of powder, wire, and furnace parts for the production of solid electrolyte capacitors (Chen et al., 1996; Cunningham, 1995). Capacitors containing tantalum require a higher purity than can be achieved after crushing and leaching. The primary impurities of concern are oxygen, sodium, and carbon because resistivity increases with oxygen content, and carbon and sodium have been directly correlated to DC leakage of anodized, sintered tantalum pellets (Miller, 1959; Chen et al., 1996). To achieve a suitable powder the metal is then presintered in a vacuum furnace ($\leq 5 \times 10^{-2}$ Pa or 4×10^{-4} mmHg) at a temperature between 1600-2000°K to remove impurities, improve flow and pellet crush strength. The agglomeration process causes the surface of the tantalum to be free of oxygen because the passivating thermal oxide layer, always present on tantalum that is exposed to oxygen, has diffused into the tantalum (Kroschwitz et al., 1997; Chen et al. 1996). Then depending on specification requirements a new thermal oxide layer is produced on the tantalum through additions of oxygen. Final milling of the passivated powder is carried out in an inert argon atmosphere using grounded equipment to avoid spontaneous combustion of the fine powder from static electricity. An additional step can be performed to deoxidize the metal further if product specifications require. The metal is mixed with a stoichiometric amount of magnesium powder in an inert atmosphere and brought to a temperature between 1200-1400°K for several hours. The Mg reacts with the oxygen that diffuses from the surface of the tantalum oxide and once all of the oxygen has reacted with the Mg, the resulting product goes through further rinsing to remove any of the unreacted Mg and magnesium oxide. The final product is vacuum packed in electrostatic safe plastic pouches to prevent uptake of atmospheric oxygen and the spontaneous ignition of the fine powder during handling.

2.3.2 Recycling

The value of tantalum scrap is approximately $25 per pound and it is estimated that 20% of the tantalum purchased is from recycled sources (Cunningham, 1995). Due to the high cost of raw material, producers are constantly researching methods to reduce loss of raw material through processing. Presently, industry recycles on average 5-50% of their starting material (Chen et al., 1996). A summary provided in Table 4 by H.C. Starck, (Chen et al., 1996) defines the by-products that result from the production of 2000 metric tons of combined oxides of Ta_2O_5 and Nb_2O_5. The data is based on an estimated 1990 world consumption of 2.7 million pounds of Ta_2O_5 and 1.9 million pounds of Nb_2O_5 (Chen et al., 1996).

Table 4 Chemical Consumption During Tantalum Processing

Input of Chemicals	Products	By-products (Waste)
4.0 mt HF	1.2 mt Ta_2O_5 in $K_2TaF_7 + Ta_2O_5$	28.0 mt Sludge containing :
6.0 mt H_2SO_4	850 mt Nb_2O_5	$CaF_2 + CaSO_4 +$
1.4 mt NH_3		$TiO_2\ nH_2O + Fe_2O_3\ nH_20$

As illustrated above, it can be noted that a substantial input of chemicals is required for minimal output of tantalum product; producing a significant amount of waste. In order to change this trend industry has implemented various recycling efforts throughout stages of the refining process. The following example is how one company in the industry is looking to minimize waste of resources. H.C. Starck developed a method that eliminates the use of H_2SO_4 in the digestion step and continues to keep it separate from HF in other steps. By separating these two mineral acid streams the process yields pure enough by-products of $CaSO_4$ and CaF_2 which are acceptable enough for feed material in other chemical processes. In addition, the company has further modified the refining process on a pilot plant scale that will eliminate the use of a second acid; this will allow the HF lost in the raffinate to be recycled (Chen et al., 1996). Another leading manufacturer of tantalum metal, Cabot Corporation, has eliminated the use of sulfuric acid completely from their refining process.

Recycling of tantalum can be conventionally processed by initially sampling the feed scrap or alloy material for purity. Material that is considered suitable for the recycling should have a tantalum content between 40-100% (Chen et al., 1996). If the material is on specification, it is degreased in a sodium hydroxide rinse and pressed. It is then remelted, forged, and rolled to a preliminary shape; 60% of this material goes for further finishing, while the remaining 40% is used as alloy additives. The 60% that goes for further finishing is degreased and pickled using NaOH, HF, and HNO_3. Upon completion of the pickling process the metal is annealed, cooled and finish rolled. This process is repeated a second time before the material is ready for packaging and shipping.

Also chlorination is an alternative method that is suitable for Ta alloys and scrap. The process is further detailed in Figure 4. The feed material is pulverized and blended with sodium chloride into a $NaCl\text{-}FeCl_3$ melt. The complete reaction is:

$$Fe(TaNb) + NaCl + 7NaFeCl_4 = (TaNb)Cl_5 + 8\ NaFeCl_3 \quad (1)$$

$$8NaFeCl_3 + 4\ Cl_2 = 8NaFeCl_4 \quad (2)$$

The reaction occurs at temperature around 600°C, evolving chlorides like $TiCl_4$ and $SiCl_4$. In addition to the formation of other chlorides, $TaCl_5$ is also evolved. Its boiling point along with $NbCl_5$ and $WOCl_4$ is between 228°C and 248°C. Upon fractional distillation of this mixture, $TaCl_5$ is then converted by hydrolysis with steam to tantalum pentoxide. The tantalum pentoxide can than go through further refinement using a vacuum-arc or electron-beam melting furnace to produce metal ingots (Kroschwitz et. al.,1997).

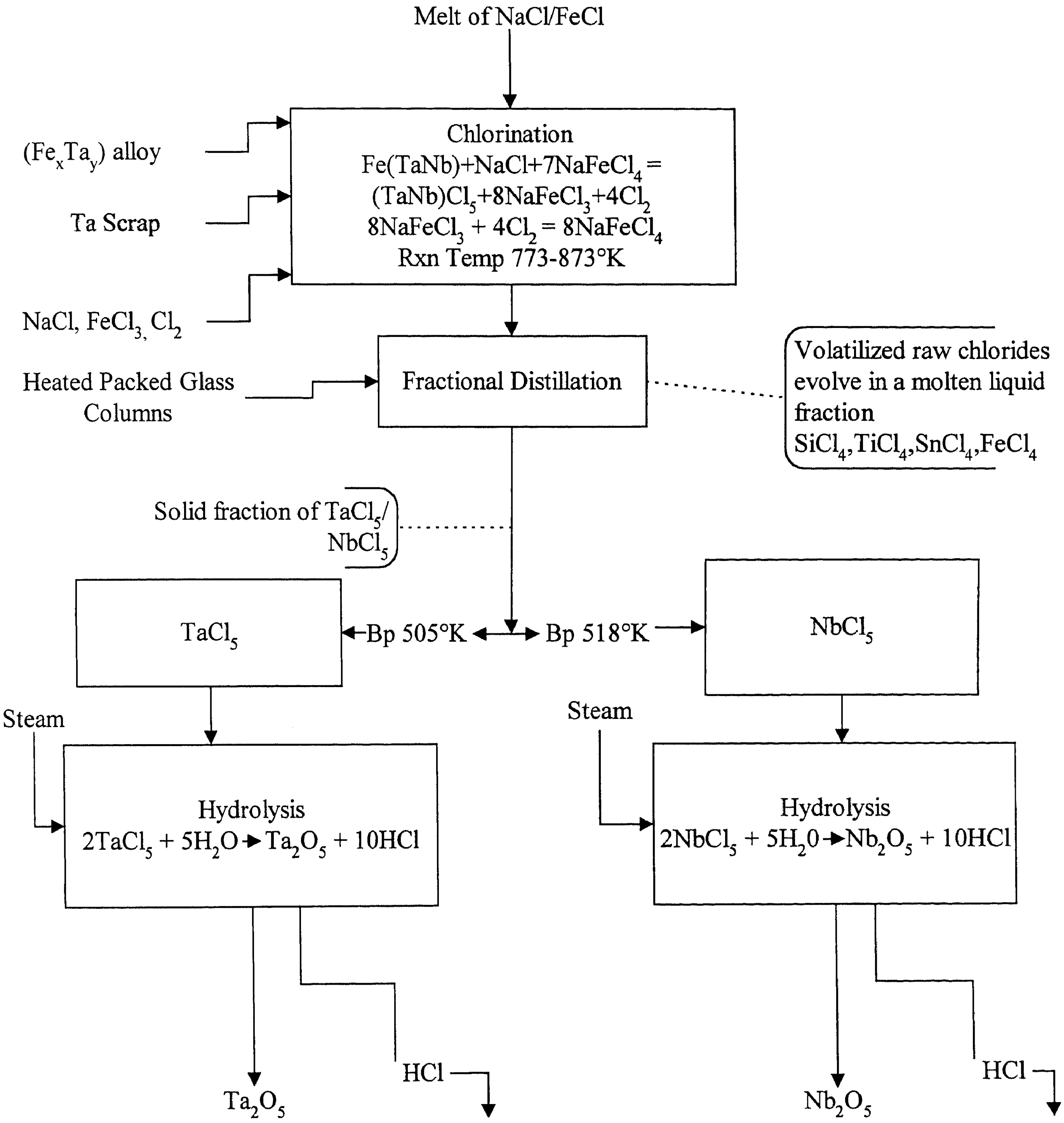


Figure 4 Recycling of Ta Compounds by Chlorination

2.4 Thermodynamic Data

To evaluate the behavior of tantalum and compounds associated with its refining, extraction, processing, and recycling, thermodynamic data is needed to model Ta in the environment. Enthalpy (ΔH°), entropy (ΔS°), and free energy (ΔG°) are used to predict if reactions will occur spontaneously in the environment under specific conditions.

Enthalpy (H) is equal to the heat content of a species under conditions of constant pressure. The change in enthalpy (ΔH) or the heat of reaction identifies whether a reaction is endothermic or exothermic and if it can proceed. When the value of ΔH is negative heat transfers to the surroundings and the reaction is referred to as exothermic. Conversely, an endothermic reaction has a positive ΔH and will absorb heat. Entropy (S), is an intensive property that describes the amount of disorder or randomness. In a solid, there is a high degree of order; the entropy is low. However, as solids change to liquids and liquids change to gases the entropy increases because the disorder of the system increases. The change in free energy $\Delta G = \Delta H\text{-}T\Delta S$ can predict whether a reaction will or will not proceed, but it can not always predict if a reaction is rapid.

2.4.1 Standard State, Thermodynamic Symbols, and Free Energy

The standard state of a substance provides a good starting point because it occurs at a temperature where the most stable form of a substance can be found. The standard state is usually 298°K and one atmosphere pressure. Thermodynamic quantities that refer to the standard state are noted by a superscript °, as in ΔH°. This ° symbol also indicates that the elemental thermodynamic quantities are in their pure state. The standard heat of formation is the heat absorbed when one mole of a substance in its standard state is formed from the most stable forms of the elements in their standard states, and is noted by a subscript $_f$. The values in the accompanying tables will help determine the equilibrium constants of tantalum and compounds associated with its refining, extraction, processing, and recycling.

Free energy (G), is a quantitative indicator of spontaneity that depends only on changes in the system and is directly related to H and S. The standard free energy of formation (ΔG_f°) is the free energy change during the formation of one mole of substance in standard state from the most stable form of the elements in their standard states. Even if values of ΔG_f° are not available, ΔG_f° can be calculated from ΔH_f° and S°. In addition, it is possible to determine whether a reaction will proceed by applying the equation $\Delta G = \Delta G^\circ + RT \ln Q$. At equilibrium ΔG is equal to zero and Q is equal to K_{eq} (equilibrium constant). Consequently, the equations of $\Delta G^\circ = -RT \ln K_{eq}$ or $K_{eq} = e^{-\Delta G^\circ/RT}$ provide the relationship between the free energy of a system and its equilibrium constant.

The thermodynamic information available in the accompanying tables provides an overview of reactions involving the formation of numerous tantalum compounds to further understand the behavior of tantalum and its species.

Table 5 Free Energies for Reactions Involving Tantalum

Reaction	Free Energy Calculations	References
$Ta_{(s)} \rightarrow Ta_{(g)}$	(2000-3000°K) $\Delta_{sub}G = 758852.1 - 6.7362 \log T - 109.62\ T$ J/mol	Chase, et al. 1985 Gerassimov, et al., 1972 Garg, et al., 1996
$Ta + C \rightarrow TaC$	$\Delta_f G = -144.58 + 2.0388\ 10^{-2}T - 5.5664 \times 10^{-3}\ T\log T$ kJ/mol formula	
$Ta^{+5} + 5/2Cl_2 \rightarrow TaCl_{5(s)}$	(298.15-4897°K) $\Delta_f G = -867.251 - 34.417 \times 10^{-3}\ T\ln T + 3.774 \times 10^{-6}T^2 - 245.915\ T^{-1} + 602.680 \times 10^{-3}T$ kJ/mol formula	
$TaCl_{5(s)} \rightarrow TaCl_{5(l)}$	(489.7-506.9°K) $\Delta_f G = -872.188 - 128.838 \times 10^{-3}\ T\ln T + 29.442 \times 10^{-6}T^2 - 245.914T^{-1} + 1184.980 \times 10^{-3}T$ kJ/mol formula	
$TaCl_{5(g)}$	(298.15-2000°K) $\Delta_f G = -771.956 - 18.447 \times 10^{-3}\ T\ln T + 3.430 \times 10^{-6}T^2 + 287.65\ T^{-1} + 310.787 \times 10^{-3}T$ kJ/mol formula	
$3/5\ Ta_{(s)} + 1/5\ Ta_2O_{5(s)} \rightarrow TaO_{(g)}$	(298-3293°K) $\Delta_f G = 194.88 - 0.15249\ T + 1.9090 \times 10^{-2}\ T\log T\ (\pm 0.3)$ (3293-5600°K) $\Delta_f G = 162.39 - 0.16262\ T + 2.4812 \times 10^{-2}\ T\log T\ (\pm 0.02)$	
$1/5\ Ta_{(cs)} + 4/5\ Ta_2O_{5(s)} \rightarrow TaO_{2(g)}$	(298-3293°K) $\Delta_f G = -197.47 - 9.4808 \times 10^{-2}\ T + 2.0512 \times 10^{-2}\ T\log T\ (\pm 0.3)$ kJ/mol formula (3293-5700°K) $\Delta_f G = -200.50 - 0.20022T + 5.0872 \times 10^{-2}\ T\log T\ (+ 0.01)$ kJ/mol formula	

Table 6 Reactions Considered for Tantalum-Water Systems at 298 K

Reactions Considered for the Tantalum-Water Systems Reactions	ΔG_f° kJ/mol	K	$\Delta E^\circ = \frac{0.059}{n} \log K$ (V)	References
$TaO_2^+ + H_2O \rightarrow HTaO_3 + H^+$	4.836	0.1422	-0.0499	Arana et al., 1995
$HTaO_3 \rightarrow TaO_3^- + H^+$	54.58	2.7×10^{-10}	-.56	
$TaO_2^+ + 5/2H_2 \rightarrow Ta + 2H_20 + H^+$	353.50	1.082×10^{-62}	-3.656	
$TaO_3^- + H^+ + 5/2H_2 \rightarrow Ta + 3H_20$	294.08	2.821×10^{-52}	-3.04	
$Ta_2O_5 + 5H_2 \rightarrow 2Ta + 5H_2O$	726.63	0.000	-	
$Ta_2O_5 + 2H^+ \rightarrow 2TaO_2^+ + H_20$	19.61	3.645×10^{-4}	-0.203	
$Ta_2O_5 + H_20 \rightarrow 2TaO_3^- + 2H^+$	138.44	5.372×10^{-25}	-1.431	
$Ta_6O_{19}^{-8} + H^+ \leftrightarrow HTa_6O_{19}^{7-}$	-6.51	13.89	0.067	Betrabet et al., 1984
$Ta_6O_{19}^{-8} + 2H^+ \leftrightarrow HTa_6O_{19}^{6-}$	-8.06	25.91	0.083	
$2H^+_{(aq)} + 2e^- \leftrightarrow H_{2(g)}$	0.000	1	0.000	Arana et al., 1995
$O_2 + 4H^+ + 4e^- \leftrightarrow 2H_20$	-474.33	1.4×10^{83}	4.90	
$H_20_{(l)} \leftrightarrow H^+_{(g)} + OH^-_{(aq)}$	79.94	9.971×10^{-15}	-0.82	Goode et al., 1993

Table 7 Reactions Considered for the Tantalum Processing

Reactions Considered for the Tantalum Processing	Temp°K	$\Delta G_f°$ kJ/mol	K	$\Delta E°$ (V)	References
Half Reactions of Initial Digestion of Impure Ta_2O_5 to form H_2TaF_7after Sn Smelting @ ~573°K $HF_{(aq)}+ H_20_{(l)} \leftrightarrow H_30^+_{(aq)} + F^-_{(aq)}$ $H_2SO_{49aq)} \leftrightarrow HSO_4^-_{(aq)} + H^+$ $Ta_2O_{5(s)} + H_20_{(l)} \rightarrow 2TaO_3^- + 2H^+$	298	19.716 -481.264 see aqueous table	3.5×10^{-4} 1.21 see aqueous table	-0.203 .004 see aqueous table	Barin, 1995 Chase et al., 1985 Goode et al., 1993 GMELIN, 1997 Chen et al., 1996
Solvent Extraction: Separation of H_2TaF_7/H_2NbF_7 Mixture from impurities with MiBk and H_2SO_4 $^*H_2TaF_7/H_2NbF_7$+ $(CH3)_2CHCH_2COCH_3 + H_2SO_4 \rightarrow H_2TaF_{7(solvent)}$+ $H_2NbF_{7(aq)}$ Steam Stripping of H_2TaF_7 from MiBk solvent $^*H_2TaF_{7(solvent)}$ + Steam $\rightarrow H_2TaF_{7(aq)}$					
Crystallization and Precipitation of H_2TaF_7 to $K_2TaF_{7(s)}$ $^*H_2TaF_{7(aq)} + 2KF_{(s)} \rightarrow K_2TaF_{7(s)} + 2HF_{(l)}$					
$^*H_2TaF_7$ Solution Rinse with NH_4OH to yield Tantalic Acid ($Ta_2O_5.H_20$) $^*H_2TaF_{7(aq)} + NH_4OH \rightarrow Ta(OH)_5 + 7NH_4F + 2H_20$					
Calcination of $Ta_2O_5.H_20$ @ ~1373°K $Ta_2O_5.H_20_{(s)}$ + Heat $\rightarrow Ta_2O_{5(s)}$					
Induction Heated Vacuum Furnace Reduction of Ta_2O_5 to Produce TaC @ ~1873-2073°K $Ta_2O_{5(s)} + 7C_{(s)} \rightarrow 2\ TaC_{(s)} + 5CO_{(g)}$		939.946	.684	-0.0097	

Table 7 (cont.) Reactions Considered for the Tantalum Processing

Reactions Considered for the Tantalum Processing	Temp°K	ΔG_f° kJ/mol	K	ΔE°(V)	References
Production of Metallic Tantalum by Reduction of K_2TaF_7 with Na @ ~1000°K $K_2TaF_7 + 5Na \rightarrow Ta + 5NaF + 2KF$	298	-3018.6	3.381	0.031	Barin, 1995 Chase et al., 1985 Goode et al., 1993 GMELIN, 1997 Chen et al., 1996
Removal of Oxygen from Ta Metal with Mg @ ~1200-1400°K $2Ta_2O_{5(s)} + 5Mg_{(s)} \rightarrow 4Ta_{(s)} + 5MgO_{(s)}$		974.73	.675	-0.010	
Recycling of Ta Compounds by Chlorination @ ~773-873°K $Fe(TaNb) + NaCl + 7NaFeCl_4 \rightarrow (TaNb)Cl_5 + 8NaFeCl_3 + 4Cl_2$ $8NaFeCl_3 + 4Cl_2 \rightarrow 8NaFeCl_4$ Fractional Distillation Yields Raw $TaCl_5$ Hydrolysis $2TaCl_{5(s)} + 5H_20 \rightarrow Ta_2O_{5(s)} + 10HCl_{(g)}$		-4356.811	5.803	.045	

*No Values of ΔH°, ΔS°, ΔG° available for H_2TaF_7, Tantalic Acid

CHAPTER 3

ECOLOGICAL RISK ASSESSMENT "FRAMEWORKS"

3.1 Introduction

Estimating the risk and impact to an ecological environment as the result of anthropogenic activity (i.e., chemical spill) is an evolving process. As environmental awareness has improved so has ecological risk assessment (ERA). The ERA process has developed from assessing the impact of a single contaminant on a single receptor to assessing impacts of multiple contaminants to an entire ecosystem (Renner, 1996).

Presently there is no consensus on a comprehensive framework for conducting an ERA (Power and McCarty, 1998). Therefore, the ecological risk assessment process relies significantly upon professional knowledge, experience, and political and social influence and other EPA protocol (Renner, 1996).

Many "frameworks" have been developed to provide guidelines for conducting an ecological risk assessment and as a consequence, results of an assessment may vary depending upon which framework is followed. Power and McCarty (1998) compared and contrasted seven such frameworks focusing on ones that dealt strictly with environmental aspects of risk assessment and decision making. The frameworks evaluated were developed by the following organizations: U.S. Risk Commission (1997), Canadian Standards Association (CSA, 1996), U.S. National Research Council (NRC, 1996), U.K. Department of the Environment (U.K. DOE, 1995), Australia/New Zealand (ANZ, 1995), U.S. EPA (1992), and the Ministry of Housing Physical Planning and Environment Netherlands (MHPPE, 1989) (Power and McCarty, 1998). The prime objectives of the frameworks evaluated varied from assessing risks associated with management, characterization, analysis, and reduction, to environmental decision-making depending on the organization. Though the framework objectives were developed from different organizations they all are based on applying scientific methods are necessary and all uncertainties must be clearly stated (Power and McCarty, 1998). However, they differ in how science and uncertainty should be quantitatively or qualitatively applied throughout the assessment process. For example, the MHPPE and U.S. EPA rely on scientific studies toward final risk estimation where as the U.K. DOE, NRC, and U.S. Risk Commission believe that scientific studies are important but not entirely objective and therefore should only be incorporated into the overall risk assessment (Power and McCarty, 1998). In general, these organizations believe that a framework that relies primarily on technical information has a tendency to minimize the importance of societal view (Power and McCarty, 1998).

According to Power and McCarty (1998) the overall trend in ecological risk assessment is more toward a qualitative approach because of concerns with data and extrapolation inadequacies. They believe that this trend is the result of the premise that, "a lack of understanding of risk and inability to predict it precisely mandate a more cautious approach to management issues." As a result of improved environmental awareness, modifications to earlier ecological assessment frameworks is an on going process (Power and McCarty, 1998).

3.2 Ecological Risk Assessment

Ecological risk assessment is a method of extrapolating chemical data from various information sources to determine how individual and complex groups of organisms will react to the introduction of a toxin into their environment. The Environmental Protection Agency (EPA) has established a basic *"Framework for ecological risk assessment"*. The three components of the framework include problem formulation, analysis, and risk characterization (Hoffman et al., 1995). The objective of problem formulation is to develop a conceptual model that identifies assessment endpoints (i.e., animal and plant receptors in the ecosystem), data needs (i.e., aquatic and terrestrial toxicity data, site-characteristics), and the analyses (i.e., specific risk and environmental models) to be used (Hoffman et al., 1995). The analysis phase of an ecological risk assessment includes characterization of exposure to the stressor (e.g., tantalum). The final component, risk characterization, tests the conceptual model with a stressor or stressors resulting in a ranking of the stressor (Hoffman et al., 1995).

According to Jørgenson et al. (1998), an ecological risk assessment can be divided into fundamental steps. The first two steps involve data gathering to define the hazards associated with a substance and how those hazards relate to dose and response. Subsequently, a predicted no effect concentration (PNEC) is calculated as a baseline for the assessment. In step three, the credibility of the data obtained from laboratory tests or empirical estimations is tested for determining the uncertainty factors. These factors usually range from 10-10,000 and are generally based on the amount of data available and quality of the reference(s). The next step is evaluation of the substance in its setting (i.e., processing, environment, etc.) and is followed by defining the predicted environmental concentration (PEC). This PEC is a quantitative value based on sampling or modeling. After a PEC has been established, the relative risk of the substance is estimated by using its risk quotient, which is a ranking determined from the ratio of the PEC to PNEC. A risk quotient is otherwise known as an ecological or environmental hazard quotient and relies on the benchmark data applied. For example, it is not uncommon to use lowest observed adverse effect level (LOAEL) or no observed adverse effect level (NOAEL) both of which may be based on toxicity data, such as lethal doses (Sample, 1996). Step seven, risk classification, provides a means to quantify a risk as unacceptable, partially unacceptable, or highly unacceptable. The final steps include examining the social issues and setting a policy.

Because exposure can vary within different wildlife species and sampling cannot always be conducted, allometric equations were developed to extrapolate exposure factors to determine contaminant intake and dose (EPA, 1993). As with humans, animal wildlife can be exposed to contaminant through inhalation, ingestion, and dermal contact. These allometric equations based on mean data (e.g., metabolic rates) are taxonomic specific; they were primarily designed for terrestrial animals (i.e., birds and mammals), because of data availability (EPA, 1993). When applied, for example, they may require body weight conversion for individuals within a population that are at different developmental stages. The allometric and dose estimate equations account for food ingestion, water intake, inhalation rates, surface areas (dermal contact) and metabolic rates (EPA, 1993). An applied daily dose (ADD) is then determined from these equations (see Chapter 5, Section 5.3.1). The exposure estimation procedure developed for birds and animals is currently accepted for use on reptiles and amphibians as well (EPA, 1993;

Sample et. al, 1997). Dose estimation for terrestrial and aquatic plants relies on the application of bioaccumulation and bioconcentration factors. Simply, these factors reflect partitioning from the surrounding aqueous medium (discussed further in Chapters 5 and 6).

3.3 Ecotoxicological Models

Jørgensen et al. (1998) defines six classes of ecotoxicological models. A food chain (food web) dynamic model follows a toxic substance throughout an ecosystem. This model is designed to evaluate how interactions between organisms can be affected by the presence of a contaminant. Static models assume minimal seasonal variability. A dynamic model accounts for effects such as seasonal variation, contaminant transport, and variations in contaminant concentration. Ecotoxicological models in population dynamics relate contaminant concentration and fluctuations in population by including bioaccumulation, contaminant uptake and excretion, chronic effects, and additional side effects from contaminant degradation. In the last class of models, contaminant transport and fate are predicted throughout an ecosystem.

To determine whether a model is appropriate to evaluate the ecological impact of replacing chromium with tantalum or some other effective coating in the lining of gun barrels, a critical review of available ecological models was conducted. The initial screening process identified a number of models developed for environmental issues related to transport, risk, and life cycle analysis: CALTOX, CHEMS-1, Ecosys4, EUSES LEVEL-1, MEPAS, MMSOILS, RESRAD-BASELINE, RESRAD-CHEM, RESRAD-ECORISK, SIMAPRO, WEAP/MEPAS, and Pacific Northwest National Laboratories

(PNNL) Columbia River Comprehensive Impact Assessment. The U.S. EPA's National Risk Management Research Laboratory (NRMRL) is in the process of developing TRACI, a Tool for the Reduction and Assessment of Chemical Impacts, but this model will not be available for another year. Table 8 provides a condensed review of each of the above listed models. Boustead is another model that may be relevant but was not obtained because it is cost prohibitive (~$15,000 distributed by Consoli Consulting, Inc., Medea, PA). It should also be noted that Sandia National Laboratories (SNL) EcoSys4 was evaluated based on the manual.

Subsequent evaluation of demonstration versions including software, resulted in a short list of models designed specifically for ecological risk assessment. Upon completion of the model evaluation, the following models were selected for this preliminary ecological risk assessment: CHEMS-1, RESRAD-ECORISK, and PNNL CRCIA (discussed in Chapter 5).

3.4 Ecological Assessments

The framework and objectives of a particular ecological risk assessment determine the methods developed and utilized for conducting the site evaluation. Idaho National Engineering and Environmental Laboratory (INEEL) developed and utilizes a "tiered" assessment process to evaluate the effect of contaminant releases (VanHorn et al. 1998a,b,c). Their process begins as a conservative preliminary assessment (screening level ERA); within the first phase they conduct a site characterization (VanHorn et al. 1998a,b,c). The specific goals of the screening phase are to identify the specific site(s) and contaminants of concern for subsequent sampling (VanHorn et al. 1998a,b,c).

Table 8 Initial Model Review List

Model Name	Developer	Designed Function	Ecological Risk Assessment Component	References
Boustead	Dr. Ian Boustead	▪ Life-cycle analysis	Not Known	Menke et al., 1996
CalTOX™	The University of California, Davis in Cooperation with Lawrence Livermore National Laboratory for the Office of Scientific Affairs Department of Toxic Substances Control, California EPA.	▪ Risk assessment model that relates chemical concentration in soil, adjacent air, surface water, sediments, and ground water to risk of an adverse effect in humans	No	*CalTOX*™, 1994
CHEMS-1	The Center for Clean Products and Clean Technologies, University of Tennessee for the U.S. National Risk Management Research Laboratory, Cincinnati, Ohio.	▪ Chemical ranking and scoring utilizing TRI data and annual pesticide usage data ▪ Originally designed to select safer substitutes for chemical processes ▪ Assessment of chemical hazards to human health and the environment in the event of a release	Yes	Swanson et al., 1997 Davis et al., 1994
EcoSys4	Sandia National Laboratories operated by Sandia Corporation, a subsidiary of Lockheed Martin, for the U.S. Department of Energy (DOE) Albuquerque, NM.	▪ Design for environment (DFE)/life cycle analysis (LCA) based tool ▪ Composed of environmental impact, life cycle inventory, virtual environmental design, and pollution prevention analyses	No (Model was reviewed to evaluate its environmental impact component.)	Wheelis et al., 1997
LEVEL-1	Mackay, D. "Multimedia Environmental Models: The Fugacity Approach" Lewis Publ., CRC Press Boca Raton, Fl, 1991.	▪ Fugacity-based environmental equilibrium partitioning ▪ Chemical behavior and concentration	No	Mackay, 1991
MEPAS	Pacific Northwest National Laboratory (PNNL) operated by Battelle Memorial Institute for the U.S. DOE.	▪ Estimates the human exposure and health risk associated with chemical and radiological releases from hazardous waste sites ▪ Comparative screening tool	No	Mills et al., 1997 Laniak et al., 1997 Buck et al., 1995

Table 8 (cont.) Initial Model Review List

Model Name	Developer	Designed Function	Ecological Risk Assessment Component	References
MMSOILS	Center For Exposure Assessment Modeling, U.S. Environmental Protection Agency.	▪ Estimates the human exposure and health risk associated with chemical and radiological releases from hazardous waste sites ▪ comparative screening tool	No	Mills et al., 1997 Laniak et al., 1997 Buck et al., 1995
PNNL (CRCIA) Ecological Risk Model	Pacific Northwest National Laboratory operated for the U.S. DOE by Battelle Memorial Institute.	▪ Ecological risk model developed for Columbia River Comprehensive Assessment (CRCIA) that evaluates inorganic, organic, and radiological contaminant effects in coastal environments	Yes	PNNL, 1998
RESRAD-BASELINE	Argonne National Laboratory (ANL) Environmental Assessment Division, operated by the University of Chicago for the U.S. DOE.	▪ Radiological and chemical human health cancer risk assessment ▪ Assist in development of baseline risk in terms of human health	No	Mills et al., 1997 Laniak et al., 1997 Buck et al., 1995 Yu et al., 1997
RESRAD-CHEM	ANL Environmental Assessment Division, operated by the University of Chicago for the U.S. DOE.	▪ Risk assessment tool designed establish clean-up criteria for contaminated soils	No	Yu et al., 1995
RESRAD-ECORISK	ANL Environmental Assessment Division, operated by the University of Chicago for the U.S. DOE.	▪ Estimate risks from contaminant exposure to ecological receptors ▪ Methodologies based on RESRAD-CHEM	Yes	Cheng, 1998
SimaPro	Pré Consultants, The Netherlands	▪ Life-cycle assessment model	No	Menke et al., 1996 Simapro 4.0, 1997
TRACI	Presently under development at the U.S. EPA Risk Reduction Laboratory. Anticipated beta release June 1998.	▪ Tool for the reduction and assessment of chemical impacts to the environment	Under development	None
USES 1.0 (EUSES)	European Union Collaborative Effort	▪ Human and ecological risk assessment	Yes	Linders et al., 1995

PNNL also is applying a tiered assessment process for the Hanford Nuclear Testing Facility. The CRCIA model discussed in Chapter 5 is a deterministic model designed to identify areas that would require further assessment.

Hall et al. (1998) approached ecological risk assessment using a probability distribution comparison method. They used concentrations of copper and cadmium found in the Chesapeake Bay Watershed and surrounding surface waters in laboratory toxicity studies. When Hall et al. (1998) observed a toxicity effect (e.g., LC_{50} or EC_{50}), they concluded a potential risk exists. Fish exposure to copper caused such effects as disruption in cell division, reduction in egg production, alteration in gills, kidney and other tissues. On the other hand, exposure from cadmium (at lower concentrations) resulted in skeletal deformities and disruptions in metabolic rates.

As discussed earlier, the preliminary risk assessment conducted in this thesis, relies exclusively on using existing toxicity data (Chapter 4) and allometric equations.

CHAPTER 4

ENDPOINTS, TOXICITY, AND ECOSYSTEMS

4.1 Introduction

An ecological risk assessment requires selecting endpoints, describing the affected environment, and identifying the contaminant's most likely sources of release into the environment (Suter et al., 1993). Collectively, these preliminary activities form a predictive ecological risk assessment. An *assessment endpoint,* "is a quantitative or quantifiable expression of the environmental receptor to be at risk (e.g., local extinction of the spotted owl)"(Suter et al., 1993). A *measurement endpoint* "is a quantitative summary of the results of a biological monitoring study, toxicity test, or other activity intended to reveal the effects of a hazard (e.g., LC_{50})" (Suter et al., 1993). Because it may not always be possible to directly measure an *assessment endpoint*, a *measurement endpoint calculated* from a surrogate receptor (e.g., avian predator: American kestrel) can be substituted to extrapolate contaminant effects to the species of interest (e.g., American bald eagle). To aid with the selection of an endpoint, Suter et al. (Suter et al., 1993) defined five general criteria that an endpoint should satisfy: *1. Societal relevance, 2. Biological relevance, 3. Unambiguous operational definition, 4. Accessibility to prediction and measurement, and 5. Susceptibility to the hazardous agent. Societal relevance* is subjective and is based on the values placed on the endpoint by the community (public/scientific/decision makers)(Suter et al., 1993). For instance, chlorofluorocarbons (CFCs) were commonly used as refrigerants until it was determined that release of CFCs into the atmosphere results in stratospheric ozone depletion.

Subsequently, pressure from various communities caused legislation to be enacted to restrict and eventually eliminate the use of CFCs. The *biological relevance* of an endpoint may be defined as species significance to an ecosystem (Suter et al., 1993). For example, zooplankton may not appear to be of importance to society, but are a biologically important food source to higher level species in aquatic ecosystems. Suter et al. (1993) believe that an *unambiguous operational definition* is a clearly defined endpoint that prevents risk assessment results from becoming too ambiguous. In the endpoint selection process, it is also important to define the *accessibility to prediction and measurement* of endpoints (e.g., was the data obtained from laboratory tests, field studies, or was it predicted by an algorithm). Ultimately, before an endpoint can be included in the ecological risk assessment, it must demonstrate a *susceptibility to the hazardous agent*.

The environmental description for an ecological risk assessment is the ecosystem of concern and its susceptible receptors inherent within specific boundaries. Usually, an environmental description is based on a representative site where a potential release may occur. For purposes of this study, the ecosystem receptors are based on ones included by RESRAD-ECORISK and Columbia River Comprehensive Risk Assessment (CRCIA) models previously evaluated and recommended for use.

Identifying sources of contaminant release in the environment includes properly characterizing the effects of emissions; for example, directly measuring emissions from pipes or stacks (routine emissions)(Suter et al., 1993). Conversely, measuring indirect sources (i.e., leachates of heavy metals) are more difficult due to difficulty identifying a contaminant source, accidental release, the effects of varying weather patterns, and other natural phenomena. Because limited field data are available for tantalum emissions, in this study, predictive methods (or data from an existing Superfund site) were used to quantify sources and released concentrations.

This chapter identifies data required to apply CHEMS-1, RESRAD-ECORISK, and the risk component of the Columbia River Comprehensive Impact Assessment (CRCIA) for predicting the ecological risk of tantalum, chromium, and molybdenum in the environment. The preliminary ecological risk assessment will be discussed in Chapter 5 was accomplished by using CHEMS-1 to rank contaminant toxicity, RESRAD-ECORISK to evaluate soil contaminant risks to five select terrestrial receptors, and the CRCIA to predict the contaminant effects to a diverse ecosystem. The data needed to use these models include toxicity information, ecosystems receptors, associated endpoints, and currently accepted regulatory contaminant concentrations.

Current toxicity and benchmark information for species of tantalum, chromium, molybdenum, niobium, and vanadium is presented in section 4.2. Section 4.3 is an overview of the selected ecosystems and associated endpoints, and Section 4.4 identifies methods and sources for predicting endpoints. The chapter concludes with a summary of the existing data available and the gaps that can be addressed with prediction methods.

4.2 General Toxicity Overview (Ta, Cr, Mo, V)

As discussed earlier, in the Earth's crust, tantalum is 54th in order of prevalence (2.0 milligrams/kilogram [mg/kg]) and tantalite $(FeMn)(Ta,Nb)_2O_6$ is its primary mineral source (Kroschwitz et al., 1997). Tantalum is predominantly mined in conjunction with a closely related mineral columbite, $(FeMn)(Ta,Nb)_2O_6$ (Kroschwitz et al., 1997). Current toxicity research indicates that metallic tantalum is completely inert to body fluids and tissue. Tantalum metal has been used in surgical implants, suture wire, cranial repair plates and x-ray diagnostics (Gold, 1997; Kroschwitz, et al., 1997). Available toxicity and regulatory information is presented for tantalum and its species in Tables 9 and 10, respectively. As seen in Table 9, there are no data for tantalum species in the liquid phase. Section 4.4 presents prediction methods for estimating lethal doses and concentration. For tantalum pentoxide (Ta_2O_5), the lethal dose administered via ingestion expected to cause death to 50% of a rat population (LD_{50}) is 8000 mg/kg. Hexavalent chromium (CrO_3) is two-fold greater in toxicity than tantalum. Human exposure to dusts containing metallic tantalum has been reported to result in eye and mucous membrane irritation. An animal study performed on beagles demonstrated that after inhalation of metal powder (~4μm diameter), the beagles were capable of "rapidly" clearing it from their tracheobronchial region (Gold, 1997). Inhalation of particulates (i.e., dusts) is the primary route of exposure to tantalum. Exposure can occur during tantalum mining, refining, and processing, however, studies have also identified trace amounts of tantalum in sources of asbestos, and dusts of cement, coal, foundry, and welding (Gold, 1997). Lewis (1996) reported that with respect to industrial safety, tantalum has caused dermal injuries, however, he did not specify or reference the type of injury, compound, or duration of exposure. No ingestion data are available other than the lethal dose (LD_{50}), lethal concentration (LC_{50}), and toxic dose low (TD_{Lo}), which are presented in Table 9. Little is known about tantalum in the environment, however, based on current toxicity experiments on rats, tantalum poses less risk than chromium (Gehartz, 1985; Lewis, 1996).

Table 9 General Toxicity Data

Species	Route of Exposure (Receptor)	LD_{50} (mg/kg)	LC_{50} (mg/L)	Toxic Dose Low (TD_{Lo})	References
$Ta_{(s)}$	implant (rat)	~4000-40,000	~500-5000	3760 mg/kg	Lewis, 1996; RTECS, 1997
$TaCl_{5(s)}$	oral (rat) intraperitoneal (rat)	1,900 75	~500-5,000	NA	
$Ta_2O_{5(s)}$	oral(rat) intraperitoneal (rat) oral (mouse)	8,000 ~>5,000 ~>4,000	~500-5,000	NA	Lewis, 1996; RTECS, 1997; Gold, 1997; CTC, 1998
$K_2TaF_{7(s)}$	oral (rat) intraperitoneal (rat) oral (mouse)	2,500 375 110	~<100	NA	Lewis, 1996; RTECS, 1997
$Cr_{(s)}$	oral (rat)	~<400	~<100	intravenous (rat)2160 µg/kg ETA implant (rat)1200 ug/kg ETA implant (rabbit)75 mg/kg ETA	Gerhartz, 1985; Lewis, 1996
$CrCl_3$	oral (rat) intraperitoneal (mouse) skin (g.pig) intraperitoneal (g.pig) Freshwater fish	1,870 434 202* 200* NA	~<100 inhalation (mouse) 31,500 µg/m^3 (48h)minnows, static, 400 mg/L (48h) trout, static > 1,000 mg/L (48h) ides, static, 300 mg/L	intraperitoneal (mouse) 44,600 µg/kg TER intratesticular (rat) 12,668 µg/kg REP	

Table 9 (cont.) General Toxicity Data

Species	Route of Exposure (Receptor)	LD$_{50}$ (mg/kg)	LC$_{50}$ (mg/L)	Toxic Dose Low (TD$_{Lo}$)	References
$CrCl_3 \cdot 6H_2O$	Oral (rat) intraperitoneal (mouse) intravenous (mouse)* intravenous (rabbit)* intravenous (frog)*	1,790 285 1,602* 576* 374*	~<100	NA	Lewis, 1996
CrF_3	oral (g.pig) subcutaneous (frog)	150 420*	~<100	NA	
CrO_3	oral (rat) oral (mouse) intraperitoneal (mouse) subcutaneous (mouse)	80 127 14 20	~<100	subcutaneous (mouse) 20 mg/kg TER intravenous (hamster) 7500 µg/kg REP	
CrN_3O_9	oral (rat) oral (mouse) intraperitoneal (mouse) subcutaneous (mouse)	3,250 2,976 110 3,232	~<100	NA	Gerhartz, 1985; Lewis, 1996
$Na_2Cr_2O_7 \cdot 2H_2O$	oral (rat)	160	~<100	NA	Gerhartz, 1985
$K_2Cr_2O_7$	oral (mouse) intraperitoneal (mouse) intramuscluar (rabbit)	180 32 11	(earthworm) no lethal effects at 1000	intraperitoneal (mouse) 30 mg/kg TER 60 mg/kg REP	
Mo	intraperitoneal (rats) intratracheal (rabbit)	114-117 *70	~<100	(mouse) 448 mg/kg TER (rat) 6050 µg/kg REP	Lewis, 1996; Mark et al., 1981
MoO_3	oral (rat) subcutaneous (mouse)	125 94	(bluegill)>87<120 mg/L (rainbow trout) >65<87 mg/L	4750	Gerhartz, 1985; Lewis, 1996; Mark et al., 1981

Table 9 (cont.) General Toxicity Data

Species	Route of Exposure (Receptor)	LD$_{50}$ (mg/kg)	LC$_{50}$ (mg/L)	Toxic Dose Low (TD$_{Lo}$)	References
Nb	oral (mouse)	~4,000-40,000	~500-5000	NA	Lewis, 1996
NbCl$_3$	oral (rat) intraperitoneal (rat) oral (mouse) intraperitoneal (mouse)	1400 40 829 61	~<100	NA	
Nb$_2$O$_5$	oral (mouse)	>4,000	~500-5000	NA	
VaCl$_2$	oral (rat)	540	~<100	NA	
V$_2$O$_5$	oral (rat) intraperitoneal (mouse) subcutaneous (rat) oral (mouse) subcutaneous (mouse)	10 12 14 23 10	11.09 mg/L (male) 4.3 mg/L (female)	intravenous (mouse) 10,900 mg/kg TER	Gerhartz, 1985; Lewis, 1996

Hazard Rating- Sax's number assigned to identify the level of toxicity or hazard: (3) indicates LD$_{50}$ below 400 mg/kg or an LC$_{50}$ below 100 ppm, or material is highly flammable or highly reactive, (2) indicates LD$_{50}$ below 400 mg/kg-4000 or an LC$_{50}$ of 100-500 ppm, or material is flammable or reactive, (1) indicates LD$_{50}$ 4000-40,000 mg/kg or an LC$_{50}$ of 500-5000 ppm, or material is combustible or some reactivity hazard (Lewis, 1996).

LD$_x$- a lethal dose administered through a route other than respiration, that is expected to cause death of X% of a test population (Lewis, 1996). General classification for rat may be used: highly toxic <25; 25< toxic < 200; <200 harmful <2000 (Jøregensen et al., 1998).
LC$_x$- a lethal concentration of a material administered to a species through the respiratory route that results in death of X% of a test population (Lewis, 1996).
TD$_{lo}$- toxic dose low, the lowest dose of a material introduced by any route other than inhalation, over any given period of time and reported to produce any toxic effect in humans or to produce carcinogenic, neoplastigenic, or teratogenic effects in animals or humans (Lewis, 1996).
*__LD$_{Lo}$__-lethal dose low, lowest dose other than the LD$_{50}$ of a material introduced by any route other than inhalation, over any period of time in one or more divided portions and reported to have cause death in humans or animals (Lewis, 1996).

NA- no data available.
ETA- equivocal tumorgenic agent (Lewis, 1996).
TER- teratogenic effects (Lewis, 1996).
REP- reproductive effects (Lewis, 1996).

Table 10 Regulatory Data

Species	OSHA PEL(mg/m^3)	NIOSH PEL(mg/m^3)	References
$Ta_{(s)}$	5.0	NA	Gold, 1997
$TaCl_{5(s)}$	NA	NA	Lewis, 1996; RTECS, 1997
$Ta_2O_{5(s)}$	5.0	NA	Gerhartz, 1985; Lewis, 1996; RTECS, 1997
$K_2TaF_{7(s)}$	2.5	2.5	Lewis, 1996; RTECS, 1997
Cr	1.0	0.5	Gerhartz, 1985; Lewis, 1996; EPA, 1997.
Cr(II)	0.5	0.5	
Cr(III)	0.5	0.5	
Cr(VI)	0.1	1.0 $\mu g/m^3$	
Chromite ore	NA	.025	
Mo	5.0 (soluble) 15.0 (insoluble) 10.0 (total dust) 5.0 (respirable)	5.0 (soluble) 10.0 (insoluble)	Gerhartz, 1985; Lewis, 1996
MoO_2	10.0 (dust)	10.0	Lewis, 1996
MoO_3	5.0 (soluble) 15.0 (insoluble)	5.0	Lewis, 1996; Sullivan et al., 1992
Vanadium Ore	0.05	0.05	Gerhartz, 1985; Lewis, 1996
$VaCl_2$	0.05	0.05	
V_2O_5	0.05 (dust)	0.05	

OSHA PEL-Occupational Safety and Health Administration Permissible Exposure Limit (Enforceable by Federal Law).

NIOSH PEL-National Institute of Occupational Safety and Health Permissible Exposure Limit (Not Enforceable by Federal Law).

Niobium and vanadium toxicity and regulatory data are presented in Tables 9 and 10. Because niobium and vanadium metals have similar physical and chemical properties to tantalum, these metals will be considered for potential surrogates when tantalum data are not available. Niobium is commonly found in mineral form associated with tantalum (Kroschwitz et al., 1997). Lewis (1996) reports dermal exposure to niobium results in eye and skin irritation in humans; and it can cause kidney damage when ingested, but Lewis did not identify the associated exposure levels. Niobium has also been observed to cause a moderate fibrogenic effect in the lungs after intratracheal administration to mice (Lewis, 1996).

Vanadium is considered to be one of the most common trace elements found in the earth's crust and is present at a mean concentration of 165 mg/kg (Kroschwitz et al., 1997). This element is mined primarily from roscoelite, montroseite, carnotite, tyuyamunite, francevillite, corbusite, vanadinite, descloizite, mottramite, patronite, and magnetite (Kroschwitz et al., 1997). Background concentrations of vanadium in air have been observed to be as great as 1 nanogram/cubic meter (ng/m^3) (Gerhartz, 1985). Higher levels have been recorded in areas where combustion of coal and heavy fuel oil occur (Gerhartz, 1985). Vanadium is commonly used in the steel industry, acute exposure to vanadium dusts results in eye and upper and lower airway irritation. Vanadium pentoxide is the most prevalent form found in water; it ranges in concentration from 0.1 to 220 μg/L in freshwater and 0.3 to 29 μg/L in seawater. The dust of this oxide is recognized to be poisonous by ingestion, intraperitoneal, subcutaneous, intratracheal, and intravenous routes of exposure (Lewis, 1996). Furthermore, this oxide is nearly 100% absorbed via inhalation and is recognized to be an experimental teratogen and mutagen (Gerhartz, 1985; Lewis, 1996; EPA, 1997). In other forms, for example, vanadate (VO_3^-), it has been observed to be a potent inhibitor of the sodium-pump, an enzyme system common in eukaryotic organisms, causing renal dysfunction, but there are no existing studies to indicate this occurs in humans (Lewis, 1996; Sullivan, 1992). Acute poisoning of animals by ingestion of vanadium compounds can cause nervous disturbances, paralysis, respiratory failure, convulsions, and even death (Gerhartz, 1985; Lewis, 1996). At high temperatures, volatilized vanadium fumes are highly toxic (VO_x) (Gerhartz, 1985; Lewis, 1996; Sullivan, 1992).

Concentrations of chromium in soil are dependent on geological conditions; typically it ranges between 5 and 1500 mg/kg and averages 50 mg/kg (Gerhartz, 1985; EPA, 1997). Chromium concentration in drinking water supplies ranges between 0.1 and

35 µg/L (EPA, 1997a), and in ocean water ranges between 0.2 and 50 µg/L (EPA, 1997a). Under the 1996 Safe Drinking Water Act amendment, the maximum contaminant level (MCL) for hexavalent chromium is 0.1 mg/L (Pontius, 1997).

Chromium can be found in the environment in three major forms. Metallic chromium has been determined to be of a limited risk to human health and is therefore not well characterized in terms of exposure and health effects (EPA, 1997; Kroschwitz et al., 1997). Trivalent chromium, the most common form found in soil, is a micronutrient. The minimum human daily requirement has not been quantified, however, as measured by the glucose tolerance test, a daily ingestion of 50 to 200 µg/day (based on 0.0007 to 0.003 mg Cr (III)/ kg body weight /day) has been estimated to be adequate (EPA, 1997). Trivalent chromium has no established toxicity and does not absorb easily through the skin (Sullivan et al., 1992); long term studies of exposures to low levels of chromium in animals have not resulted in any adverse health effects. However, as with any substance, exposure to large quantities of chromium (III) may result in a toxic effect.

Hexavalent chromium can be easily absorbed through the skin resulting in dermal ulcers (Sullivan et al., 1992). Acute exposure by inhalation and ingestion of mists and dusts has been correlated to ulcers and perforations of the nasal septum (Gehartz, 1985 and Lewis 1996). Chronic toxicities include irritation of the gastrointestinal tract and adverse effects to the liver and kidney. Furthermore, long-term inhalation has been attributed to throat and lung cancer in factory workers. Therefore, hexavalent chromium is a confirmed human carcinogen, and is considered to be poisonous by ingestion, intraperitoneal, and subcutaneous routes of exposure (Lewis, 1996). As a result, based on information extrapolated from epidemiological and animal research, the U.S. EPA has mandated acceptable toxicity thresholds and maximum allowable and recommended exposure levels (Tables 9 and 10).

Molybdenum (Mo) is commonly used in metallurgy and as a catalyst in chemical processing (Sullivan et al., 1992). Primarily mined from molybdenite (MoS_2), molybdenum is present in the earth's crust at about 10^{-4} % (Kroschwitz et al., 1997). Molybdenum is considered to be an essential micronutrient (U.S. National Academy of Sciences acceptable human intake 0.15 to 0.5 mg/d); leguminous plants require it for nitrogen fixation, and humans and animals require it as a cofactor for enzymes (EPA, 1997; Sullivan et al., 1992). Toxicity of molybdenum is solubility dependent. The more soluble the molybdenum compound, the easier it can be absorbed into a human or ecological receptor (Sullivan et al., 1992). Limited acute toxicity information on molybdenum exists, however, fumes from arcing molybdenum metal have been documented to cause respiratory irritation in animals (EPA, 1997 and Sullivan et al., 1992). Molybdenum trioxide (MoO_3) irritates the mucous membranes of animals and humans (eyes, nose, and throat) and causes digestive disturbances in animals (Gehartz, 1985, Sullivan et al., 1992). Chronic toxicity data on animals is limited, but a level of 5 to 10 ppm is considered conservatively safe for cattle and sheep (Gerhartz, 1985); ingestion of higher concentrations of molybdenum has been reported to induce kidney disease, liver disfunction, and bone and joint disorders (Gerhartz, 1985; Lewis, 1996; Sullivan et al., 1992). Clinical measurement of exposure to toxic concentrations of molybdenum is a deficiency in copper.

The above information was used for applying the CHEMS-1 ranking model to compare chromium, molybdenum, and tantalum toxicities. Methods for estimating metal toxicity data for additional potential species produced or released in the lifecycle process will be addressed in Section 4.3. For a more comprehensive ecological risk assessment, RESRAD-ECORISK and the CRCIA models provide the ability to assess risks to specific ecosystems and their receptors (Cheng, 1998 and PNNL, 1998). The data required for these models is discussed in the next section.

4.3 Ecosystems

The ecosystem receptors for Argonne National Laboratory's (ANL) RESRAD-ECORISK code are presented in Table 11. ANL selected these receptors because they are common to many regions in the United States, specifically Department of Energy (DOE) sites. Table 11 also presents the associated endpoints, no-observable-adverse effect levels (NOAEL), which are defined as the maximum dose administered to a test species that did not produce an adverse effect. I obtained these endpoints from Oak Ridge National Laboratory studies for chromium, molybdenum, and vanadium (Sample et al., 1996). As presented in the table, when endpoint data were not available for a receptor, surrogates and conversion factors were used to determine the appropriate NOAELs (Sample et al., 1996). The use of conversion factors will be presented in Section 4.4. Current literature surveyed revealed that no NOAELs have been established for any tantalum compounds. Therefore, vanadium data were used as the surrogate species for tantalum in addressing any modeling endpoint gaps. As mentioned earlier, these elements are from the same group in the Periodic Table (VB) and therefore, have similar physical and chemical properties.

Table 11 RESRAD-ECORISK Receptors with Associated Endpoints (Sample et al.,1996)

<table>
<tr><th colspan="5">Endpoint Determination of Cr</th></tr>
<tr><th>Receptor</th><th>Surrogate</th><th>Species</th><th>CF</th><th>NOAEL (mg/kg/day)</th></tr>
<tr><td>American robin</td><td>black duck</td><td>$CrK(SO_4)_2$</td><td>1</td><td>1</td></tr>
<tr><td>Mallard</td><td>black duck</td><td>$CrK(SO_4)_2$</td><td>1</td><td>1</td></tr>
<tr><td>White-tailed deer</td><td>rat</td><td>Cr(VI)</td><td>0.278</td><td>0.92</td></tr>
<tr><td>White-footed mouse</td><td>rat</td><td>Cr(VI)</td><td>1.99</td><td>6.55</td></tr>
<tr><td>Eastern cottontail</td><td>rat</td><td>Cr(VI)</td><td>0.73</td><td>2.41</td></tr>
<tr><th colspan="5">Endpoint Determination Mo</th></tr>
<tr><td>American robin</td><td>chicken</td><td>$MoNa_2O_4$</td><td>1</td><td>3.50</td></tr>
<tr><td>Mallard</td><td>chicken</td><td>$MoNa_2O_4$</td><td>1</td><td>3.50</td></tr>
<tr><td>White-tailed deer</td><td>mouse</td><td>MoO_4</td><td>0.14</td><td>0.04</td></tr>
<tr><td>White-footed mouse</td><td>mouse</td><td>MoO_4</td><td>same as test surrogate</td><td>0.28</td></tr>
<tr><td>Eastern cottontail</td><td>mouse</td><td>MoO_4</td><td>0.36</td><td>0.10</td></tr>
<tr><th colspan="5">Endpoint Determination V</th></tr>
<tr><td>American robin</td><td>mallard duck</td><td>VSO_4</td><td>1</td><td>11.4</td></tr>
<tr><td>Mallard</td><td>mallard duck</td><td>VSO_4</td><td>1</td><td>11.4</td></tr>
<tr><td>White-tailed deer</td><td>rat</td><td>$NaVO_3$</td><td>0.278</td><td>0.055</td></tr>
<tr><td>White-footed mouse</td><td>rat</td><td>$NaVO_3$</td><td>1.99</td><td>0.389</td></tr>
<tr><td>Eastern cottontail</td><td>rat</td><td>$NaVO_3$</td><td>0.734</td><td>0.143</td></tr>
</table>

NOAEL-No observable adverse effect level, applied daily dose reported to produce no-observed adverse-effects levels in the receptor species (mg/kg/day)

(CF)- conversion factor for a test receptor NOAEL to a NOAEL for a given ecosystem receptor.

Tables 12a, 12b, and 12c present the CRCIA ecosystem receptors and associated endpoints used to determine the ecological risk of hexavalent chromium at the 560 square mile Hanford nuclear production and research facility located adjacent to the Columbia River in Washington (PNNL, 1998). The ecology of the Hanford Reach area has been studied over the past fifty-years, therefore, comprehensive data were available to aid in the selection of the most susceptible ecological receptors. An LD_{50} or LC_{50} for a receptor (or surrogate) was used to obtain (with and without bioconcentration factor) the associated LOAEL (the lowest dose used in a test that produced an observed adverse effect) and LOAEC (the lowest concentration used in a test that produced an observed adverse effect), respectively. Specifically, these lowest doses used in a test that produced an observed adverse effect were obtained by dividing the LC or LD by 15 (Sample, 1996 and PNNL, 1998). During the screening assessment of the Hanford site, molybdenum and vanadium were determined not to be of concern, because these elements did not exceed background concentrations (PNNL, 1998). Therefore, the data for these metals are not presented here.

Table 12a CRCIA Terrestrial Plant and Fungi Receptors and Endpoints (PNNL, 1998)

Terrestrial Plant Receptor	Surrogate Species (no conversion factor used)	LOAEC µg/kg/day Chromium (VI)
Soil Concentration		
Black Cottonwood	general plants	1000
Fern	general plants	1000
Mulberry	general plants	1000
Reed Canarygrass	general plants	1000
Fungi	general plants	1000
Water Concentration		
Tule	bulrush	5000
Columbia Yellowcress	water-hyssop	5000
Dense Sedge	bulrush	5000
Rushes	bulrush	5000

Table 12b CRCIA Terrestrial Animal Receptors and Endpoints (PNNL, 1998)

Terrestrial Receptors	Chromium (VI) based on a rat surrogate with a conversion factor	
Animals	LD_{50} µg/kg	LOAEL µg/kg/day
American coot	20000	1333
American kestrel	20000	1333
American White Pelican	20000	1333
Bald eagle	20000	1333
Beaver	6988	466
Bufflehead	20000	1333
California quail	20000	1333
Canada goose	20000	1333
Cliff swallow	20000	1333
Common snipe	20000	1333
Coyote	7451	497
Forster's tern	20000	1333
Great Blue Heron	20000	1333
Harvest mouse	42896	2860
Lizards (side-blotched)	20000	1333
Mallard	20000	1333
Mule deer	5876	392
Muskrat	14589	973
Northern harrier	20000	1333
Raccoon	9581	639
Weasel	21797	1453
Western aquatic garter snake	20000	1333
Woodhouse toad (adult)	20000	1333

LOAEL- the lowest dose used in a test that produced an observed adverse effect, $LD_{50}/15$.

Table 12c CRCIA Aquatic Receptors and Endpoints for Cr(VI) (PNNL, 1998)

Aquatic Receptor	Surrogate			Chromium (VI)	
	Receptor[a]	Endpoint[b]	BCF	LC_{50} (µg/L)	LOAEC (µg/L/d)[c]
Animals					
Carp			1000	91200	6080
Channel catfish			1000	10000	667
Clams	Mytilus edulis	EC_{50}	120	4500	300
Columbia pebblesnail	Lymnaea acuminata		430	5970	398
Crayfish	Procambarus clarkii	LC_{40}	450	500000	33333
Fresh water shrimp	Asellus aquaticus			3957	264
Large-scale/Mountain sucker	carp		1000	91200	6080
Mayfly	Clioperla clio		450	101300	6753
Mountain whitefish	rainbow trout		1000	69000	4600
Mussels	Mytilus edulis	EC_{50}	430	4500	300
Pacific lamprey (juvenile)	rainbow trout		1000	3400	227
Rainbow trout (adult)			1000	69000	4600
Rainbow trout (larvae)			1300	350	23
Rainbow trout eggs (eggs)		LC_{72}	1300	12200	813
Salmon (adult)	Oncorhynchus tshawytscha		1000	111000	7400
Salmon (eggs)	Salvelinus fontinalis	LC_{72}	1300	350	23
Salmon (larvae)	Oncorhynchus tshawytscha		1300	111000	820
Smallmouth bass	Micropterus salmoides	TL_m	1000	195000	10960
Water flea				400	10
White sturgeon	carp			91200	6080
Woodhouse toad (tadpole)			1000	49290	3286
Plants					
Periphyton		EC_{50}	16000	1000	67
Phytoplankton		EC_{50}	23000	150	10
Water millfoil		IL_{50}		9600	640

[a] When direct endpoint values for the aquatic receptors of concern were not available, surrogate receptors were used (PNNL, 1998).

[b] Surrogate endpoints were selected when LC_{50} data was not available for the receptor of interest.

[c] For purposes of the CRCIA study LOAEC values were derived by dividing the corresponding LC_{50} values, or their surrogate values, by 15. However, where LOAEC values from the literature were found to be smaller than the derived values, these literature values were used. In addition, some of the LOAEC values were based on surrogate endpoints and surrogate receptors of concern (PNNL, 1998).

LOAEC-lowest observable adverse concentration of contaminant that produces a toxic effect.

BCF- Bio-concentration factor is the equilibrium distribution of the contaminant between the organism and water.

EC_{50}- effective concentration resulting in 50% reduction in cell growth rates.

TL_m- the median tolerance, concentration of a toxicant at which m% of the test organisms survives (Jøregensen et al., 1998).

To address gaps in toxicity information, prediction methods were used to estimate required receptor endpoints; these are discussed in the next section.

4.4 Estimation Methods

In the survey, not all CRCIA ecosystem receptors had tantalum, molybdenum, and vanadium LD_{50}'s. However, Suter et al. (1996) and others (Efroymson et al., 1997a; 1997b; Sample et al., 1996) performed comprehensive literature surveys and developed methods for estimating NOAELs and LOAELs for wildlife receptors based on U.S. EPA's methodology for deriving human toxicity values (Sample et al., 1996). NOAELs and LOAELs can be obtained by using the body weight adjustment factors and the surrogate NOAELs (or LOAELs) as shown in the following equation:

$$NOAEL_{wildlife} = NOAEL_{test}\left(\frac{bw_{test}}{bw_{wildlife}}\right)^{0.25}$$

where the $NOAEL_{wildlife}$ (or $LOAEL_{wildlife}$) represents the ecosystem receptor of concern, the $NOAEL_{test}$ (or $LOAEL_{test}$) is the surrogate test species for which the NOAEL (or LOAEL) is available, and *bw* represents their respective body weights (EPA, 1995). The (0.25) exponent is a scaling factor used to account for the physiological functions of different species' metabolic rates (Sample et al., 1996). When LOAELs are the only endpoint available for wildlife or laboratory receptors, than NOAELs can be estimated by applying an uncertainty factor (UF) of ≤ 10 as follows (Sample et al., 1996):

$$NOAEL = \frac{LOAEL}{\leq 10}$$

Error increases when estimating a NOAEL or LOAEL from an LD_{50} because there is no standard correlation between LD_{50} and NOAEL that can be applied to all contaminants (Sample et al., 1996). However, if both an LD_{50} and NOAEL (or LOAEL) are available for the same contaminant the following ratio can be used to estimate a NOAEL $_{wildlife}$ (Sample et al., 1996):

$$NOAEL_{wildlife} = LD_{50\,wildlife} \times \frac{surrogate\ NOAEL}{surrogate\ LD_{50}}$$

According to (Jøregensen et al., 1998), the following characteristics have been proposed to correlate metal properties to an LD_{50} (or LC_{50}), these include but are not limited to, ionization potential (SP), stability of metal complexes, solubility of sulfides (log S), and Pauling's electronegativity (Jøregensen et al., 1998). For example, the standard ionization potential (SP) and solubility of sulfides (log S) can be used in estimating an LD_{50} for white mice as shown in the following equation:

$$\log LD_{50} = -0.63 \times SP - 1.0$$

$$\log LD_{50} = -0.21 \times \log S + 0.75$$

Another parameter widely used is the bioconcentration factor (BCF), which is the ratio of the concentration of contaminant in an organism to the concentration in the test medium (e.g., water or air) at equilibrium (Jøregensen et al., 1998). A BCF can be estimated by using the following relationship (Sample et al., 1996):

$$\log BCF = 0.76 \log K_{ow} - 0.23$$

where log K_{ow} represents the octanol-water partition coefficient used to describe the bioaccumulation potential of a lipophilic compound in an organism's cell walls (Cockerham et al., 1994). The K_{ow} is only applicable for organic contaminants. For inorganics, the BCF is estimated using the water solubility (K_{so} mg/L) of a contaminant (Sample et al., 1996):

$$\log BCF = 2.791 - 0.564 \log K_{so}$$

In addition to the correlations developed by Sample et al. (1996) and Jøregensen et al. (1998) presented in this section, data from laboratory and field studies was applied to establish contaminant effects on terrestrial plants, sediments and associated biota, soil and litter invertebrates, and other heterotrophic processes (Suter et al., 1996; Efroymson et al., 1997a,b; Sample, et al., 1996; PNNL, 1998). Additional correlations for evaluating an LD_{50} (or LC_{50}) are also recommended modeling (Jøregensen et al., 1998).

4.5 Summary

The toxicity data presented within this section was be used in the CHEMS-1 ranking model to establish a general comparison between tantalum, chromium, and molybdenum. Additional toxicity information not available but required to assess the impact of using tantalum, molybdenum, or chromium are estimated by the methods discussed above. Furthermore, by using data obtained from ORNL and PNNL's CRCIA study, surrogates, and estimation methods, a more comprehensive ecological risk assessment was conducted with RESRAD-ECORISK and CRCIA models.

CHAPTER 5

PRELIMINARY ECOLOGICAL RISK ASSESSMENT

5.1 Introduction

A preliminary ecological risk assessment was conducted to assess life cycle implications of replacing chromium plating with tantalum coatings. The three models critically evaluated were the University of Tennessee CHEMS-1model, Argonne National Laboratory RESRAD-ECORISK code, and Pacific Northwest National Laboratory Columbia River Comprehensive Impact Assessment. The evaluation of each model includes their background, algorithms used in the model, parameter valuation, toxicity data employed for benchmarks, and model application, limitations and summary.

5.2 CHEMS-1 Background

The CHEMS-1(Chemical Hazard Evaluation for Management Strategies) scoring and ranking system developed by industry and regulators (Davis et al., 1994; Swanson et al.,1997) was selected to evaluate the ecological toxicity posed by tantalum, chromium, and molybdenum. This scoring and ranking system designed to compare contaminant toxicity endpoints is considered an initial screening step in selecting a safer substitute for electroplated chromium. CHEMS-1 is not intended to be a quantitative measure of hazard or risk; it simply is a method of consolidating data so that a relative comparison can be made (Davis et al., 1994; Swanson et al.,1997). As identified by the authors of the model, the accuracy of the CHEMS-1 tool is dependent on toxicity data availability or accurate estimates thereof (Davis et al., 1994; Swanson et al.1997). Lack of data is an obstacle for any chemical ranking system or ecological model, and estimates may not accurately represent chemical behavior in the environment (Davis et al., 1994 and Swanson et al.,1997).

The following presents an evaluation of the model using tantalum, chromium, molybdenum, and vanadium data, and includes an overview of the model algorithm, the data selection process, model application, a discussion of its limitations, and a summary of our conclusions.

5.2.1 Algorithm and Methods

According to Swanson et al. (1997) the screening method ranks contaminants based on toxicity and environmental persistence. To calculate a hazard value the algorithm combines data from terrestrial toxicity (rat oral LD_{50}), acute aquatic toxicity (fathead minnow LC_{50}), and chronic aquatic toxicity (fathead minnow no observable effect level, NOEL) tests (Table 13). Subsequently, the product of the toxicity hazard value summation and the persistence hazard value results in a total hazard value that can be compared and ranked against other contaminants (Table 13). The persistence component within the algorithm assumes that biochemical oxygen demand (BOD) and hydrolysis degradation for metals can be quantified. Because these effects are not plausible with metals, both were excluded. Consequently, the bioconcentration factor (BCF) was the only exposure factor used for persistence (bioaccumulation). The BCF describes equilibrium between contaminants in the aquatic organism and the aqueous phase (Davis et al. 1994, Swanson et al., 1997; Suter et al., 1993; ECOTOX, 1998; Jørgensen, et al., 1998).

Table 13 Toxicity Data to Hazard Value Conversion (Davis et al., 1994 and Swanson et al.,1997)

Terrestrial (Rat)	**Aquatic (Fathead minnow)**		**Bioconcentration Factor**
Oral LD_{50}	**Acute aquatic toxicity**	**Chronic aquatic toxicity**	**BCF**
For $LD_{50} > 5000$ mg/kg: **$HV_{OR} = 0$** For 5 mg/kg $< LD_{50} \leq 5000$ mg/kg: **$HV_{OR} = 6.2 - 1.7(\log D_{50})$** For $LD_{50} \leq 5$: **$HV_{OR} = 5$**	For $LC_{50} \geq 1000$ mg/l **$HV_{FA} = 0$** For 1 mg/l $\leq LC_{50} < 1000$ mg/l: **$HV_{FA} = -1.67(\log LC_{50}) + 5.0$** For $LC_{50} < 1$ mg/l: **$HV_{FA} = 5$**	**$NOEL = 0.05(LC_{50})$** For NOEL >100 mg/l **$HV_{FC} = 0$** For 0.1 mg/l < NOEL ≤ 100 mg/l: **$HV_{FC} = 3.33 - 1.67(\log NOEL)$** For NOEL ≤ 0.1 mg/l: **$HV_{FC} = 5$**	For log BCF ≤ 1.0: **$HV_{BCF} = 1$** For 1.0 ≤ log BCF < 4.0: **$HV_{BCF} = 0.5 \log BCF + 0.5$** For log BCF > 4.0: **$HV_{BCF} = 2.5$** *The BCF component was excluded if no data was available.

The following is the CHEMS-1 algorithm:

$$HV_{Total} = \sum HV_{Environmental\ Effects} \times HV_{Bioconcendration\ Factor}$$

Applying the BCF's to represent environmental persistence of the inorganic contaminant in terrestrial animals is not appropriate and is a limitation of the model.

The environmental effect component as discussed earlier is designed to include terrestrial and aquatic toxicity based on rat and Fathead minnow data exclusively. However, if data is not available other data can be used and the selection process is addressed in the following text section. In this section, procedures applied to select toxicity data and BCFs are discussed along with the data applied to evaluate the model.

5.2.2 Terrestrial Toxicity Data Selection

The median lethal dose resulting in the death of 50% of a population after 14 days (LD_{50}) is a common endpoint used in laboratory studies to measure toxicity to mammals, birds, and other vertebrates' (Walker et al., 1996). Extrapolation of data from laboratory studies to wildlife is common practice because when compared to the amount of laboratory studies conducted few wildlife toxicity studies have evaluated a species during its entire lifetime (Sample et al., 1996). However, the following data limitations should be considered: First, the variation in physiological or biochemical factors between species, such as, uptake, metabolism, and disposition (Sample et al., 1996); second, inbreeding of laboratory animals can cause sensitivity or resistance to a particular contaminant (Sample et al., 1996). Sample et al. (1996) also noted that, "behavioral and ecological parameters (e.g. stress factors such as competition, seasonal changes in temperature or food availability, diseased states, or exposure to other contaminants) may make a wildlife species' sensitivity to an environmental contaminant different from that of a laboratory or domestic species." Third, exclusively relying on a mortality endpoint may not accurately reflect effects of a contaminant or combination of contaminants. To illustrate, in addition to mortality, contaminants can also affect reproduction, development, and population dynamics (Sample et al., 1996).

Relying on rat or other rodent toxicity data to represent all wildlife effects is a limitation of the CHEMS-1 model and is an inherent problem within risk assessment. The practice of extrapolating data between species is controversial but since all species have not been tested, the assessor's only choice is to make assumptions (Suter et al., 1993). Davis and Swanson et al. (1994,1997) preferred to select the most sensitive rodent toxicity value if data is available for more than one species. However, to minimize inconsistency caused by data extrapolation, rat data was applied exclusively (Table 14).

Davis and Swanson et al. (1994,1997) reported their primary sources for data are the on-line Hazardous Substances Data Bank and the Registry of Toxic Effects of Chemical Substances. They also used ambient water criteria and related documents available from the U.S. Environmental Protection Agency (U.S. EPA). In addition, I reference Oak Ridge National Laboratory's (ORNL) *Toxicological Benchmarks for Wildlife: 1996 Revision* and *Sax's Dangerous Properties of Industrial Materials* (Sample et al., 1996, Lewis, 1996). The U.S. EPA Ecological Toxicity (ECOTOX) Database was consulted, however at this time the Aquatic Toxicity Effects Data (AQUIRE) Database is the only component considered current (ECOTOX, 1998).

Table 14 Terrestrial Toxicity LD_{50} Data (rat)

Analyte	LD_{50} (mg/kg)	References
$Ta_{(s)}$	~4,000-40,000	ECOTOX, 1998
$TaCl_{5(s)}$	1,900	Sample et al., 1996; Lewis, 1996; RTECS, 1998; Gehartz, 1985
$Ta_2O_{5(s)}$	8,000	
$K_2TaF_{7(s)}$	2,500	
$Cr_{(s)}$	~<400	Sample et al., 1996
$CrCl_3$	1,870	
$CrCl_3 \cdot H_20_{(l)}$	1,790	
$Cr(NO_3)_3$	3,250	
CrO_3	80	
$Na_2Cr_2O_7 \cdot 2H_2O$	160	
MoO_3	125	Lewis, 1996; RTECS, 1998; Gehartz, 1985
$NbCl_3$	1400	Lewis, 1996
$VaCl_2$	540	
V_2O_5	10	Lewis, 1996; RTECS, 1998

5.2.3 Aquatic Toxicity Data Selection

Davis and Swanson et al. (1994,1997) developed a data hierarchy selection process with the 96-hour flow-through test for calculation of the median lethal concentration (LC_{50})

for *Pimephales promelas (Fathead Minnow)* as the preferred test to represent aquatic toxicity (Table 15). However, if data is not available, Davis and Swanson et al. (1994,1997) apply the following hierarchy to select the toxicity value: 2) a flow-through 96-hour LC_{50} data for another freshwater fish; and 3) a static 96-hour *Fathead minnow* test or a static 96-hour test for another freshwater fish. Our survey revealed that aquatic toxicity data were available for chromium and chromium compounds, molybdenum trioxide, vanadium pentoxide and one species of tantalum (potassium tantalum oxide). The primary source for aquatic toxicity data was the U.S. EPA Database (ECOTOX). The confidence in these values is relatively high based on scoring criteria established by the U.S. EPA, that includes a completeness of methods and results (ECOTOX, 1998).

Additional information was also obtained from the benchmark data applied by Pacific Northwest National Laboratory with Columbia River Comprehensive Impact Assessment model, (PNNL, 1998) and Oak Ridge National Laboratory's aquatic biota toxicity study (Suter et al., 1996). As stated above, Davis and Swanson et al. (1994,1997) preferred that minnow data for 96-hour flow-through experiments be utilized over other species of freshwater fish. Therefore, the algorithm was applied with the 96-hour vanadium pentoxide LC_{50} data as a surrogate for tantalum, because of the availability of *Fathead minnow* toxicity data. However, the ECOTOX (1998) database includes data for *Oncorhynchus mykiss (Rainbow trout, donaldson trout)* of 4330 μg/L from a 28-day toxicity study conducted for potassium tantalum oxide; for comparison purposes, the algorithm was also run using that information. Running the CHEMS-1 model with the potassium tantalum oxide LC_{50} will help demonstrate the significant impact of limited toxicity data and the use of surrogates in applying CHEMS.

Table 15 Aquatic LC_{50}Toxicity Data (ECOTOX,1998)

Species Latin Name	Test Duration (days)	Concentration (µg/L)	Documentation code[2]
CAS: 1313-27-5 Molybdenum trioxide (MoO_3)			
Pimephales promelas (Fathead minnow)	4	628,000	C
		70,000	M
		370,000	M
CAS: 12030-91-0 Potassium Tantalum Oxide (Formula Not Known)			
Oncorhynchus mykiss (Rainbow trout,donaldson trout)	28	4,330	C
CAS: 1314-62-1 Vanadium pentoxide (V_2O_5)			
Pimephales promelas (Fathead minnow)	4	1,850	C
		13,000	M
		55,000	M
CAS: 7440-47-3 Chromium (Cr)			
Pimephales promelas (Fathead minnow)	4	52000	C
		37000	C
CAS: 10025-73-7 Chromium chloride ($CrCl_3$)			
Pimephales promelas (Fathead minnow)	4.00-30	43 –632	M(NR)[1]
Oncorhynchus mykiss (Rainbow trout,donaldson trout)	4	11200	M
CAS: 10141-00-1 Chromium potassium sulfate ($CrK(SO_4)_2$)			
Pimephales promelas (Fathead minnow)	4	29000	C
		27000	C
		5070	C
		67400	C

[1] **NR**-Not Reported, no statistically derived endpoint was reported.

[2] **Documentation Code** = C, "thorough methods and results documentation was presented. The computerized documentation score was between 86-100 points; **Code = M**, documentation is generally satisfactory, but one or more pieces of information are missing from either the methods or results sections, such as test duration or endpoints were not calculated. The computerized documentation score was between 51-85 points; **Code = I**, insufficient methods and results documentation. The computerized documentation score was less than 51 points (ECOTOX,1998)." "The documentation code indicates the type and completeness of methods documentation and results presentation accompanying the data. Documentation coded assignments range from detailed documentation to summary format. Although a documentation code of "C" does not signify that these data are better than test data receiving a documentation code of "I", it does give you a means of determining the level of confidence associated with those test records. The documentation code is assigned by the software based on various database elements from a total score of 100. Points are assigned to fields with entries and no points are given if the entry is blank or not reported (ECOTOX,1998)."

Table 15 (cont.) Aquatic LC_{50}Toxicity Data (ECOTOX,1998)

Species Latin Name	Test Duration (days)	Concentration (µg/L)	Documentation code[2]
CAS: 7775-11-3 Sodium chromate (Na_2CrO_4)			
Oncorhynchus mykiss (Rainbow trout,donaldson trout)	4	27300	C
		46800	C
		65500	C
		7600	C
		12800	C
		25900	C
		45000	C
		3400	C
		7500	C
		13000	C
		20200	C
		53200	C
		29500	C
		15600	C
		>600000	C
7789-00-6 Potassium chromate (K_2CrO_4)			
Pimephales promelas (Fathead minnow)	4	46000	M
		39800	C
		45600	C

[1] NR-Not Reported, no statistically derived endpoint was reported.

[2] **Documentation Code** = **C**, "thorough methods and results documentation was presented. The computerized documentation score was between 86-100 points; **Code** = **M**, documentation is generally satisfactory, but one or more pieces of information are missing from either the methods or results sections, such as test duration or endpoints were not calculated. The computerized documentation score was between 51-85 points; **Code** = **I**, insufficient methods and results documentation. The computerized documentation score was less than 51 points (ECOTOX,1998)." "The documentation code indicates the type and completeness of methods documentation and results presentation accompanying the data. Documentation coded assignments range from detailed documentation to summary format. Although a documentation code of "C" does not signify that these data are better than test data receiving a documentation code of "I", it does give you a means of determining the level of confidence associated with those test records. The documentation code is assigned by the software based on various database elements from a total score of 100. Points are assigned to fields with entries and no points are given if the entry is blank or not reported (ECOTOX,1998)."

During the study, direct access to the ECOTOX database was not available and required the assistance of the systems administrator to conduct the queries. As a result, a complete review of the toxicity studies and related comments selected by the U.S. EPA was unavailable. Also it was not possible to differentiate which toxicity values were based on flow through or static tests. In an effort to conduct the most conservative evaluation, the lowest toxicity value for a given species either the Fathead minnow or Rainbow trout was applied (although all data are presented).

5.2.4 Bioconcentration Factor (BCF) Data Selection

The presence of metals in estuarine environments is common. Heavy metals can be present in the sediment or the water column depending on their speciation. In some instances these metals are necessary for an organism's survival. For example, zinc is a necessary cofactor of enzymes (Cockerham et al.,1994). Although metals have been found to bioaccumulate in organism's, most do not biomagnify through the foodchain (Cockerham et al.,1994). However, experiments have demonstrated hydrophobic alkyl metals will biomagnify in higher vertebrates (Hoffman et al.,1995). The BCF, as defined by Davis and Swanson et al. (1994,1997) is the ratio of the chemical concentration in an aquatic organism to its concentration in water at equilibrium conditions and is designed to reflect an aquatic organisms assimilation of inorganic pollutants. The bio-availability of the contaminant can vary as a function of the physical characteristics of the element, the aqueous phase composition, and an organism's taxon, biochemistry, and lipid content (Hoffman, 1995).

Organism biochemistry can influence the BCF, because a contaminant may follow similar biochemical pathways that have evolved in an organism to assimilate essential nutrients. For example, it has been demonstrated that organisms with calcareous skeletons, exoskeletons, or shells will accumulate lead and strontium in higher amounts than organisms without these structural features, because these metals follow similar chemical pathways as calcium (Walker et al., 1996).

In addition, methyl mercury, which is hydrophobic, has a much greater tendency to be bioaccumulated then inorganic mercury, because the organic form will accumulate more readily in aquatic organisms with higher lipid contents (Newman et al., 1991). Water characteristics such as pH and organic content can have a direct effect on the solubility of metals; as the pH decreases some metals become more soluble, and as a result more bio-available (Lithner et al., 1995; Newman et al., 1991). Additionally, aquatic species may accumulate higher concentrations of metals to supplement and adapt to their ecosystem's nutrient deficiency. As a result, an organism may maintain a naturally high residual inorganic concentration.

Table 16 presents the BCF data applied to CHEMS-1 for chromium compounds. Because aquatic BCF data was only available for experiments conducted with chromium compounds on Rainbow trout it should be noted that if data for Fathead minnow were available the algorithm results might change. No additional BCF data were available for any other inorganics of interest and fish species.

5.2.5 Hazard Characterization

Table 17 presents individual hazard values and the total hazard value. The first and third columns present the analyte form tested to calculate terrestrial/aquatic toxicity respectively. As stated previously, little aquatic toxicity data were available for tantalum.

Table 16 Chromium BCF Values for Oncorhynchus mykiss (Rainbow trout)(ECOTOX,1998)

Analyte	Duration	BCF	Log BCF	Documentation Code
CAS: 7778-50-9 Chromic Acid, Dipotassium salt	180	17.4	1.24	C
	180	9.8	0.99	C
	180	2.8	0.45	C
CAS: 7440-47-3 Chromium	24	1.34	0.13	M
	24	1.27	0.10	M
		1.03	0.01	
		1.22	0.09	
	30	1.03-1.22		
	30	1.13 (Geometric Mean)	0.05	M

Documentation Code = C, "thorough methods and results documentation was presented. The computerized documentation score was between 86-100 points; **Code** = **M**, documentation is generally satisfactory, but one or more pieces of information are missing from either the methods or results sections, such as test duration or endpoints were not calculated. The computerized documentation score was between 51-85 points; **Code** = **I**, insufficient methods and results documentation. The computerized documentation score was less than 51 points (ECOTOX,1998)."

However, because vanadium and tantalum are within the same group of the Periodic Table, and therefore possess similar physicochemical properties (Clements et al.,1993), vanadium pentoxide, was applied as a surrogate. Furthermore, the algorithm was also executed applying potassium tantalum oxide, because it is the only aquatic data available for tantalum. A significant limitation of CHEMS-1, as demonstrated in Table 18 for the overall ranking of hazard values, is that applying a surrogate such as vanadium pentoxide for the aquatic hazard can significantly impact the ranking of compounds.

Table 17 Hazard Value

Analyte (Terrestrial)	HV_{mam}	Analyte (Aquatic)	HV_{fc}	HV_{fa}	HV_{BCF}	HV_{TOTAL}	Range
$Ta_{(s)}$	0.08	$KTaO_3$	3.94	4.43	1.00	8.45	4.77-9.69
	0.08	V_2O_5	5.06	4.55	1.00	9.69	
	0.08		3.64	3.14	1.00	6.86	
	0.08		2.60	2.09	1.00	4.77	
$TaCl_{5(s)}$	0.63	$KTaO_3$	3.94	4.43	1.00	9.00	5.32-10.24
	0.63	V_2O_5	5.06	4.55	1.00	10.24	
	0.63		3.64	3.14	1.00	7.41	
	0.63		2.60	2.09	1.00	5.32	
$Ta_2O_{5(s)}$	0.00	$KTaO_3$	3.94	4.43	1.00	8.37	4.69-9.61
	0.00	V_2O_5	5.06	4.55	1.00	9.61	
	0.00		3.64	3.14	1.00	6.78	
	0.00		2.60	2.09	1.00	4.69	
$K_2TaF_{7(s)}$	0.42	$KTaO_3$	3.94	4.43	1.00	8.79	5.11-10.04
	0.42	V_2O_5	5.06	4.55	1.00	10.04	
	0.42		3.64	3.14	1.00	7.21	
	0.42		2.60	2.09	1.00	5.11	
MoO_3	2.64	MoO_3	2.63	1.92	1.00	7.18	3.79-7.18
	2.64		0.83	0.33	1.00	3.79	
	2.64		1.21	0.71	1.00	4.56	
$VaCl_2$	1.55	V_2O_5	5.06	4.55	1.00	8.35	6.24-8.35
	1.55		3.64	3.14	1.00	8.34	
	1.55		2.60	2.09	1.00	6.24	
V_2O_5	4.50	V_2O_5	5.06	4.55	1.00	14.11	9.19-14.11
	4.50		3.64	3.14	1.00	11.28	
	4.50		2.60	2.09	1.00	9.19	
$Cr_{(s)}$	1.78	Cr	2.64	2.13	1.00	6.55	6.55-7.04
	1.78		2.88	2.38	1.00	7.04	
$CrCl_3$(III)	0.64	$CrCl_3$ *Rainbow trout*	3.75	2.37	1.00	6.76	5.03-10.67
$CrCl_3$(III)	0.64	$CrCl_3$ *Fathead minnow*	5.00	5.00	1.00	10.64	
$CrCl_3$(III)	0.64	$CrKO_8S_2$(III)	3.06	2.56	1.00	6.26	
	0.64		3.11	2.61	1.00	6.36	
	0.64		4.33	3.82	1.00	8.79	
	0.64		2.45	1.95	1.00	5.03	
$CrCl_3{\cdot}H_20_{(l)}$(III)	0.67	$CrCl_3$	5.00	5.00	1.00	10.67	
	0.67	$CrKO_8S_2$(III)	3.06	2.56	1.00	6.29	
	0.67		3.11	2.61	1.00	6.39	
	0.67		4.33	3.82	1.00	8.82	
	0.67		2.45	1.95	1.00	5.07	

Table 17 (cont.) Hazard Value

Analyte (Terrestrial)	HV_{mam}	Analyte (Aquatic)	HV_{fc}	HV_{fa}	HV_{BCF}	HV_{TOTAL}	Range
CrN_3O_9(III)	0.23	$CrCl_3$	5.00	5.00	1.00	10.23	10.23-11.85
	1.85		5.00	5.00	1.00	11.85	
CrO_3(VI)	2.96	Na_2CrO_4(VI)	3.10	2.60	1.12	9.71	4.18-13.09
	2.96		3.10	2.60	1.00	8.67	
	2.96		2.71	2.21	1.12	8.83	
	2.96		2.71	2.21	1.00	7.88	
	2.96		2.47	1.97	1.12	8.28	
	2.96		2.47	1.97	1.00	7.40	
	2.96		2.35	1.84	1.12	8.01	
	2.96		2.35	1.84	1.00	7.15	
	2.96		3.65	3.15	1.12	10.94	
	2.96		3.65	3.15	1.00	9.77	
	2.96		3.14	2.64	1.12	9.79	
	2.96		3.14	2.64	1.00	8.74	
	2.96		2.74	2.24	1.12	8.89	
	2.96		2.74	2.24	1.00	7.94	
	2.96		4.62	4.11	1.12	13.09	
	2.96		4.62	4.11	1.00	11.69	
	2.96		4.04	3.54	1.12	11.80	
	2.96	Na_2CrO_4(VI)	4.04	3.54	1.00	10.54	
	2.96		3.64	3.14	1.12	10.91	
	2.96		3.64	3.14	1.00	9.74	
	2.96		3.32	2.82	1.12	10.20	
	2.96		3.32	2.82	1.00	9.10	
	2.96		2.62	2.12	1.12	8.62	
	2.96		2.62	2.12	1.00	7.70	
	2.96		3.05	2.55	1.12	9.58	
	2.96		3.05	2.55	1.00	8.55	
	2.96		3.51	3.01	1.12	10.62	
	2.96		3.51	3.01	1.00	9.48	
	2.96		0.86	0.36	1.12	4.69	
	2.96		0.86	0.36	1.00	4.18	
	2.96	K_2CrO_4(VI)	2.73	2.22	1.12	8.86	
	2.96		2.73	2.22	1.00	7.91	
	2.96		2.83	2.33	1.12	9.09	
	2.96		2.83	2.33	1.00	8.12	
	2.96		2.73	2.30	1.12	8.95	
	2.96		2.73	2.30	1.00	7.99	
$Na_2Cr_2O_7 \cdot 2H_2O$(VI)	2.45	Na_2CrO_4 (VI)	3.10	2.60	1.12	9.14	3.77-12.62
	2.54		3.10	2.60	1.00	8.25	
	2.54		2.71	2.21	1.12	8.36	
	2.54		2.71	2.21	1.00	7.47	
	2.54		2.47	1.97	1.12	7.82	
	2.54		2.47	1.97	1.00	6.98	

Table 17 (cont.) Hazard Value

Analyte (Terrestrial)	HV$_{mam}$	Analyte (Aquatic)	HV$_{fc}$	HV$_{fa}$	HV$_{BCF}$	HV$_{TOTAL}$	Range
$Na_2Cr_2O_7 \cdot 2H_2O$(VI)	2.54	Na_2CrO_4 (VI)	2.35	1.84	1.12	7.54	3.77-12.62
	2.54		2.35	1.84	1.00	6.73	
	2.54		3.65	3.15	1.12	10.47	
	2.54		3.65	3.15	1.00	9.35	
	2.54		3.14	2.64	1.12	9.33	
	2.54		3.14	2.64	1.00	8.33	
	2.54		2.74	2.24	1.12	8.43	
	2.54		2.74	2.24	1.00	7.52	
	2.54		4.62	4.11	1.12	12.62	
	2.54		4.62	4.11	1.00	11.27	
	2.54		4.04	3.54	1.12	11.34	
	2.54		4.04	3.54	1.00	10.12	
	2.54		3.64	3.14	1.12	10.44	
	2.54		3.64	3.14	1.00	9.33	
	2.54		3.32	2.82	1.12	9.73	
	2.54		3.32	2.82	1.00	8.69	
	2.54		2.62	2.12	1.12	8.15	
	2.54		2.62	2.12	1.00	7.28	
	2.54		3.05	2.55	1.12	9.11	
	2.54		3.05	2.55	1.00	8.14	
	2.54		3.15	3.01	1.12	9.74	
	2.54		3.15	3.01	1.00	8.70	
	2.54		0.86	0.36	1.12	4.22	
	2.54		0.86	0.36	1.00	3.77	
$Na_2Cr_2O_7 \cdot 2H_2O$(VI)	2.54	K_2CrO_4 (VI)	2.73	2.22	1.12	8.39	
	2.54		2.73	2.22	1.00	7.49	
	2.54		2.83	2.33	1.12	8.63	
	2.54		2.83	2.33	1.00	7.70	
	2.54		2.73	2.30	1.12	8.48	
	2.54		2.73	2.30	1.00	7.57	

5.2.6 Limitations

Figure 5 and Table 18 present the graphical representation and overall ranking of the Maximum and Minimum HV$_{Total}$'s. This ranking was different than anticipated; because of the hazards associated with hexavalent chromium, I expected it to score the highest. However, as presented in Figure 5 and Table 18, vanadium pentoxide scored the most hazardous. In addition it was expected that similar compounds (and combinations)

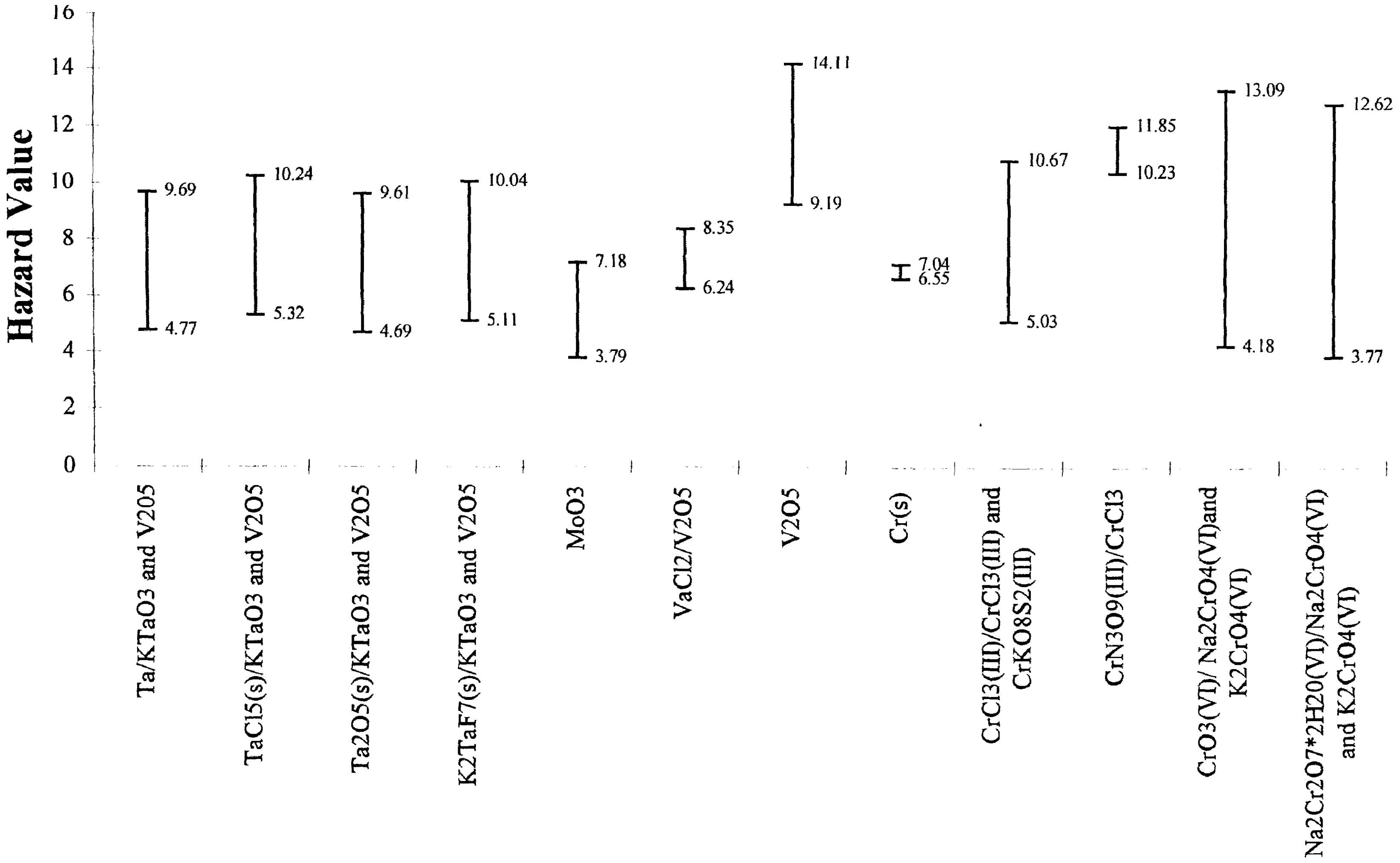


Figure 5 Maximum and Minimum Hazard Value Comparison

Table 18 Compound Ranking

Species Category (Terrestrial/Aquatic)	Normalized Score (14.11 being the Greatest HV)
V_2O_5/V_2O_5	100
CrO_3/Na_2CrO_4	93
$Na_2Cr_2O_7*2H_2O/Na_2CrO_4$	89
CrN_3O_9(III)/$CrCl_3$	84
$CrCl_3*H_20_{(l)}/CrCl_3$	75
$CrCl_3/CrCl_3$ *Fathead minnow*	75
$TaCl_{5(s)}/V_2O_5$	73
$K_2TaF_{7(s)}/V_2O_5$	71
$Ta_{(s)}/V_2O_5$	69
$Ta_2O_{5(s)}/V_2O_5$	68
CrO_3/K_2CrO_4	64
$TaCl_{5(s)}/KTaO_3$	64
$CrCl_3*H_20_{(l)}/CrKO_8S_2$	63
$CrCl_3/CrKO_8S_2$	62
$K_2TaF_{7(s)}/$ $KTaO_3$	62
$Na_2Cr_2O_7*2H_2O/(K_2CrO_4)$	61
$Ta_{(s)}/$ $KTaO_3$	60
$Ta_2O_{5(s)}/$ $KTaO_3$	59
$VaCl_2/V_2O_5$	59
MoO_3/MoO_3	51
$Cr_{(s)}/Cr$	50
$CrCl_3/CrCl_3$ *Rainbow trout*	48

would fall within the same range of values. In contrast, forms of hexavalent chromium ranked both at the top and bottom of the table thus, creating an issue as to the reliability of the method. If for example, the method were to be applied without comparing different toxicity values for the same compound the conclusions of the test may incorrectly overestimate or underestimate hazards associated with a contaminant. This fact places the reliability of the ranking method and its application highly variable.

As with any other ranking or modeling method, CHEMS-1 is based on the selection and the reliability of the toxicity data used and application of an appropriate surrogate. The utilization of quantitative structure activity relationships (QSAR) to predict relative toxicity was developed first in pharmacology, and was than adopted to evaluate organic toxicity in the environment (Tatara et al.,1997). The study of inorganic toxicants (metals) is relatively new when compared to organic QSAR methods. QSARS are designed to relate fundamental characteristics of a contaminant to an observed toxicity either through the use of a surrogate or molecular characteristic (Tatara et al.,1997).

General prediction of relative metal toxicity based on ion characteristics is possible but further research is needed (Tatara et al.,1997). Therefore, settling for vanadium as a surrogate for tantalum may be appropriate. However, not enough information is available at this time to make any conclusion. Another limitation within most models and in particular CHEMS, is that it is only effective in evaluating single substance criteria, derived from single-substance toxicity data; as a result neglecting mixtures (Weltje,1998).

Additional issues that may cause CHEMS-1 to be misleading include applying the BCF to the entire algorithm. The BCF is intended to evaluate the process of accumulation of chemicals by fish and other aquatic animals through non-dietary routes. Therefore, application to terrestrial animals is inappropriate. Similarly, although Davis and Swanson et al. (1994,1997) recommend using BOD and hydrolysis degradation factors for metals, an element is non-biodegradable.

5.2.7 Summary

An evaluation of applying CHEMS-1 to tantalum, molybdenum, vanadium and chromium data was conducted to rank and score contaminant toxicity and exposure potential. Certain components such as BOD and hydrolysis were excluded, because these components do not accurately represent inorganics. Originally, it was believed that hexavalent chromium would rank the most hazardous. However, the results of the model presented in Table 18 indicate that the vanadium compounds, in particular vanadium pentoxide, presents the greatest hazard. Then, as expected hexavalent chromium follows as the next greatest hazard. Overall an approximate ranking was accomplished and based on the data gathered, tantalum presents less of a hazard than hexavalent chromium. However, it should be recognized that only using two animals to represent ecosystem toxicity, the numerical closeness of the hazard values, and the influence of a surrogate compound question the reliability of this model. Therefore, I emphasize that an assessor who intends on applying this model to evaluate inorganics be very skeptical of the results. Moreover, selection of a proper surrogate is essential; if the surrogate is inappropriate it can be misleading. A surrogate should have similar physical and chemical characteristics so that when it is applied it can be expected to behave similarly to the contaminant of interest. However, a limitation is that even if a surrogate is closely related to the contaminant of concern, it may not present the most accurate representation. As in the case of tantalum compounds, the use of vanadium pentoxide increases the hazard value above chromium.

As previously discussed, during the aquatic toxicity selection process, the ideal toxicity values were to be obtained from *Pimephales promelas (Fathead minnow)* 96-hour flow-through or other freshwater fish flow through studies. Data selection is subjective and falls upon the judgment of the risk assessor to select values he believes to be appropriate. Furthermore, it should also be noted, that I did not have full access to the ECOTOX database, as a result, preventing a more thorough evaluation. For example, the full database does identify if the toxicity study conducted applied flow through or static testing methods. Therefore, the lowest toxicity value available (greatest hazard value) was selected for ranking purposes.

5.3 RESRAD-ECORISK Background

The RESRAD-ECORISK code was designed to assist with ecological risk assessment of contaminated soil (Cheng, 1998): the more site information available, the more comprehensive the assessment. The code can be easily modified to site-specific characteristics of a contaminated area. However, for purposes of evaluating the model, default values within the code were used and are based on data collected by Argonne National Laboratory (ANL), Oak Ridge National Laboratory (ORNL), the United States Environmental Protection Agency (U.S. EPA), and others (Sample et al., 1996;EPA, 1993c; Yu et al., 1993;EPA, 1998;EPA, 1983). To characterize risk, an ecological hazard quotient (EHQ) is calculated from the ratio of the estimated receptor's exposure to a contaminant (i.e., applied daily dose [ADD]) to the measurement endpoint (i.e., no-observed-adverse-effects level [NOAEL]) (Cheng, 1998). Code parameters and derivation of the ADD and the NOAEL are explained further within the accompanying text.

Because the code is not amenable to changes or additions in the contaminant database, tantalum could not be evaluated. Only chromium and vanadium were evaluated, and as such are considered as surrogates for molybdenum and tantalum, respectively. The following section presents an evaluation of the code using chromium and vanadium data; and includes a general overview of the code ecological risk algorithms, assessment of benchmarks, code parameters, receptor exposure input, application and results, limitations, and a summary of our conclusions and recommendations for improvement.

5.3.1 Algorithms and Methods

A receptor's exposure to a contaminant can occur through single or multiple pathways depending on its behavior, diet, and characteristics of the ecosystem. The code accommodates the various media in which food sources exist and allows the user to activate different combinations of these media to which the receptor is exposed (Cheng, 1998). However, the only pathway of exposure for the terrestrial animals considered by the code is ingestion, which is accounted for through terrestrial vegetation, invertebrates, soil, and water (Cheng, 1998). The code developers have not included inhalation and dermal exposure pathways, which may be satisfactory for most metal contaminants but it is a limitation nonetheless. Five terrestrial animals are the only receptors used in this model: American robin, Mallard duck, White-tailed deer, Eastern cottontail rabbit, and the White-footed mouse. At this time, it is not possible to modify the receptor database (Cheng, 1998).

The RESRAD code uses the applied daily dose (ADD) equation to assess contaminant exposure to wildlife through ingestion. However, this equation along with others was developed by the U.S. EPA (1993) to evaluate exposure through inhalation, ingestion, and dermal routes. The following equation alone was used by ANL to estimate the contaminant dose (through ingestion) for the receptors evaluated within their code (Cheng, 1998):

$$ADD_k = (C_k \times DF_k \times SU \times NIR_k)$$

where:

ADD = Applied daily dose (mg·kg^{-1}day^{-1})
k = Media index (i.e., invertebrates, soil, vegetation, and water)
C = Average contaminant concentration in the medium that is contaminated (mg·kg^{-1})
DF = Fraction of total diet (unitless)
SU = Site use factor: [(area of contamination) ÷ (receptor home range area)]
NIR = Normalized ingestion rate: [ingestion rate (IR) kg·day^{-1} ÷ body weight (BW)kg]

The fraction of the total diet and normalized ingestion rate is based on data collected by the U.S. EPA (1993). Without actual site data, estimation of environmental concentrations (EECs) that could cause a measurable effect to a receptor was required. As a result, data provided by the New Jersey Department of Environmental Protection (NJDEP) and representative of actual site contamination were used (NJDEP,1998). At a defunct electroplating site 4550 mg/kg for Cr(VI) was found to be the greatest concentration present in soils (NJDEP,1998). Therefore, in considering a worst case scenario, this concentration was used to represent both chromium and vanadium levels.

The rationale for selecting equivalent concentrations was to examine similar releases into the environment.

A common methodology within ecological risk assessment is to extrapolate data from laboratory studies to wildlife (Suter et al., 1993 and Sample et al., 1996). The U.S. EPA's *Wildlife Handbook* provides information on characteristics common to selected wildlife including birds, mammals, amphibians, and reptiles. Reported within the handbook is information such as normalizing factors (e.g., body weight, metabolic, and growth rates), contact rate factors (e.g., oral, inhalation, or dermal routes), and population dynamics (e.g., social organization, home range/territory size, population density, annual fecundity, mortality, and longevity) (EPA, 1993). Furthermore, the handbook also provides allometric and exposure estimation equations that can be applied to assess risk to wildlife. Allometry, the study of the relationship between physiological and physical parameters of an organism, can include but is not limited to, data on food ingestion as it relates to metabolic rate and the energy required for growth and reproduction. Equations (e.g., ADD) are commonly applied to estimate exposure factors when actual site data on receptor exposure are not available. Exposure estimation equations are used to estimate exposure to wildlife through a variety of routes (e.g. oral, inhalation, or dermal). However, RESRAD-ECORISK only considers the ingestion pathway. The RESRAD code developers (Cheng, 1998) considered only the ingestion pathway as the greatest exposure for terrestrial receptors.

5.3.2 Benchmarks

No-observed-adverse-effects levels (NOAELs) benchmarks are derived from experiments conducted on laboratory animals, and are the highest dose applied that did not result in a measurable adverse effect (Cockerham et al., 1994). Toxicity data are limited for wildlife; consequently, NOAELs are estimated from laboratory studies and by extrapolating toxicity data such as LD_{50} values for domestic or laboratory animals to wildlife (Sample et al., 1996). Extrapolation of toxicity data immediately introduces uncertainty into any model. As a general rule, organisms with smaller bodies have a tendency to detoxify faster than larger ones, because of their higher metabolisms; however, there are exceptions (Sample et al., 1996). If for example, the toxic effect is produced by a primary metabolite, the detoxification process may be disrupted (Sample et al., 1996). Generally, because smaller animals have a tendency to detoxify rapidly (i.e., mice), application of data to larger animals (i.e., deer) may significantly underestimate a risk. Correcting for body weight and varying metabolic rates, wildlife NOAELs can be estimated for an untested species by the following equation (Sample et al., 1996) presented earlier:

$$NOAEL_{wildlife} = NOAEL_{test}\left(\frac{bw_{test}}{bw_{wildlife}}\right)^{0.25}$$

where the $NOAEL_{wildlife}$ represents the ecosystem receptor of concern, the $NOAEL_{test}$ is the surrogate test species for which the NOAEL is available, and bw represents their respective body weights (Sample et al.,1996; EPA,1993). The (0.25) exponent is a scaling factor used to account for the physiological functions of different species' metabolic rates, and was obtained empirically by Sample et al. (1996). The current RESRAD-ECORISK code applies the U.S. EPA 1994 (Cheng, 1998) version of the above equation with a (0.33) exponent to represent relative body surface area as opposed to revised body surface area (0.25) exponent (Sample et al.,1996). It was determined by Sample et al. (1996) that the species metabolic rate revised value more was a more appropriate scaling factor to determine the influence of body surface area on metabolic rate. Therefore, I applied the revised method with the (0.25) scaling factor in the RESRAD code. The algorithm that Sample et al. (1996) apply to calculate the NOAELs for wildlife avian species defaults to a body weight ratio raised to a zero exponent, based on empirical relationships resulting from tests conducted on birds using LC_{50} data for 37 pesticides. Avian body weight scaling factors for the 37 contaminants did not vary significantly from 1, therefore, Sample et al. (1996) concluded that 1 was the most appropriate scaling factor for interspecies extrapolation among birds. Table 19 lists body weights of common surrogates used for toxicity testing and the receptors considered by the RESRAD-ECORISK code.

Table 19 Surrogate and Receptor Body Weight

Contaminants	Surrogate[a]	Body Weight (kg)	Receptor[b]	Body Weight (kg)
Cr_2O_3 K_2CrO_4 $NaVO_3$	Rat	0.35	White-footed mouse	0.0212
			Cottontail Rabbit	1.2200
			White-tailed deer	73.3
*$CrK(SO_4)_2$	Black duck	1.25	American robin	0.077 ± 0.00036 SE Both M/F
			Mallard Duck	1.1340
VSO_4	Mallard duck	1.134	American robin	0.077 ± 0.00036 SE Both M/F
			Mallard Duck	1.1340

*Note: Same default NOAEL data for Cr(III) and Cr(VI) were applied for avian receptors, therefore test species are not shown for Cr(VI) [Sample et al., 1996]. M-Male, F-Female, SE-Standard Error only available for those presented (EPA,1993).

[a] Sample et al., 1996
[b] Cheng, 1998

During the development of toxicological benchmarks for wildlife, Sample et al. (1996) placed emphasis on toxicity studies that were concerned with effects other than mortality, such as reproduction and developmental impact. Rather than relying on the mortality endpoint exclusively, a more meaningful approach to ecological risk assessment is to consider both acute and chronic effects caused by a contaminant (VanHorn,1998). For example effects such as, tumor formation (carcinogenic), birth defects (genetic), and reduced litter size (reproductive) to persistent and bio-accumulative contaminants such as metals may be more important in assessing quality of life and population effects.

The following example presents a demonstration of the data and NOAEL calculation used for Cr(III) as Cr_2O_3 (Sample et al., 1996):

Test Species: Rat
Body weight: 0.35 kg
Food Consumption: $0.028\ kg{\cdot}d^{-1}$ (derived from an allometric equation)
Study Duration: 90 day and 2 year
Endpoint: reproduction, longevity
Exposure Route: oral in diet
Dosage: 1%, 2%, or 5% of diet (no effects observed at any dose level)

Calculations:
NOAEL:

$$\left(\frac{50{,}000\ mg\ Cr_2O_5}{kg\ food} \times \frac{28\ g\ food}{day} \times \frac{1\ kg}{1000\ g}\right) \div 0.35\ kg\ BW = 4000\ mg \cdot kg^{-1} \cdot a$$

$0.6842 \times 4000\ mg\ Cr_2O_3\ kg{\cdot}d^{-1}$ or $2737\ mg\ Cr(III)\ kg{\cdot}d^{-1}$

Comments: Although no effects were seen at any dose level, the maximum dose was considered to be the chronic NOAEL.

Because the code allows for benchmark modification, revised 1996 benchmarks based on studies conducted by Sample et al. (1996) (Table 20 and Table 21) were entered into the code for the hazard quotient calculations.

Table 20 NOAEL Surrogate Toxicity Data (Sample et al., 1996)

Analyte Form	Test Species	NOAEL($mg{\cdot}kg^{-1}{\cdot}d^{-1}$)
Cr_2O_3	Rat	2737.00
$CrK(SO_4)_2$	black duck	1.00
K_2CrO_4	Rat	3.28
$NaVO_3$	rat	0.21
VSO_4	mallard duck	11.40

Table 21 RESRAD-ECORISK Receptors and Associated NOAELs (Sample et al., 1996)

Receptor	Analyte	NOAEL ($mg{\cdot}kg^{-1}{\cdot}d^{-1}$)
	Cr (III)	
American robin	Cr(III) as $CrK(SO_4)_2$	1.0
Mallard	Cr(III) as $CrK(SO_4)_2$	1.0
White-tailed deer	Cr(III) as Cr_2O_3	768.0
White-footed mouse	Cr(III) as Cr_2O_3	5466.0
Eastern cottontail	Cr(III) as Cr_2O_3	2011.0
	*Cr (VI)	
American robin	Cr(VI)	1.0
Mallard	Cr(VI)	1.0
White-tailed deer	Cr(VI) as K_2CrO_4	0.92
White-footed mouse	Cr(VI) as K_2CrO_4	6.55
Eastern cottontail	Cr(VI) as K_2CrO_4	2.41
	V	
American robin	VSO_4	11.4
Mallard	VSO_4	11.4
White-tailed deer	$NaVO_3$	0.055
White-footed mouse	$NaVO_3$	0.389
Eastern cottontail	$NaVO_3$	0.143

* hexavalent chromium compound was not specifically identified.

5.3.3 Site Characteristic Parameters

The code includes default site-parameter values, based on site data from the U.S. DOE, U.S. EPA, U.S. Department of Agriculture, U.S. Department of the Interior, U.S. Department of Defense, and other references (Yu et al., 1993a,b). However, parameters can be modified to site-specific characteristics. The code uses the following categories for the parameters: *contaminated zone parameters, cover and contaminated zone hydrological data, saturated zone hydrological data, unsaturated strata hydrological data, distribution coefficients,* and *air-particulates.* Site-characteristics should be reviewed thoroughly so that the code parameters can be modified accordingly. Parameters such as, distribution coefficients can vary over many orders of magnitude depending on the soil type, pH, redox potential, presence of other ions, and soil organic content. A discussion of the code parameters follows.

The *contaminated zone* as defined within the code, is an area that contains soil concentrations above background and is buffered from natural background levels by at least 100 meters. Code developers (Cheng,1998 and Yu et al., 1993a,b) recommend that contaminant concentrations clearly exceed background levels, and samples should be taken from a variety of up-gradient or offsite locations. U.S. EPA Region 9 preliminary remediation goals (PRGs) and general metal background levels are provided as a general reference for sites contaminated with chromium, vanadium, or molybdenum (Table 22) (EPA 1998). An area is considered contaminated, if the chemical concentration in a soil sample exceeds the level of the mean background level by two times the standard deviation (Cheng, 1998 and Yu et al., 1993a,b).

The primary parameters of the contaminated zone and their corresponding default

Table 22 Contaminant Concentration Comparison (EPA, 1983 and 1998)

Contaminant	PRGs EPA Region 9		Background	
	Residential Soil (mg/kg)	Industrial Soil (mg/kg)	Range (mg/kg)	Mean (mg/kg)
Total Cr [1:6 for Cr(VI): Cr(III)]	210	450	1-1,000	100
Cr (VI)	30	64		
Mo	370	9400	0.2-5	2
V	520	13,000	20-500	100
V_2O_5	670	17,000		
VSO_4	1500	37,000		

values are presented in Table 23. The thickness of the contaminated zone as defined by the code is the distance from the surface of the soil, to the depth beneath the surface where the contaminant exceeds the background (Cheng, 1998 and Yu et al., 1993a,b). As stated previously the representative contaminant concentration that was used was based on actual chromium site data obtained from an unpublished report provided by the NJDEP. The code can evaluate a maximum of 25 contaminants (assuming the contaminant is in the database) per run and assumes that the contaminated zone is uniform with a finite contaminant concentration (Cheng, 1998). The length of the contaminated zone parallel to aquifer flow is used to evaluate dilution of contaminated water into an aquifer. The amount of time that has elapsed between the placement of chemical wastes on-site and its characterization can be defined within a range of hours up to 100,000 years.

Table 23 Contaminated Zone Parameters Default Values (Cheng,1998)

Parameter	Code Default Value
Area of the contaminated zone (m^2)	10,000
Thickness of the contaminated zone (m)	1
Length of contaminated zone parallel to aquifer flow (m)	100
Time since material placement (yrs)	0
Initial soil concentration (mg/kg)	4550

Hydrological data assists with predicting contaminant mobility within the soil. Calculation of the flux from the soil phase requires defining the zone characteristics, such as soil porosity, erosion, and hydraulic conductivity (Cheng, 1998). Soil porosity can vary significantly within the strata (Yu et al., 1993) (Table 24). By definition, total porosity is the ratio of the soil pore volume to a total volume of a sample (Cheng, 1998 and Yu et al., 1993). In this evaluation, the zone porosity initially used is based on coarse sand material (0.4). The effective porosity accounts for tortuosity; the effective path for transport.

Other parameters listed in Table 24 like the hydraulic conductivity, evapotranspiration coefficient, annual precipitation, b parameter, and runoff coefficient are all used to calculate chemical leaching. The b parameter is a component of the universal soil loss equation (Yu et al., 1993). It is applied to predict the water content in the soil layer. The b exponent is a soil specific fitting parameter of the volumetric water saturation equation that can only be determined experimentally (Yu et al., 1993). However, values are available for most general soil types and can be obtained from tables within the ANL handbook (Yu et al., 1993). The following is the volumetric water saturation ratio, R_S, equation:

$$R_S = \left(\frac{I_r}{K_{sat}}\right)^{\left(\frac{1}{2b+3}\right)}$$

where I_r is the infiltration rate and K_{sat} is the saturated hydraulic conductivity. For preliminary screening the code defaults to a silty loam value.

Table 24: Hydrological data and Zone Strata Parameters (Cheng, 1998 and Yu et al., 1993)

Parameter	Code Value	*Range
Density (g/cm^3) dry	1.6	1.1 - 1.6
Total porosity	0.4	0.03 - 0.57
Effective porosity	0.2	0.01 - 0.47
Exponential b parameter	5.3	4.05 – 11.40
Saturated and Uncontaminated /Unsaturated Strata Parameters hydraulic conductivity (m/yr)	100	10^{-7} - 10^{7}
Chromium Compounds K_d (cm^3/g)	560	30 – 1500
Vanadium K_d (cm^3/g)	100	
Depth drilled below water table for groundwater sample (m)	10 (below water table)	
Erosion rate (m/yr)	1×10^{-3}	
Precipitation (m/yr)	1	
Saturated zone hydraulic gradient	.02	
Evapotranspiration coefficient	0.6	
Cover/Contaminated zone hydraulic conductivity (m/yr)	10	
Runoff coefficient	0.2	
Cover depth (m)	0	
Unsaturated zone strata thickness (m)	4	
Watershed area for nearby stream or pond (m^2)	1×10^{-6}	

*Common ranges are included for reference (Yu et al., 1993).

The run-off coefficient is the fraction of precipitation that does not penetrate the topsoil; however, no loss is assumed for irrigation water. If a site is near a water source such as a watershed area for a nearby stream or pond, the code estimates a dilution factor for the surface water pathway (Cheng, 1998 and Yu et al., 1993). The ratio of the contaminated zone area to the watershed area is the dilution factor (Cheng, 1998 and Yu et al., 1993). The contaminated zone erosion rate represents the average volume of soil removed as a result of natural phenomena (i.e., wind, rain, running water, etc.) (Cheng, 1998; Yu et al., 1993).

The bulk density of dry soil from the contaminated zone is the ratio of the mass of the solid phase of dry soil to its total solid and pore volume (Cheng, 1998 and Yu et al., 1993). Because the code defaults to a cover zone porosity value describing sandy material, a value of 1.6 g/cm^3, which is commonly applied to describe the bulk density of sandy soils, was defaulted to as well (Cheng, 1998; Yu et al., 1993). The ranges of bulk density typically observed in soils are also provided in Table 24 (Yu et al., 1993).

The site parameters presented in Table 24 can describe up to five different horizontal strata including a layer of clean soil that can exist over the contaminated layer (Cheng, 1998). The only essential parameter required to activate additional strata is the thickness parameter(s). If the contaminants of interest were buried at the site, this would be appropriate, however, for immediate evaluation of receptor exposure to a contaminant, cover depth was modified to zero.

The distribution coefficients describing contaminant partitioning and availability are provided for chromium and vanadium contaminants, 560 cm^3/gm and 100 cm^3/gm, respectfully. One critical limitation with this code is the use of one partitioning value for both forms of chromium. This default is grossly inaccurate as these two species behave very differently in the environment (Kroschwitz et al., 1997). For demonstration, code values were used as these were specific for the soil system considered and defined by the developers (Cheng, 1998). In the second stage of this work, contaminant distribution processes will be examined and modeled.

The soil-mixing layer depth defaulted to within the code is 0.15 m (Cheng, 1998). A value of 0.9 m for the root depth is used, because most plants for which nutrients can be obtained usually extend less than 1.0 m below the surface (Yu et al., 1993). The soil-mixing layer is a component used in conjunction with particulate characteristics to account for contaminant deposition onto terrestrial plants. Table 25 presents the air-particulate characteristics used to assess mass loading to soils. This mass loading is the ratio of airborne particulates to contaminated soil, and is a dilution effect to contaminated soils. According to code developers (Cheng, 1998), the default value of 2.0×10^{-4} g·m^{-3} is a conservative estimate, because it considers both short periods of high mass loading and sustained periods of normal activity (i.e., heavy equipment) on a site (Cheng, 1998). The dilution length is used to assist in estimating the effect clean soil blown in from outside the contaminated site has in diluting the contaminated material (Cheng, 1998). A default value of 3.0 m is used as it is the geometric mean of boundaries commonly used in particulate modeling (0.03 to 250 m) (Cheng, 1998). The mass loading for foliar deposition is the air/soil particulate concentration ratio, specified as the average mass loading to foliage of airborne contaminated soil particles in a garden during the growing season (Yu et al., 1993b). Typically, the depth of the soil mixing layer assists in calculating "the depth factor for the dust inhalation and soil ingestion pathways for foliar deposition (Cheng, 1998)." However, the code does not account for terrestrial plant toxicity.

5.3.4 Receptor Exposure Parameters

Other parameters used in the code that can be modified are receptor ingestion rates, diet

Table 25 Air-Particulate Parameters

Parameter	Code Default Values
Mass loading for particulates (g/m^3)	2.0×10^{-4}
Dilution length for airborne dust (m)	3.0
Wind speed in mixing zone (m/s)	2.0
Mass loading for foliar deposition (g/m^3)	1.00×10^{-4}
Depth of soil mixing layer (m)	0.15

fractions, and body weights. The diet fractions are dimensionless parameters that define the relative composition of a receptor's diet (Cheng,1998). For instance, a receptor's diet may be composed of one-third vegetation, one-third invertebrates, and one-third water. The code also includes a parameter that considers a receptor home range, the area of the receptor's habitat. The default values obtained for the code were based on values presented in U.S. EPA *1993 Wildlife Exposure Factors Handbook* (EPA, 1993). A site use factor is determined in the code by dividing the contaminated zone area by a receptor's home range area (Cheng, 1998). These parameters are used to derive the ADD and were presented earlier in section 1.1. Table 26 presents the characteristics specific to each receptor used in the code for assessing contaminant uptake and exposure:

Table 26 Receptor Exposure Parameters

Parameter	Robin	Mallard	Deer	*Rabbit*	Mouse
Diet fraction Vegetation	0.550	0.2400	1.000	0.937	0.4100
Diet fraction Soil	0.100	0.0200	NA	0.063	0.0200
Diet fraction Invertebrates	0.350	0.7400	NA	NA	0.5700
Home range (ha)	0.340	580.0000	16.200	3.129	0.0615
Ingestion rate of food (kg/day)	0.093	0.3277	4.674	0.562	0.0055
Ingestion rate of water (L/day)	0.011	0.0641	4.720	0.118	0.0046
Body weight (kg)	0.077	1.1340	73.300	1.220	0.0212

5.3.5 Risk Characterization Results

Once the physical and chemical characteristics of the site and receptors are fully understood, a hazard quotient is calculated by dividing the ADD_{Total} by a benchmark. As discussed earlier RESRAD code developers are applying NOAELS as opposed to lethal doses, which is the preferred method for evaluating risks to an ecosystem. The ecological hazard quotient (EHQ) is calculated using the following equation:

$$\text{EHQ} = \text{ADD}_{\text{Total}} \div \text{Benchmark NOAEL}$$

The EHQ provides a risk characterization as shown in Table 27 (Cheng, 1998). Based on the value, the level of risk to a receptor provides a guideline for risk assessment decisions.

Table 27 EHQ risk characterization

EHQ Value Range	Risk Characterization
0.0001-1.0	Potential risk to receptor
1.0-10.0	Slight potential adverse risk to receptor
10.0-100.0	Moderately high potential adverse risk to receptor
>100.0	Extreme adverse risk to receptor

Vanadium, Cr(III), and Cr(VI) contamination were evaluated simultaneously so that their impact on the total hazard quotient could be compared. However, the code is still in the beta testing stage, and the developers are currently addressing problems I had in using this code. For example, I was unable to evaluate risks posed to the mallard duck at this time. In addition, because of the limited graphical capabilities within the code, results from the summary report were imported to Excel for formatting and presentation purposes. A summary report is produced upon completing an evaluation. Within the summary report are the contributing fractions of each medium (i.e., soil, water, invertebrates, and vegetation) to the total hazard quotient for each contaminant. Identification of the contributing media to a receptor's diet focuses the ecological risk assessment on areas that present the greatest risk. For example, Figure 6 displays invertebrates as the greatest contributing medium to the American robin hazard quotient for all three metals, even though vegetation is the greatest fraction of its diet (Table 26). In addition, contaminant transport affects the relative contribution as contaminants become more available via leaching or diffusion. Figures 6-9 illustrate the medium contributions to the total hazard quotient for the robin, deer, rabbit, and White-footed mouse receptors at 10 years. A limitation with avian (American robin) benchmark methodology can be seen in Figure 6: the media contributions for Cr(III) and Cr(VI) are identical even though these metals behave differently in the environment. Specifically, Cr(VI) is more mobile than Cr(III), as the precipitates of the latter have very small solubilities (Tölgyessy, 1993; Stumm and Morgan, 1995). Furthermore, benchmarks applied for calculating the ecological hazard quotients for both metals are the same for avian species (i.e., American robin).

As seen in these Figures (6-9), water does not contribute to the hazard quotient for any of the receptors, because up to 10-years contaminants have not yet reached surface waters. Medium contributions for the Eastern-cottontail rabbit demonstrate that soil is the most significant medium (Figure 8), even though vegetation is the rabbit's primary dietary component (Table 26). For the rabbit at 10 years, vegetation contributed a dose of 0.1722 $mg \cdot kg^{-1} \cdot d^{-1}$ as opposed to 42.05 $mg \cdot kg^{-1} \cdot d^{-1}$ for soil. Consequently, even though metal uptake is greater in the root then the shoot of the plant (Gupta et al., 1994), exposure via ingestion of vegetation is much less than that of soil. The contribution of vegetation intake to the hazard quotient is determined in the code by the soil-to-plant transfer factor. For example, the soil-to-plant transfer factor for the chromium is 2.5×10^{-4} as opposed to 1.3×10^{-3} for vanadium. The influence of the chromium and vanadium factors is demonstrated in Figures 6 and 8, where vegetation contributes 0.24% for vanadium as opposed to the 0.02% for chromium. Transfer factors are important in determining the ecological impact of contaminants.

In Figure 10, the hazard quotient versus time is presented and compared for receptor exposure to Cr(III), Cr(VI), and V. The figure is in semi-log scale to highlight and differentiate the effect of the three contaminants. As demonstrated in Figure 10, an extreme risk exists (Table 26) for the robin as a consequence of exposure to all three contaminants. Because the input parameters and benchmarks are equivalent for Cr(III) and Cr(VI), there is no means of distinguishing risks between the two. Therefore, comparing the three contaminants, the chromium compounds present a greater potential to cause adverse effects to the American robin over time, as the greater vanadium NOAEL results in a smaller EHQ.

The EHQ for the White-tailed deer indicated that vanadium presented a greater risk than the chromium contaminants. However, up to 500 years for each contaminant the EHQ is less than 1. Therefore, risk characterization is defined as a "potential risk" to a deer (Cheng, 1998). For the White-tailed deer, the Cr(III) NOAEL of 768 $mg \cdot kg^{-1} \cdot d^{-1}$ (Table 21) is so large that the resulting EHQ is less than 10^{-5}. Similarly, the EHQ for the rabbit and White-footed mouse indicated that as with the deer, vanadium presented the greatest risk and trivalent chromium presented the least. In fact, vanadium exposure is characterized as an extreme risk to both the rabbit and mouse. On the other hand, Cr(VI) resulted in a moderately high risk, and Cr(III) is considered only a potential risk. As discussed earlier, the dimensionless soil-to-plant transfer factor is greater for vanadium than for Cr(III) and Cr(VI); the greater transfer factor results in an increase in

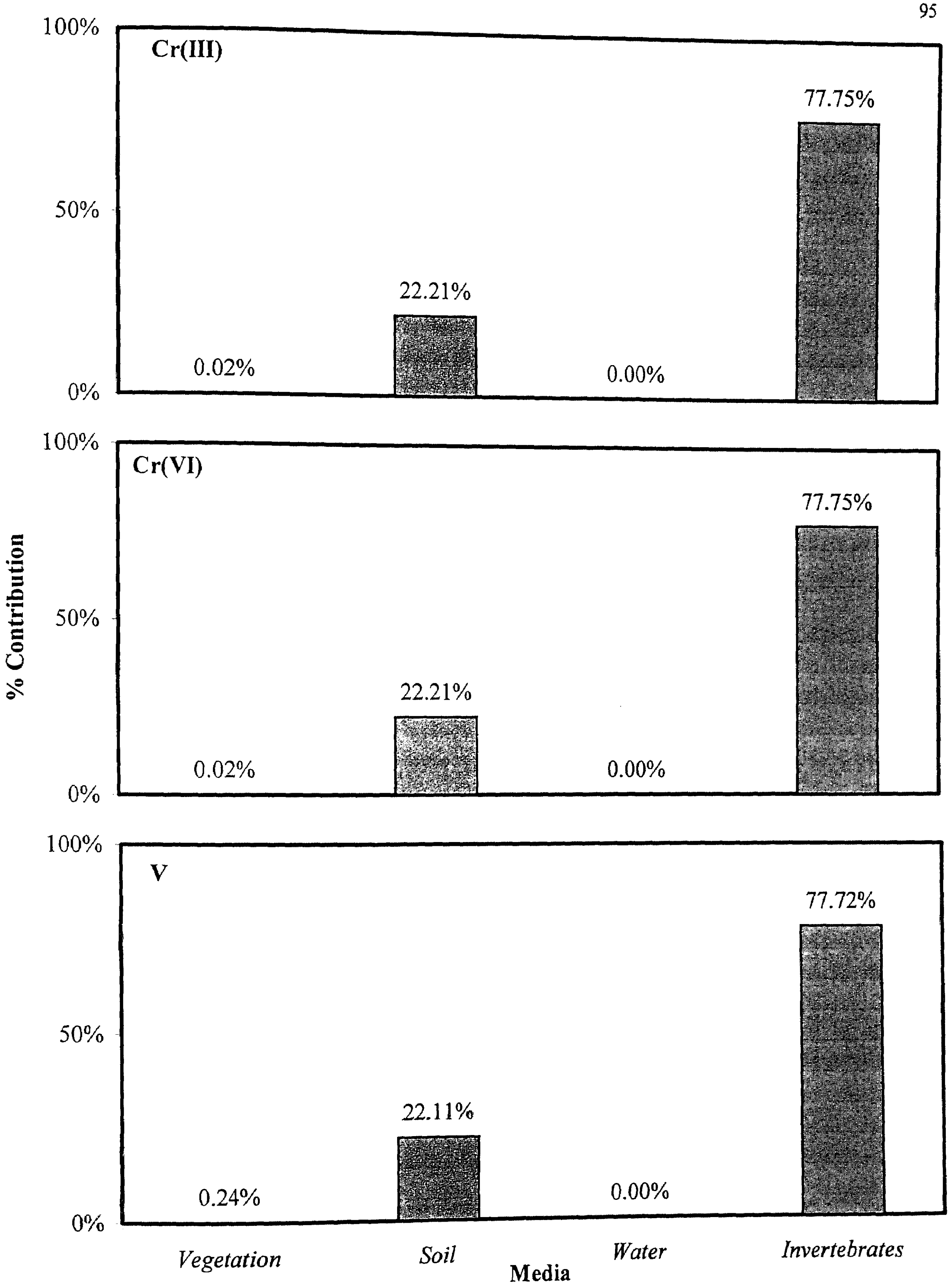


Figure 6 Percent Contribution of Each Medium to the Hazard Quotient for the American robin at 10 years

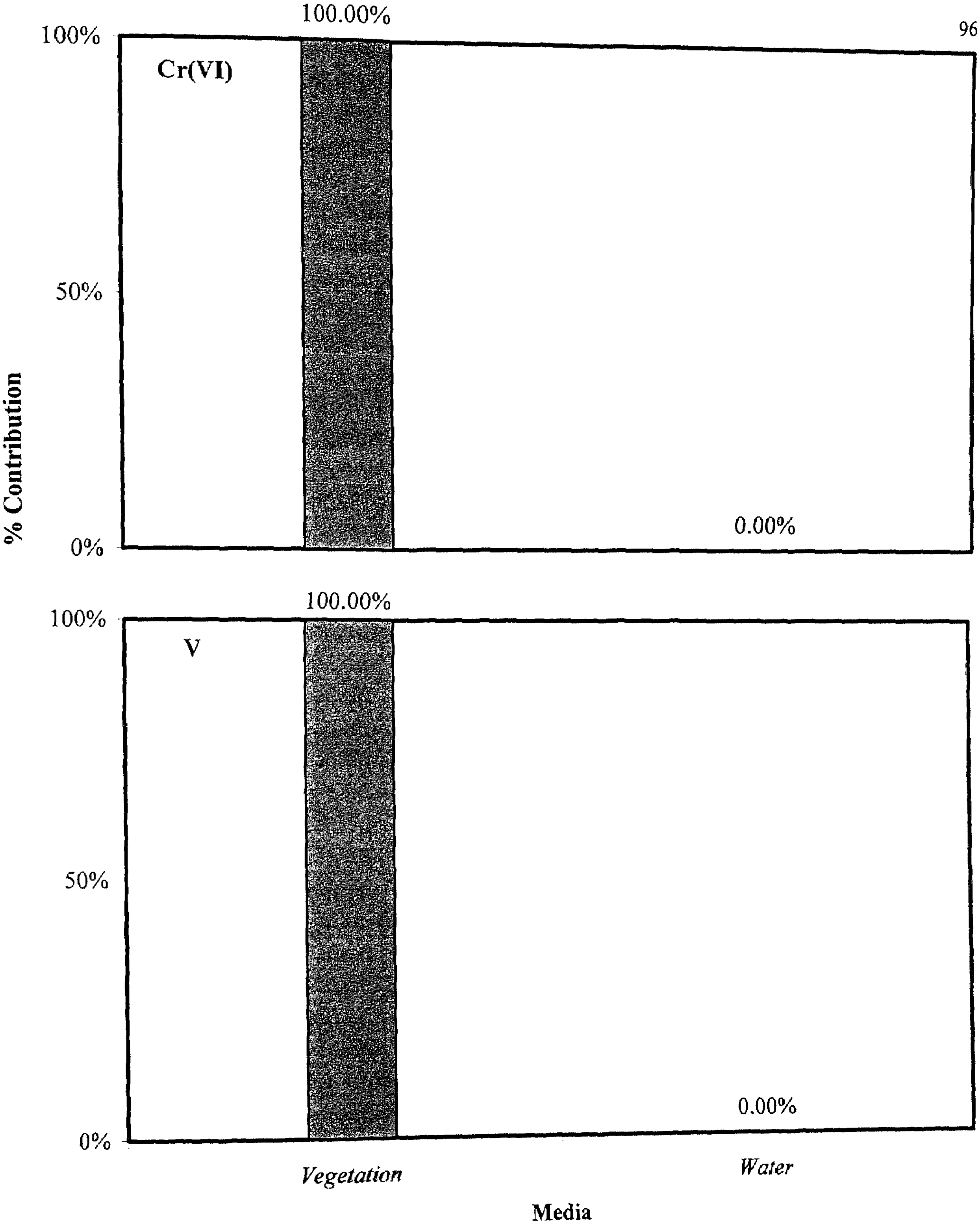


Figure 7 Percent Contribution of Each Medium to the Hazard Quotient for the White-tailed deer at 10 years

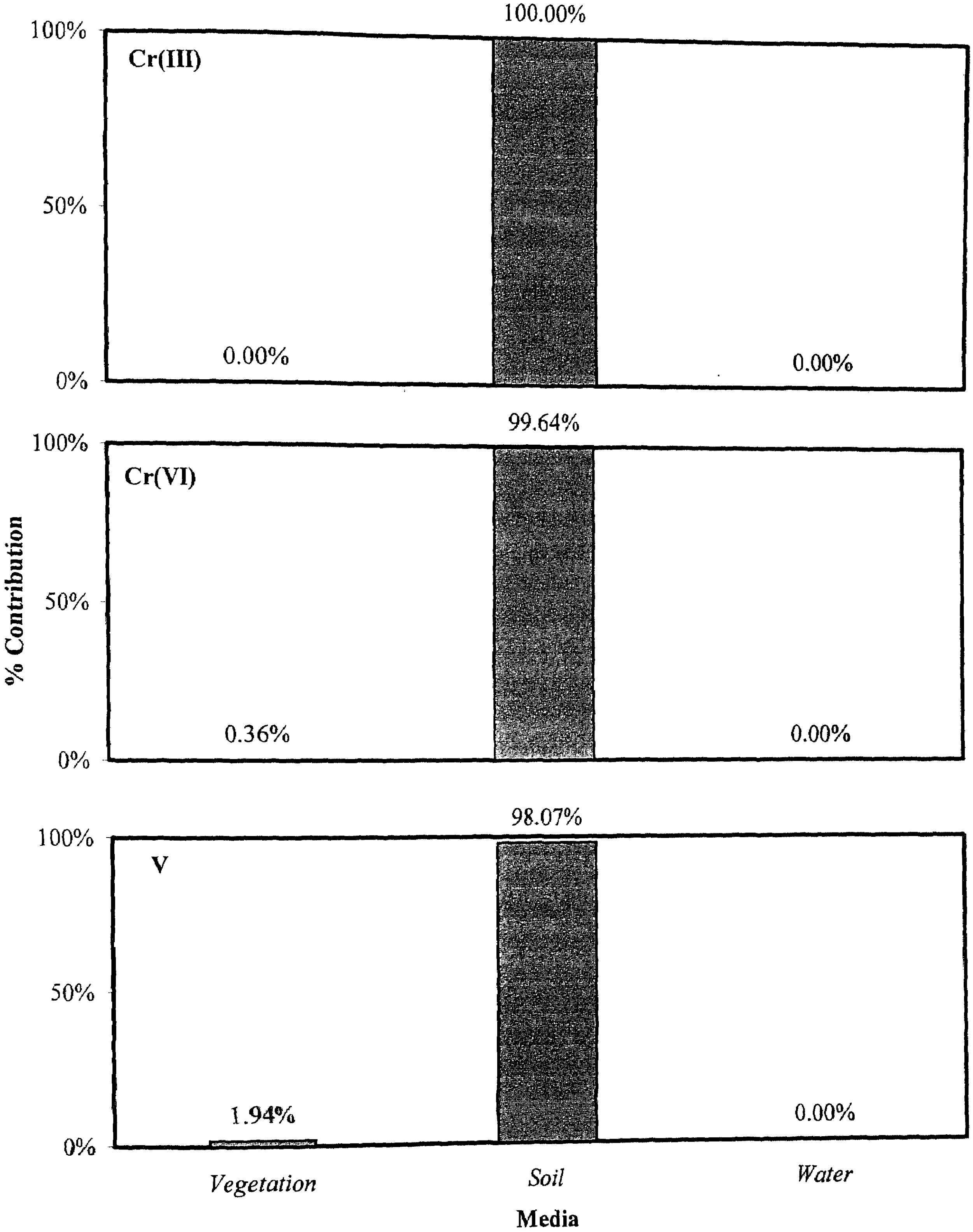


Figure 8 Percent Contribution of Each Medium to the Hazard Quotient for the Eastern cottontail Rabbit at 10 years

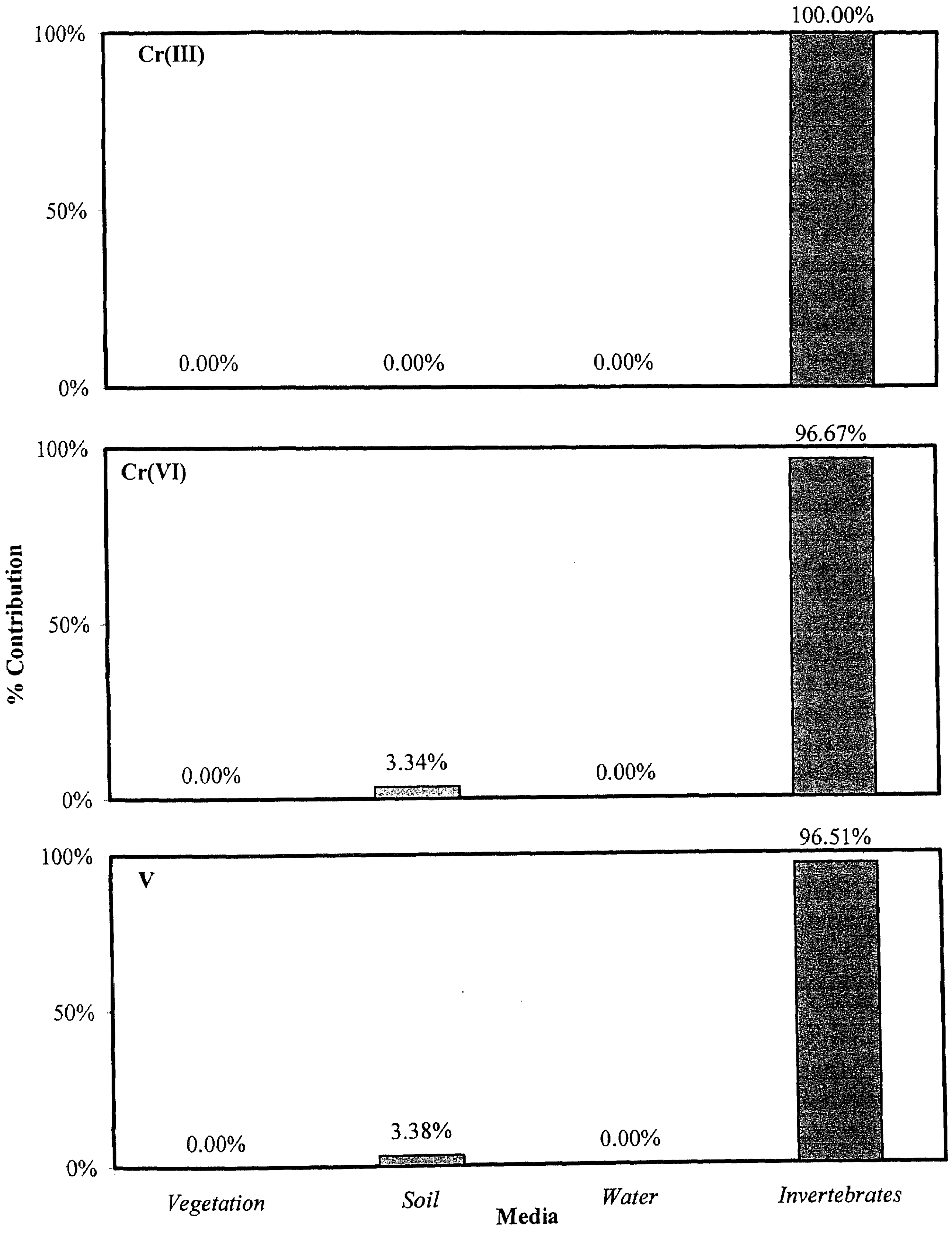


Figure 9 Percent Contribution of Each Medium to the Hazard Quotient for the White-footed mouse at 10 years

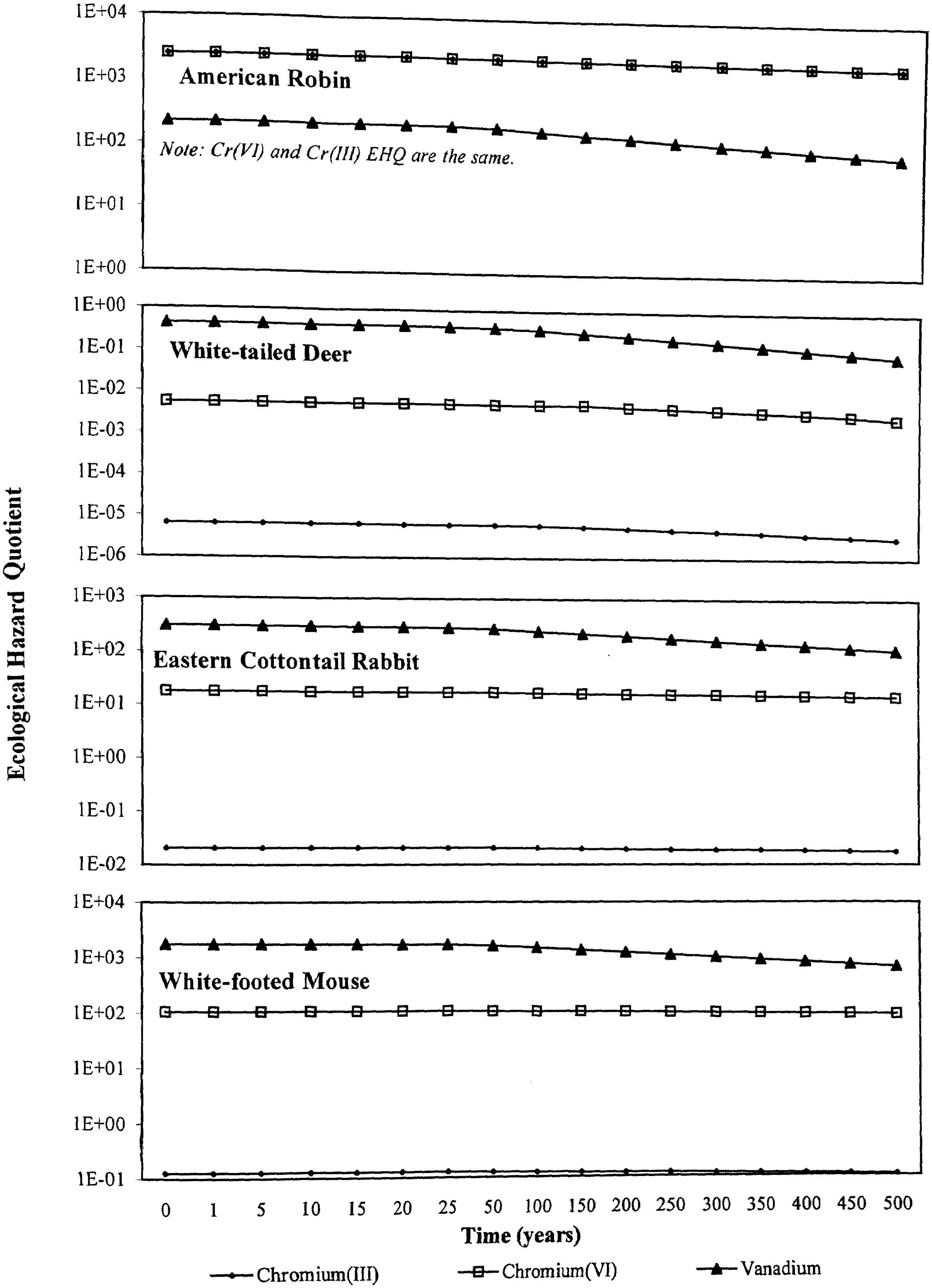


Figure 10 Hazard Quotient as a Function of Time

contaminant uptake in the plant. Subsequently, because the rabbits diet consists predominantly of vegetation (approximately 93%, Table 26), the possibility for vanadium ingestion increases. Furthermore, vanadium has the lowest benchmark (0.143mg·kg^{-1}·d^{-1}) of the three metals.

Overall, the risks were found to be greatest for the American robin with all metals contributing as extreme adverse effects. The Eastern cottontail and White-footed mouse exposure to vanadium and Cr(VI) fell into extreme and moderately high risks, respectively. Similar results were found for the White-footed mouse. Lastly, the White-tailed deer observed the least amount of risk from these contaminants, where all risks resulted as "potential".

5.3.6 Sensitivity Analysis

A sensitivity analysis (Figure 11) was performed on select parameters within the code. The following equation was applied as a sensitivity factor (Cheng,1998):

$$F = 1 + \frac{\%}{100}$$

The 900% range used results in a factor of 10. The code runs three iterations applying the following guidelines:

- iteration one is application of the code with the original parameter value;
- iteration two repeats iteration one and then multiplies the selected parameter by the sensitivity factor; and
- iteration three again repeats the first iteration and then divides the parameter by the sensitivity factor.

To better understand the influence of parameters within the code, the sensitivity analysis was implemented by applying the maximum and minimum for parameters discussed in section 6.3.3 (Table 24); these include soil density, total and effective porosity,

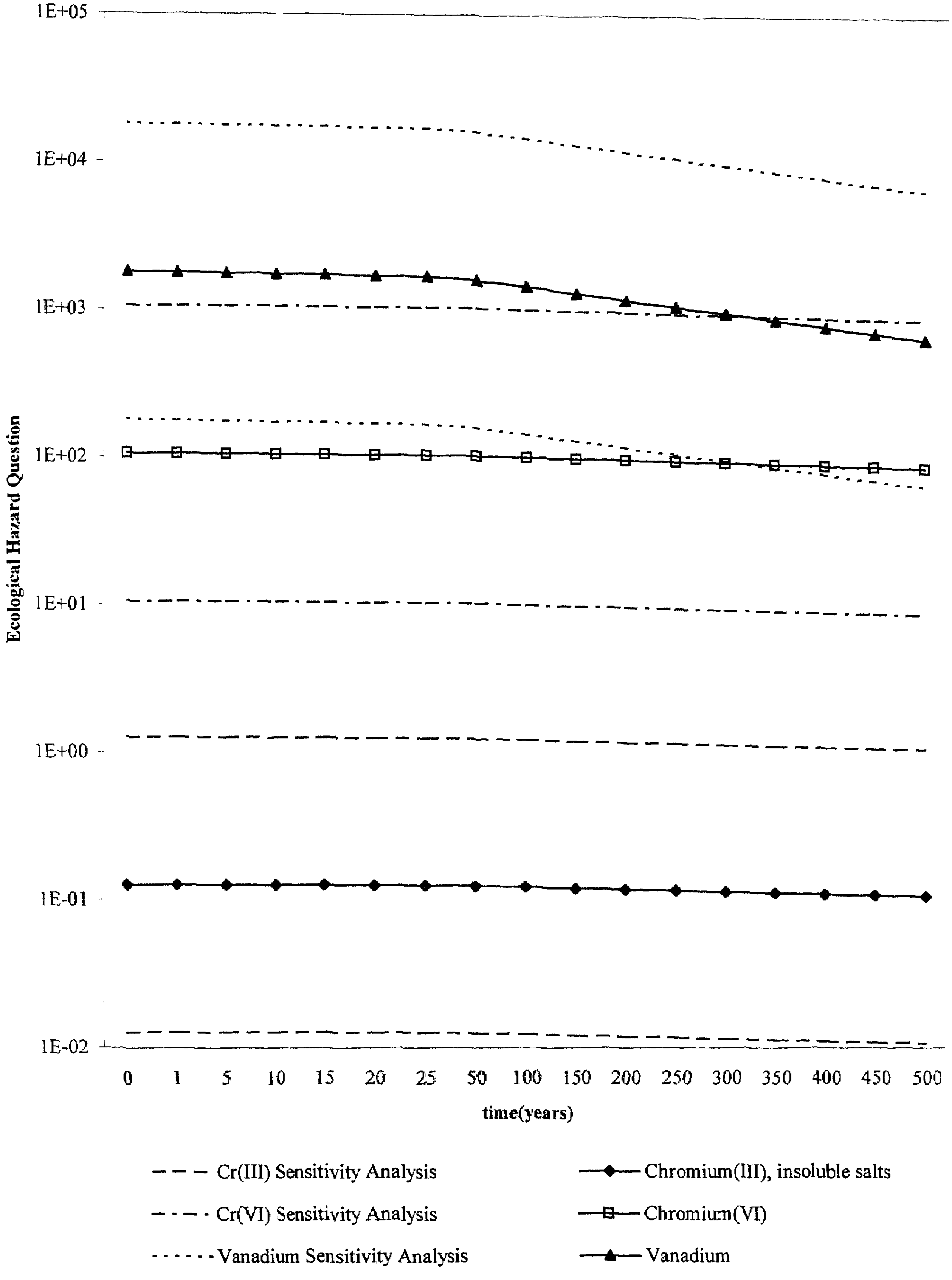


Figure 11 White-footed mouse Sensitivity Analysis

exponential b, hydraulic conductivity, and distribution coefficients. In Figure 11, results from applying a 900% range to the distribution coefficient are presented. The lines above and below the resulting hazard quotients on the graph represent the effect of the distribution coefficient, K_d. As seen in the figure, the K_d influences the EHQ by an order of magnitude. Furthermore, for the White-footed mouse, the resulting EHQ effected risk characterization. For example, initial conditions for Cr(VI) resulted in a "moderately high potential to adverse risk", however, when the K_d was increased by a factor of 10, the risk characterization changed to "extreme adverse risk ". Conversely, when the K_d was reduced by a factor of 10, risk characterization of exposure to Cr(VI) was a "slight potential adverse risk". The effect demonstrates that the distribution coefficients have a significant impact on contaminant transport as well as EHQ. Sensitivity analysis of other parameters including soil density, total and effective porosity, exponential b, and hydraulic conductivity parameters had little to no impact on the EHQ.

5.3.7 Limitations

RESRAD-Code developers selected five terrestrial animals to represent a cross section of species throughout the U.S. However, in the current version I was unable to obtain results for the mallard duck, and as a result the developers are addressing this. While the model is useful in itself for assessing risks to the five prevalent animals, it also is a limitation because the code cannot be modified to evaluate different animals. The code is also limited because it only considers vegetation as a medium for exposure and not as a potential receptor. Even though plants are a food source, exposure and uptake may negatively impact plant growth and habitat as well (Newman et al., 1991). Including the effects to plants is important for a comprehensive ecological risk assessment.

Furthermore, the code is only designed to evaluate soil contamination and does not account for potential contaminant effects to aquatic organisms. In fact, neither aquatic plants nor animals are considered in this model; this presents a problem when conducting assessments of metals, because aquatic environments and in particular sediments are very likely sinks for contamination. As stated in the introduction, the code is limited by its contaminant database; only those can be weighed in their model. Accordingly, application of surrogates to represent a contaminant of concern adds additional uncertainty to the results. Although exposure through ingestion occurs by one of four media, a receptor's exposure is only considered and evaluated through this pathway. Dermal absorption and inhalation may not present as significant a threat relative to ingestion, they are nonetheless exposure pathways. The current version of the code runs only as an MS-DOS program, which from a user standpoint complicates data transfer. Reformatting of the reports was required to view the text and tables.

5.3.8 Summary

Even though risk characterization for the mallard duck is not possible at this time, the code produced an output for the four other terrestrial receptors. Risks posed to a receptor were found to be greatest for the American robin, where all metals resulted in extreme adverse effect risk characterization. While extreme risks were found for the Eastern cottontail and White-footed mouse from exposure to vanadium, moderately high risks were observed for exposure to Cr(VI). On the other hand, the White-tailed deer received the least amount of risk from these contaminants, where all risk resulted as "potential".

Chromium and vanadium species were applied as surrogates to estimate the potential ecological risk from molybdenum and tantalum, respectively, because of their corresponding grouping within the Periodic Table. Using Cr(VI) (or Cr[III]) and vanadium sulfate as a surrogate for molybdenum (Mo) and tantalum (Ta), respectively, resulted in an extreme risk to the robin. On the other hand, using sodium vanadate and Cr(III) as a surrogates for Ta and Mo, respectively, resulted in risks ranging from potential to moderately high for the Eastern cottontail rabbit, White-footed mouse, and White-tailed Deer (Table 28). Employing surrogates when chemical and toxicity data are lacking is questionable and may mislead the ecological risk characterization process. Because Mo is stable as MoO_3, Cr_2O_3 species may be the best surrogate. Therefore, an additional area of concern within this code or any ecological risk assessment is the use of surrogates and proper selection of ones similar in terms of properties as well as speciation. Overall, results from this assessment indicate that vanadium and chromium species posed similar risks, depending on the form present.

Table 28 Overall Risk Characterization

Receptor	Analyte	Risk Characterization
American Robin	$CrK(SO_4)_2$	Extreme
	[a]Cr(VI)	
	VSO_4	
White-tailed Deer	Cr_2O_3 K_2CrO_4 $NaVO_3$	Potential
Eastern Cottontail Rabbit	Cr_2O_3	Potential
	K_2CrO_4 $NaVO_3$	Moderately High
White-footed Mouse	Cr_2O_3	Potential
	$NaVO_3$	Potential to Moderately High
	K_2CrO_4	Moderately High

[a]Cr(VI) analyte not specified(Sample et al., 1996)

Based on these surrogates, tantalum and molybdenum contaminated soil presented a limited risk to the deer, and tantalum contaminated soil posed a greater risk to the rabbit and mouse than molybdenum contamination. For all contaminants, an extreme risk was found for the robin.

Even though the ecological risk component of the code is based on relatively simple models and is designed exclusively for soil assessments, applying a transport model with an applied daily dose is a useful template for building a more comprehensive ecological risk model. Recommended features for this type of code include addition of algorithms to account for dermal and inhalation routes of exposure, and access to modify the receptor and contaminant databases, which would include introduction of terrestrial and aquatic vegetation as well as animal receptors. Also, the code input and output requires a more user friendly interface for graphical and spreadsheet software. Lastly, the code cannot account for synergistic or additive affects that can result from exposure to multiple contaminants.

5.4 CRCIA Background

The ecological risk model developed by Pacific Northwest National Laboratory (PNNL) is designed to address how exposure to organic, inorganic, and radiological contaminants can affect a coastal habitat. This model stems from a collaborative effort between PNNL, U.S. DOE, U.S. EPA, Washington State Department of Ecology, and other organizations to assess risks posed by chemical and radiological releases from the Hanford Nuclear test facility on the Columbia River ecology. The model uses dose and uptake estimation equations to calculate burdens to plants and animals in both aquatic and terrestrial communities (PNNL, 1998). The algorithms of the model are linked via an Excel spreadsheet to calculate the "body burden concentration" that is then compared to a benchmark (i.e., LOAEL) to predict an ecological hazard quotient.

The sample version provided by PNNL evaluated effects of zinc contamination to the coastal community. The objective of the present case study is to use available physical and toxicological data for chromium, molybdenum, vanadium, and tantalum species for assessing ecological risks posed by these contaminants on the coastal habitat of the Columbia River. Included is an overview of the model algorithms and data selection process, results from its application, a discussion of its limitations, and a summary of conclusions and recommended tools for improvement.

5.4.1 Algorithms and Methods

The CRCIA committee members considered the following factors during algorithm selection: pathways by which a species may be exposed, degree of contact that a species may potentially have with contaminated media, and the potential for an animal to uptake a contaminant (PNNL, 1998). Animal exposure, referred to as contaminant body burdens, are primarily based on dermal, inhalation, and ingestion exposure (PNNL, 1998).

Terrestrial plant exposure is based on equilibrium partitioning and includes the effects of rain splash, root and foliage partitioning via soil vapor, and foliage adsorption from soil. These parameters when combined yield a total internal plant burden and are also incorporated into the total burden ingested by a herbivore (PNNL, 1998). Plant concentration (C_i in mg/kg) via uptake from rain splash (C_{par}), soil vapor (C_{pav}), and particulates (C_{pap}) is determined by the following equation:

$$C_i = EC_i \times K_i$$

where EC_i (mg/m^3) is the medium concentration (i.e., rain, soil vapor, particulates) and K_i (m^3/kg) is the corresponding partition coefficient. Plant concentration from root uptake (C_{pau}) is determined from:

$$C_{pau} = EC_{soil} \times B_v \times (1 - f_w)$$

where B_v is the plant bioconcentration factor and f_w is the plant tissue water weight fraction (PNNL,1998). The total internal plant concentration (C_{pai}) is the sum of the foliage uptake by soil vapor (C_{pav}) and the root uptake (C_{pau}). The total burden to a herbivore is the sum of the four pathways. Aquatic plant exposure is also based on equilibrium partitioning with the aqueous phase where a bioconcentration factor is applied.

On the other hand, an applied daily dietary (ADD) intake through dermal, inhalation, and ingestion routes was used for terrestrial animal exposure to a contaminant (PNNL, 1998). The ADD, like that for the RESRAD-Code, is based on algorithms that were originally developed for assessing human exposure but were determined to be appropriate for terrestrial mammals (Hope, 1995). Accordingly, separate algorithms are employed to address the contribution of each pathway to the daily dose and body burden calculation. Dermal exposure for a terrestrial animal is determined in the code by combining the estimated body burden concentration from sediment/soil (C_{dersi}) and water (C_{derwi}). These body burdens are derived from the respective absorbed daily contact dose

(D_i mg/kg·d) and the contaminant-specific depuration rate for species (k_{ei} d^{-1}):

$$C_i = D_i / k_{ei}$$

The sum of the two is the total body burden from dermal exposure. The total daily dermal absorbed dose (D_{Total}) is the sum of the absorbed daily contact dose from the sediment/soil and water. Terrestrial animal body burden from contaminant exposure via vapor (C_{ivi}) and particulate inhalation (C_{ipi}), and ingestion of water (C_{ingw}), soil (C_{ings}), and food (C_{ingf}) is determined by the following:

$$C_i = D_i \text{ x } \alpha_i \ / \ k_{ei}$$

where D_i is the ADD based in the respective medium, α_i is the absorption factor, and k_{ei} is the depuration rate. A total body burden for inhalation is the sum of the vapor and particulate concentrations, just as the total body burden for ingestion is the sum of three components.

Aquatic animal exposure is based on a daily dietary intake occurring by ingestion (i.e., food, sediment, and water) and respiration (i.e., gills). The general aquatic burden calculation is based on a mass balance and includes feeding on prey (from sediment):

$$dV_i/dt = k_{ui} \ (b_{pore} \text{ x } EC_{pore} + b_{surface} \text{ x } EC_{surface}) + \Sigma \ (P_{ij} \text{ x } \alpha_{ij} \text{ x } I_{ij} \text{ x } V_j) - (K_i + G_i)V_i$$

where,

- V_i is body burden in predator (metals: µg or µCi/kg dry weight ; organics: µg or µCi/g lipid)
- V_j is body burden in prey (metals: µg or µCi/kg dry weight ; organics: µg or µCi/g lipid) or in sediment (metals: µg or µCi/kg dry sediment; organics: µg or µCi/g organic carbon)

- k_{ui} is contaminant uptake from dissolved sources (metals: L/g dry weight / day; organics: L / g lipid / day)
- b_{pore} is relative exposure to pore water
- $b_{surface}$ is relative exposure to surface water ($b_{surface} = 1 - b_{pore}$)

- EC_{pore} is contaminant concentration in pore water (μg/L or μCi/L)
- $EC_{surface}$ is contaminant concentration in surface water (μg/L or μCi/L)

- P_{ij} is fraction of food source in diet
- α_{ij} is assimilation efficiency of contaminant consumed (g contaminant assimilated / g contaminant ingested)
- I_{ij} is feeding rate (organic model: g prey lipid / g predator lipid / day; metal model: g prey dry weight / g predator dry weight / day) or for sediment (organic model: g organic carbon ingested / g predator lipid / day; metal model: g sediment dry weight / g predator dry weight / day).
- K_i is loss rate of contaminant including depuration and metabolism (1/day)
- G_i is growth rate of prey (1/day)

To calculate organic and inorganic body burden, steady state conditions are assumed (PNNL, 1998):

$$V_i = [\, k_{ui} (b_{pore} \times EC_{pore} + b_{surface} \times EC_{surface}) + \Sigma (P_{ij} \times \alpha_{ij} \times I_{ij} \times V_j) \,] / (K_i + G_i)$$

In this equation $k_{ui} / (K_i + G_i)$ is simply the bioconcentration factor (BCF_i) that reflects uptake from the surrounding aqueous medium and the bioaccumulation factor (BAF_i) is $(P_{ij} \times \alpha_{ij} \times I_{ij} \times V_j) / (K_i + G_i)$. The equation then reduces to the following at steady state:

$$V_i = BCF_i \times (b_{pore} \times EC_{pore} + b_{surface} \times EC_{surface}) + \Sigma\, BAF_i$$

5.4.2 Parameters

In this section, the ecological risk parameters in these above equations are discussed. Important components of a body burden calculation are receptor physical characteristics and habits (i.e., body weight and foraging) and how efficient they are at absorbing and eliminating a contaminant. The code includes site-parameter values, based on site data from the Columbia River and the Hanford Facility. Because the code is in an Excel spreadsheet these parameters can be easily modified to site-specific characteristics. Parameters such as, distribution coefficients, and pore water concentrations, can vary over many orders of magnitude depending on the soil type, pH, redox potential, presence of other ions, and soil organic content.

As with RESRAD-ECORISK, data provided by the New Jersey Department of Environmental Protection (NJDEP) and representative of actual site contamination were used (NJDEP,1998). At a defunct electroplating site 4550 mg/kg for Cr(VI) was found to be the greatest concentration present in soils (NJDEP,1998). Therefore, in considering a worst case scenario, this concentration was used to represent all metal contaminant levels in sediment and soil. The rationale for selecting equivalent concentrations was to examine similar releases into the environment. For this case study these soil concentrations and other concentrations (EC_i) along with distribution coefficients (K_i) are listed in Table 28.

Table 28 Total Plant Burden Parameters Values (PNNL,1998)

Species	Partition of soil to plant - wet weight K_{ps1}	root-zone soil to above-ground parts B_v	plant-air partition coefficient – particulates (m^3/kg wet weight) K_{pa2}	Soil-phase concentration-estimated (μg or μCi/m^3) EC_{soil}	[a]particulate air concentration - estimated (μg or μCi/m^3) EC_{par}
Terrestrial Plants	3.40E-03	2.40E-02	3.30E+03	4.55E+06	6.40E-05

[a]particulate air concentration-estimated for Fungi (1.28E-04), Black cottonwood and Mulberry (1.28E-06).

Terrestrial animal exposure pathways include inhalation, ingestion, and dermal contact. To account for these routes, absorbed daily doses and depuration rates were required (Table 29). However, because the metal contaminants are nonvolatile, there is no exposure of gases through inhalation. Other exposure factors applied for the terrestrial animal dose estimation formulae include 0.22 for particulate inhalation, α_{pari}, and 0.01 for water, soil, and food ingestion, α_{ingi} (PNNL, 1998).

The bioaccumulation factors (BAFs) used for aquatic animals are listed in Table 30 to determine aquatic animal and plant dose directly from an aqueous solution. The BAF accounts for contaminant uptake by an aquatic animal from all routes of exposure. Aquatic receptor BAFs needed in the case study were not identified for all aquatic receptors, because some receptors are either not at a stage of development where they are capable of ingesting prey or as with plants are exposed via water respiration and transpiration. In these cases, only bioconcentration (BCFs) were used (e.g., salmon eggs) (Table 31). Similarly, for aquatic plants only BCFs are applied (Table 32).

5.4.3 Benchmarks

The lowest observed adverse effect level (LOAEL) and lowest observed adverse concentration (LOAEC) are the benchmarks used within this ecological risk assessment (PNNL, 1998). These LOAELs and LOAECs are the lowest contaminant concentrations that will produce a clinically toxic response in terrestrial and aquatic test organisms, respectfully. Following the guidelines developed by CRCIA assessors, benchmark data for the case study were gathered; if a particular receptor was unavailable, a surrogate was selected based on taxonomy, life style, and/or toxicological response similarity (PNNL, 1998).

Terrestrial animal benchmark selection is based on the LOAEL and is taken directly if available (Table 33). When LOAELs were not available one-fifteenth of the LD_{50} was used (Table 33) (PNNL, 1998). Very few LD_{50} values were available for the terrestrial animals, therefore, LD_{50} values obtained from laboratory studies on test animals were extrapolated for receptors of interest (PNNL, 1998):

$$LD_{50\,(\text{receptor})} = LD_{50\,(\text{benchmark species})} \times [\text{body weight}_{(\text{bench mark species})} / \text{body weight}_{(\text{receptor})}]$$

Table 29 Terrestrial Animal Dermal, Inhalation, and Ingestion Exposure Parameter Values (PNNL,1998)

Terrestrial Animal Receptor	Absorbed daily dermal dose - soil (µg or µCi/kg bw/day) D_{dersi}	Depuration rate (1/day) K_{ei}	Absorbed daily dermal dose – water (µg or µCi/kg bw/day) D_{derwi}	Particulate Inhalation dose (µg or µCi/kg/day) D_{ipi}	Water Ingestion dose (µg or µCi/kg-day) D_{ingw}	Soil Ingestion dose (µg or µCi/kg-day) D_{ingsi}	Food Ingestion applied		
							Herbivores (µg or µCi/kg bw/ day) D_{ingfi}	Insect and Omnivores (µg or µCi/kg bw/ day) D_{ingfi}	Carnivores (µg or µCi/kg bw/ day) D_{ingfi}
Terrestrial arthropods	8.80E-02	6.00E-01	0.00E+00	8.42E-04	0.00E+00	4.50E+03	9.10E+03	----	----
Lizards (Uta)	9.92E+01	1.20E+00	0.00E+00	1.16E-04	0.00E+00	1.44E+03	----	1.47E+03	----
Western aquatic garter snake	1.78E+02	1.20E+00	1.14E+03	6.35E-05	0.00E+00	8.63E+02	----	----	9.07E+02
Muskrat	1.67E+01	6.00E-01	2.02E+02	1.79E-04	4.01E+01	1.07E+04	1.42E+04	----	----
Beaver	5.63E+00	6.00E-01	6.82E+01	9.65E-05	2.94E+01	1.23E+03	2.41E+03	----	----
Racoon	9.40E+00	6.00E-01	1.14E+00	2.07E-05	3.41E+01	1.48E+04	----	----	1.91E+04
Coyote	5.99E+00	6.00E-01	0.00E+00	1.60E-05	3.00E+01	8.36E+03	----	----	9.00E+03
Weasel	3.97E+01	6.00E-01	0.00E+00	2.36E-04	5.14E+01	6.21E+03	----	----	7.07E+03
Mule deer	3.42E+00	6.00E-01	1.66E+00	2.90E-06	2.55E+01	1.12E+03	5.03E+03	----	----
Harvest mouse	7.66E+01	1.40E+00	0.00E+00	8.58E-04	6.21E+01	1.74E+04	----	5.76E+04	----
Woodhouse toad – adult	4.02E+00	1.20E+00	4.28E+01	1.31E-06	0.00E+00	3.95E+02	----	4.38E+02	----
American coot	1.87E+01	1.20E+00	9.97E+01	2.85E-05	2.66E+01	1.31E+05	----	1.56E+05	----
Common snipe	1.10E+01	1.20E+00	5.86E+01	1.40E-05	4.73E+01	2.39E+04	----	2.49E+04	----
Bufflehead	1.12E+01	1.20E+00	5.96E+01	1.61E-05	3.18E+01	2.76E+03	----	4.29E+03	----
Canada Goose	1.07E+01	1.20E+00	5.71E+01	1.29E-05	1.53E+01	1.48E+04	----	2.24E+04	----
Mallard	1.59E+01	1.20E+00	8.46E+01	2.54E-05	2.26E+01	1.04E+04	----	2.21E+04	----
American white pelican	8.65E+00	1.20E+00	4.61E+01	1.12E-05	1.24E+01	1.36E+03	----	2.20E+03	----
Forster's tern	1.53E+01	1.20E+00	3.26E+01	8.01E-07	4.34E+01	3.16E+03	----	4.90E+03	----
California quail	2.97E+01	1.20E+00	0.00E+00	7.84E-05	4.21E+01	4.50E+04	----	6.97E+04	----
Cliff swallow	2.96E+01	1.20E+00	0.00E+00	1.27E-06	8.37E+01	7.47E+03	----	1.04E+04	----
Great blue heron	1.24E+01	1.20E+00	1.32E+01	8.56E-06	1.77E+01	2.08E+03	----	----	3.21E+03
Bald eagle	5.32E+00	1.20E+00	4.54E+00	3.86E-07	1.53E+01	6.59E+02	----	----	9.12E+02
Northern harrier	2.18E+01	1.20E+00	0.00E+00	1.27E-06	3.11E+01	3.04E+03	----	----	3.17E+03
American kestrel	3.32E+01	1.20E+00	0.00E+00	1.70E-06	4.71E+01	5.15E+03	----	----	5.34E+03

Table 30 Aquatic Animal Bio-accumulation Factor (BAFs) (PNNL,1998)

Receptors \ *Prey*	*Sediment*	*Phyto-plankton*	*Peri-phyton*	*Water millfoil*	*Cray-fish*	*Mayfly*	*Columbia pebble-snail*	*Hyallela*	*Daphnia magna*	*Channel catfish*	*Large-scale/ mountain sucker*	*Small-mouth bass*	*Carp*	*Pacific lamprey (juvenile)*
Crayfish	4.0E-4	0.0E+0	1.1E-3	0.0E+0	0.0E+0	1.0E-4	1.9E-4	0.0E+0	0.0E+0	0.0E+0	0.0E+0	0.0E+0	0.0E+0	0.0E+0
Mayfly	1.5E-3	4.0E-3	5.3E-3	5.1E-3	0.0E+0	0.0E+0	0.0E+0	4.0E-4	4.0E-4	0.0E+0	0.0E+0	0.0E+0	0.0E+0	0.0E+0
Columbia pebblesnail	3.0E-4	0.0E+0	2.4E-3	1.0E-3	0.0E+0	0.0E+0	0.0E+0	0.0E+0	0.0E+0	0.0E+0	0.0E+0	0.0E+0	0.0E+0	0.0E+0
Clams	4.0E-4	1.0E-3	0.0E+0	0.0E+0	0.0E+0	0.0E+0	0.0E+0	7.0E-5	7.0E-5	0.0E+0	0.0E+0	0.0E+0	0.0E+0	0.0E+0
Woodhouse toad (tadpole)	2.0E-4	0.0E+0	1.3E-3	6.0E-4	0.0E+0	0.0E+0	0.0E+0	0.0E+0	0.0E+0	0.0E+0	0.0E+0	0.0E+0	0.0E+0	0.0E+0
Mussels	4.0E-4	1.0E-3	0.0E+0	0.0E+0	0.0E+0	0.0E+0	0.0E+0	7.0E-5	7.0E-5	0.0E+0	0.0E+0	0.0E+0	0.0E+0	0.0E+0
Hyallela	0.0E+0	1.8E-2	0.0E+0	0.0E+0	0.0E+0	0.0E+0	0.0E+0	0.0E+0	0.0E+0	0.0E+0	0.0E+0	0.0E+0	0.0E+0	0.0E+0
Daphnia magna	0.0E+0	4.7E-2	0.0E+0	0.0E+0	0.0E+0	0.0E+0	0.0E+0	0.0E+0	0.0E+0	0.0E+0	0.0E+0	0.0E+0	0.0E+0	0.0E+0
Channel catfish	7.0E-5	0.0E+0	2.0E-4	1.0E-4	0.0E+0	3.0E-5	0.0E+0	0.0E+0	0.0E+0	0.0E+0	0.0E+0	0.0E+0	0.0E+0	0.0E+0
Largescale/ Mountain sucker	9.0E-5	0.0E+0	3.0E-4	2.0E-4	0.0E+0	5.0E-5	0.0E+0	0.0E+0	0.0E+0	0.0E+0	0.0E+0	0.0E+0	0.0E+0	0.0E+0
Smallmouth bass	9.0E-5	0.0E+0	3.0E-4	2.0E-4	0.0E+0	5.0E-5	0.0E+0	0.0E+0	0.0E+0	0.0E+0	0.0E+0	0.0E+0	0.0E+0	0.0E+0
Carp	8.0E-5	0.0E+0	2.0E-4	2.0E-4	0.0E+0	7.0E-5	3.2E-5	0.0E+0	0.0E+0	0.0E+0	0.0E+0	0.0E+0	0.0E+0	0.0E+0
Mountain whitefish	5.0E-5	0.0E+0	6.0E-5	2.0E-4	0.0E+0	3.0E-4	2.9E-5	0.0E+0	0.0E+0	4.2E-6	4.0E-6	4.2E-6	4.0E-6	0.0E+0
White sturgeon	3.0E-5	0.0E+0	5.0E-5	0.0E+0	2.0E-5	4.0E-5	0.0E+0	0.0E+0	0.0E+0	1.6E-5	2.0E-5	1.6E-5	2.0E-5	7.0E-6
Pacific lamprey (juvenile)	1.0E-4	0.0E+0	2.0E-4	0.0E+0	0.0E+0	0.0E+0	0.0E+0	2.0E-4	2.0E-4	0.0E+0	0.0E+0	0.0E+0	0.0E+0	0.0E+0
Salmon (larvae)	5.0E-5	0.0E+0	7.0E-5	0.0E+0	0.0E+0	4.0E-3	0.0E+0	9.0E-5	9.0E-5	0.0E+0	0.0E+0	0.0E+0	0.0E+0	0.0E+0
Rainbow trout (adults)	3.0E-5	0.0E+0	0.0E+0	1.0E-4	2.5E-5	1.0E-3	3.3E-5	3.0E-5	0.0E+0	0.0E+0	0.0E+0	2.9E-5	0.0E+0	0.0E+0
Rainbow trout (larvae)	5.0E-5	0.0E+0	7.0E-5	0.0E+0	0.0E+0	4.0E-3	0.0E+0	9.0E-5	9.0E-5	0.0E+0	0.0E+0	0.0E+0	0.0E+0	0.0E+0

Table 31 Aquatic Animal Fractional Exposure to Pore Water and BCF Values for Cr(VI)

Receptor	Fractional exposure to pore water, b_{pore}	BCF(PNNL,1998)
Crayfish	5.00E-01	450
Mayfly	5.00E-01	450
Columbia pebblesnail	5.00E-01	430
Clams	5.00E-01	120
Woodhouse toad (tadpole)	5.00E-01	1000
Mussels	5.00E-01	430
Hyallela	0.00E+00	450
Daphnia magna	0.00E+00	450
Channel catfish	1.00E-01	1000
Largescale/Mountain sucker	1.00E-01	1000
Smallmouth bass	5.00E-02	1000
Carp	5.00E-02	1000
Mountain whitefish	5.00E-02	1000
White sturgeon	1.00E-01	1000
Pacific lamprey (juvenile)	1.00E+00	1000
Salmon (larvae)	2.00E-01	1000
Salmon (eggs)	1.00E+00	1300
Salmon (adults)	0.00E+00	1000
Rainbow trout (adults)	0.00E+00	1000
Rainbow trout (eggs)	1.00E+00	1300
Rainbow trout (larvae)	2.00E-01	1000

Aquatic BCF value of 10 was applied as default value for Mo, Ta, V.

Table 32 Aquatic Plant Fractional Exposure to Pore Water and BCF Values (PNNL,1998, Jøregensen,1991)

Receptor	Fractional exposure to pore water (b_{pore})	BCF Ta, V	BCF Mo	BCF Cr
Phytoplankton	0.00E+00	620	20000	23000
Periphyton	1.00E+00			16000
Water millfoil	5.00E-01			16000

CRCIA assessors determined that because obtaining LD_{50} or LC_{50} values for terrestrial and emergent plants was difficult, a contaminant concentration that caused a 20% reduction in tissue growth/yield (LOEC) was the appropriate benchmark (Efroymson et al. 1997)(Table 34). Benchmarks for fungi are based on the lowest reported LC_{50} values for the entire taxonomic group when available, if not the benchmarks are the same as terrestrial plants (Table 23) (PNNL, 1998). LOAECs are the preferred aquatic plant benchmark (PNNL, 1998). When LOAECs are not available for aquatic plants and phytoplankton, the effective concentration resulting in 50% reduction in cell growth rates, EC_{50}, were used (Table 35).

Similarly, for aquatic animals LOAEC benchmarks are preferred if available, otherwise one-fifteenth of the LC_{50} is recommended (Tables 36-38). In addition, because laboratory test results vary depending on the form of the analyte, toxicity studies resulting in the lowest value were selected (PNNL, 1998). When more than two references were available for the same endpoint and analyte, the geometric mean of the LOAEC was used (ECOTOX, 1998 and Suter et al., 1996). Most of the aquatic receptor benchmarks in Tables 35-38 were obtained from the U.S. EPA ECOTOX database; the analyte with the lowest toxicity value and most comprehensive documentation code was selected.

Table 33 CRCIA Terrestrial Animal Benchmarks (Sample et al., 1996)

Terrestrial Animal	Hexavalent Chromium (K_2CrO_4)		Molybdenum (MoO_4, MoO_3 and $MoNa_2O_4$)		Vanadium (VSO_4 and $NaVO_3$)		Tantalum	
	LD$_{50}$ µg/kg	Estimated LOAEL µg/kg/day	LD$_{50}$ µg/kg	Estimated LOAEL µg/kg/day	LD$_{50}$ µg/kg	Estimated LOAEL µg/kg/day	LD$_{50}$ µg/kg	Estimated LOAEL µg/kg/day
American coot	2.00E+04	1.33E+03	----	3.53E+04	----	1.14E+05	----	1.14E+05
American kestrel								
American White Pelican								
Bald eagle								
Beaver	6.99E+03	4.66E+02	4.21E+04	2.80E+03	3.37E+03	2.24E+02	2.69E+06	1.80E+05
Bufflehead	2.00E+04	1.33E+03	----	3.53E+04	----	1.14E+05	----	1.14E+05
California quail								
Canada goose								
Cliff swallow								
Common snipe								
Coyote	7.45E+03	4.97E+02	4.66E+04	3.10E+03	3.72E+03	2.48E+02	2.98E+06	1.99E+05
Forster's tern	2.00E+04	1.33E+03	----	3.53E+04	----	1.14E+05	----	1.14E+05
Great Blue Heron								
Harvest mouse	4.29E+04	2.86E+03		2.60E+03		3.89E+03		3.53E+04
Lizards (side-blotched)	2.00E+04	1.33E+03		3.53E+04		1.14E+05		1.14E+05
Mallard								
Mule deer	5.88E+03	3.92E+02		3.90E+02		5.47E+02	2.10E+06	1.40E+05
Muskrat	1.46E+04	9.73E+02	8.72E+04	5.81E+03	6.97E+03	4.65E+02	5.58E+06	3.72E+05
Northern harrier	2.00E+04	1.33E+03	----	3.53E+04	----	1.14E+05	----	1.14E+05
Raccoon	9.58E+03	6.39E+02	5.79E+04	3.86E+03	4.63E+03	3.09E+02	3.71E+06	2.47E+05
Weasel	2.18E+04	1.45E+03	1.32E+05	8.78E+03	1.05E+04	7.02E+02	8.43E+06	5.62E+05
Western aquatic garter snake	2.00E+04	1.33E+03	----	3.53E+04	----	1.14E+05	----	1.14E+05
Woodhouse toad (adult)								

[a]Vanadium – A NOAEL value of 11.4 was available for the avian species. The NOAEL was multiplied by an uncertainty factor of (10) (Sample et al., 1996) to calculate a LOAEL.

V was used as a surrogate for Ta for avian receptors; For avian and hepetilian species a 1:1 conversion was used (Sample et al., 1996)

An experimentally derived LOAEL using Sodium Niobate introduced orally to a laboratory mouse was applied as a surrogate for Ta to calculate the harvest mouse LOAEL.

Table 34 Terrestrial Plant Receptors and LOEC Benchmarks (Efroymson,1997)

Terrestrial Plants and Fungi	Chromium (µg/L)	Molybdenum (µg/L)	Vanadium (µg/L)	Tantalum (µg/L)
Based on Soil Concentration: Black Cottonwood	1.00E+03	2.00E+03	2.00E+03	2.00E+03
Fern				
Mulberry				
Reed canarygrass				
Fungi				
Based on Aqueous Concentration: Tule	5.00E+01	5.00E+02	2.00E+02	2.00E+02
Columbia Yellowcress				
Dense Sedge				
Rushes				

Table 35 Aquatic Plant Receptors and LOAEC Benchmarks(ECOTOX,1998)

Aquatic Plants	Chromium		Molybdenum[b]		Vanadium[b]		Tantalum[c]	
	EC_{100} (µg/kg)	LOAEC (µg/L/day)	EC_{50} (µg/kg)	LOAEC (µg/L/day)	EC_{50} (µg/kg)	LOAEC (µg/L/day)	EC_{50} (µg/kg)	LOAEC (µg/L/day)
Periphyton	[a]3.50E+02	2.3E+01	4.5E+03	3.0E+02	1.8E+03	1.2E+02	1.8E+03	1.2E+02
Phyto-plankton	3.5E+02	2.3E+01	4.5E+03	3.0E+02	1.8E+03	1.2E+02	1.8E+03	1.2E+02
Water millfoil	3.5E+03	2.3E+02	4.5E+03	3.0E+02	1.8E+03	1.2E+02	1.8E+03	1.2E+02

[a] Analyte tested was CrK_2O_7 surrogate aquatic plants are algae and phytoplankton

[b] Surrogate aquatic plant is Dinoflagellate

[c] Vanadium applied as a surrogate for Tantalum.

Table 36 Hexavalent Chromium Aquatic Animal Benchmarks (ECOTOX,1998)

Aquatic Animal (Surrogate)	LC_{50} (µg/L)	Estimated LOAEC (µg/L/day)	Analyte
Carp	1.43E+04	9.53E+02	Cr
Channel catfish	1.50E+03	1.00E+02	CrK_2O_7
Clams	7.95+E04	5.30E+03	CrK_2O_7
Columbia pebblesnail (Pond snail)	3.88E+03	2.59E+02	CrK_2O_7
Crayfish	1.76E+05	1.17E+04	CrK_2O_7
Fresh water shrimp (Opossum shrimp)	2.03E+03	1.35E+02	Na_2CrO_4
Largescale/ Mountain sucker (Razorback sucker)	3.20E+04	2.13E+03	Na_2CrO_4
Mayfly (Stonefly)	1.01E+05	6.75E+03	K_2CrO_4
Mountain whitefish (Rainbow or donaldson trout)	1.80E+02	1.20E+01	CrO_3
Mussels (Common blue, bay mussel)	4.50E+03	3.00E+02	Cr
Pacific lamprey, juvenile (Rainbow or donaldson trout)	1.80E+02	1.20E+01	CrO_3
Rainbow trout: adult, eggs, larvae			
[b]Hyallela (Amphipod)	4.20E+02	2.80E+01	CrK_2O_7
Salmon: adult, eggs, larvae	4.00E+03	2.67E+02	$Cr_2Na_2O_7$
Smallmouth bass (Largemouth bass)	1.17E+03	7.82E+01	CrO_3
[b]Water flea	7.39E+00	4.93E-01	K_2CrO_4
White sturgeon (Common, mirror, colored, carp)	1.43E+04	6.53E+02	CrO_3
Woodhouse toad, tadpole (Eastern Narrow-Mouthed Toad)	4.93E+04	3.29E+03	CrO_3

[a] Many of the LC_{50} values, or their surrogates, were not obtained from toxicity tests that tested the contaminants of concern. Instead, these were obtained from toxicity tests that tested similar contaminants. These similar contaminants were used as surrogates for the contaminants of concern.

[b] EC_{50} – Median effective concentration, effective concentration for 50% of the organisms tested; used when endpoint is not mortality (i.e. immobilization)

Table 37 Molybdenum Aquatic Animal Benchmarks (ECOTOX,1998)

Aquatic Animal (Surrogate)	LC_{50} (µg/L)	Estimated LOAEC (µg/L/day)	Analyte
Carp (Carassius auratus, Goldfish)	6.00E+04	4.00E+03	$MoNa_2O_4$
Channel catfish (Fathead minnow)	6.28E+05	4.19E+04	MoO_3
Clams (Common bay or blue mussel)	1.47E+05	9.80E+03	$H_8MoN_2O_4$
Columbia pebblesnail	6.00E+03	4.00E+02	$MoNa_2O_4$
Crayfish, Fresh water shrimp, Hyallela (Hermit crab)	2.23E+05	1.48E+04	$(NH_4)6Mo_7O_{24}\cdot H_2O$
Fresh water shrimp			
Hyallela			
Largescale/ Mountain sucker (Fathead minnow)	6.28E+05	4.19E+04	MoO_3
[b]Mayfly (Water flea)	----	8.80E+02	MoO_3
Mountain whitefish (Fathead minnow)	6.28E+05	4.19E+04	MoO_3
Mussels (Common bay or blue mussel)	1.47E+05	9.80E+03	$H_8MoN_2O_4$
Pacific lamprey, juvenile (Fathead minnow)	6.28E+05	4.19E+04	MoO_3
Rainbow trout: adult, eggs, larvae	7.30E+02	4.87E+01	MoO_3
Salmon; adult, eggs, larvae	1.00E+06	6.67E+04	$MoNa_2O_4$
Smallmouth bass (Rainbow or donaldson trout)	7.30E+02	4.87E+01	MoO_3
[b]Water flea	----	8.80E+02	MoO_3
White sturgeon (Fathead minnow)	6.28E+05	4.19E+04	MoO_3
Woodhouse toad, tadpole (Eastern narrow-mouthed toad)	9.60E+02	6.40E+01	$MoNa_2O_4$

[a] Many of the LC_{50} values, or their surrogates, were not obtained from toxicity tests that tested the contaminants of concern. Instead, these were obtained from toxicity tests that tested similar contaminants. These similar contaminants were used as surrogates for the contaminants of concern.

[b] MATC - geometric mean of No Observed Effect Concentration (NOEC) and Lowest Observed Effect Concentration (LOEC),surrogate endpoint applied in place of LC_{50}.

Table 38 Vanadium and Tantalum Aquatic Benchmarks (ECOTOX,1998)

Aquatic Animal (Surrogate)	LC_{50} (µg/L)	Estimated LOAEC (µg/L/day)	Analyte
Carp (Goldfish)	4.60E+03	3.07E+02	V_2O_5
[b]Channel catfish (Fathead minnow)	1.70E+02	1.13E+01	V_2O_5
[b]Clams	5.00E+01	3.33E+00	Vanadium
Columbia pebblesnail			
Crayfish, Fresh water shrimp, Hyallela (Water flea)	9.40E+02	6.27E+01	V_2O_5
[b]Largescale/ Mountain sucker (Fathead minnow)	1.70E+02	1.13E+01	V_2O_5
Mayfly (Water flea)	9.40E+02	6.27E+01	V_2O_5
[b]Mountain whitefish (Fathead minnow)	1.70E+02	1.13E+01	V_2O_5
Mussels	5.00E+01	3.33E+00	Vanadium
[b]Pacific lamprey, juvenile (Fathead minnow)	1.70E+02	1.13E+01	V_2O_5
Rainbow trout: adult, eggs, larvae	1.60E+02 [a](4.33E+03)	1.07E+01 (2.89E+02)	V_2O_5
[b]Salmon: adult, eggs, larvae Smallmouth bass (Pimephales promelas, Fathead minnow)	1.70E+02	1.13E+01	V_2O_5
Water flea	9.40E+02	6.27E+01	V_2O_5
[b]White sturgeon (Fathead minnow)	1.70E+02	1.13E+01	V_2O_5
Woodhouse toad, tadpole (Eastern narrow-mouthed toad)	2.50E+02	1.67E+01	V_2O_5

[a]Benchmark value for tantalum as Ta_2O_5 (only real data available)

[b]MATC-Applied as surrogate endpoint for LC_{50}.

5.4.4 Risk Characterization Results

The ecological risk is determined by evaluating the ecological hazard quotient (EHQ). A total body burden concentration is calculated for each receptor by summing the individual pathway contributions. Subsequently, an EHQ is determined by dividing the specific receptor body burden by the respective benchmark. According to the CRCIA members, an EHQ greater than one indicates that potential risk exists, and further stochastic exposure modeling methods should be applied (PNNL, 1998).

Based upon conditions and parameters previously identified, a deterministic assessment applying the guidelines established by the CRCIA committee was conducted. The overall result indicated a potential risk exists for terrestrial and aquatic plants from all contaminants (Figures 12 and 13). As seen in Figure 12, for terrestrial plants risk from hexavalent chromium is greater than risk posed by tantalum (with vanadium as the surrogate) and molybdenum. The results in Figure 13, indicate that all aquatic plants are at potential risk, with hexavalent chromium and molybdenum presenting a greater potential risk than tantalum (again vanadium was the surrogate).

As demonstrated in Figure 14, numerous aquatic animal receptors are at risk from the contaminants. For the most part, potential risks resulted from exposure to hexavalent chromium and vanadium. While overall risks posed by the metals followed the order of Cr > V > Ta > Mo. However, only three (of the twenty) terrestrial animals were at risk; the muskrat and raccoon were at potential risk from vanadium and tantalum (vanadium as the surrogate), and the American coot was at potential risk from hexavalent chromium (Figure 15). Therefore, because of the multiple receptors at potential risk, CRCIA

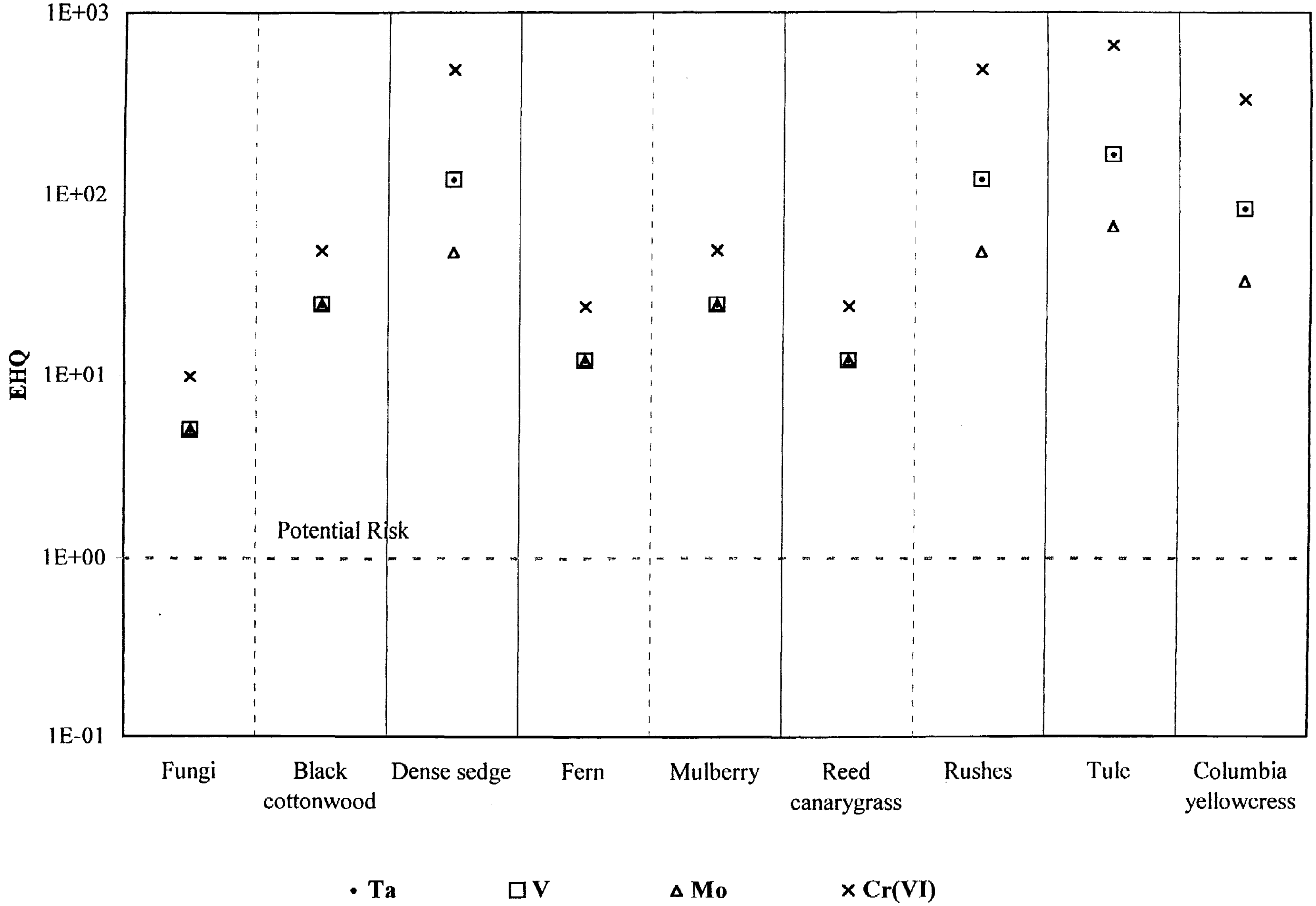


Figure 12 Terrestrial Plant EHQ

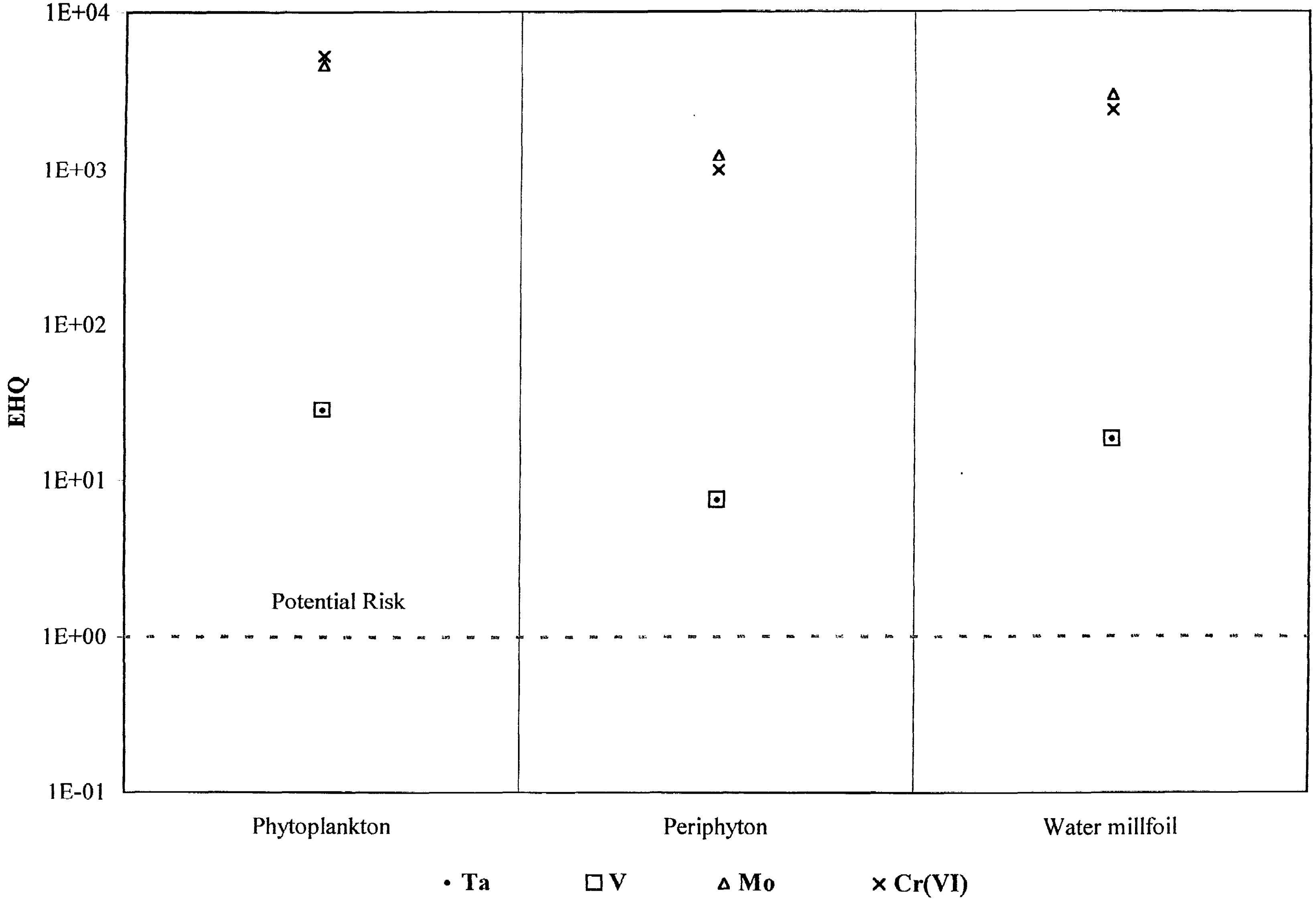


Figure 13 Aquatic Plant EHQ

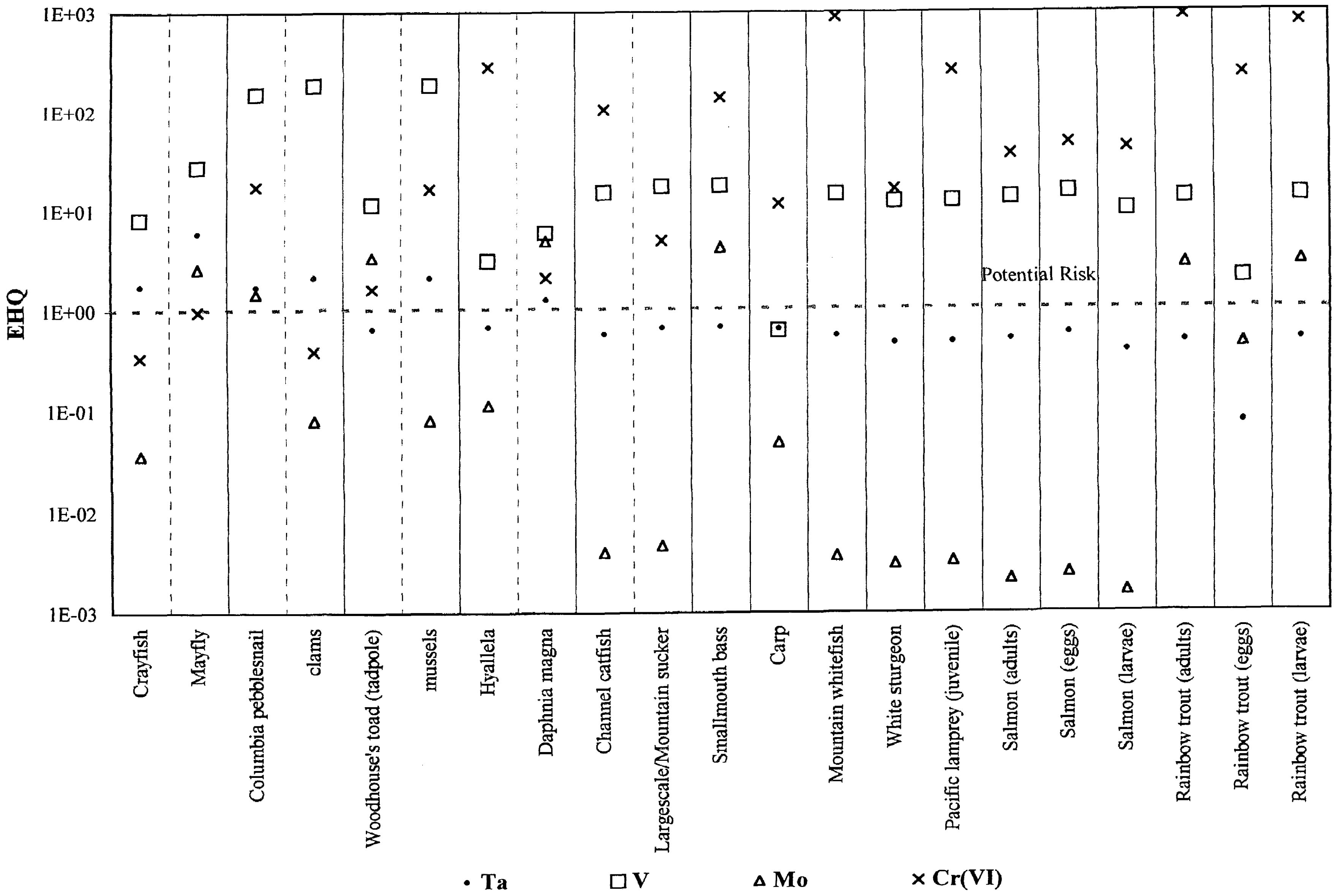


Figure 14 Aquatic Animal EHQ

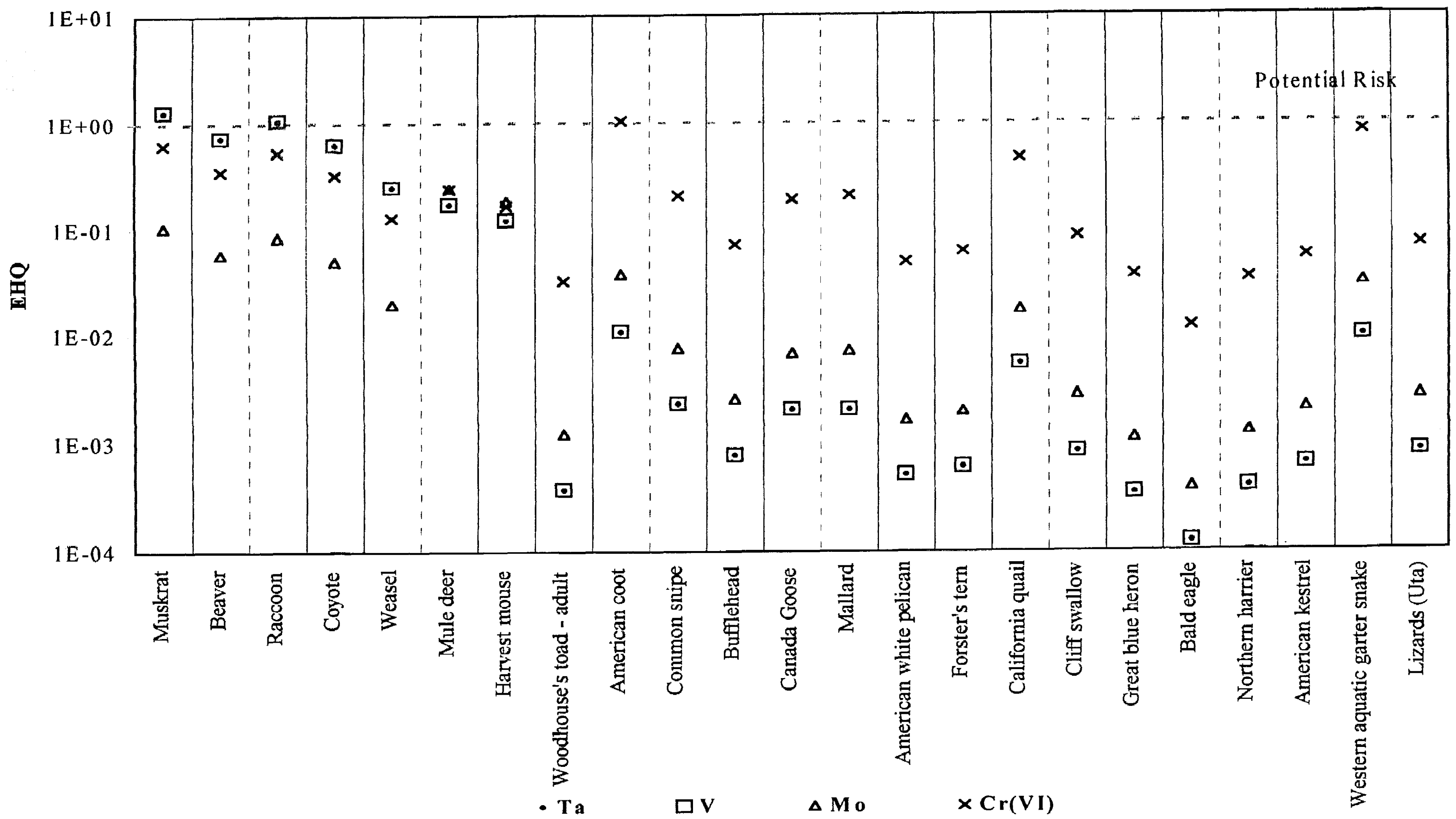


Figure 15 Terrestrial Animal EHQ

protocol deems further assessment of the contaminated site applying stochastic risk assessment methods.

5.4.5 Limitations

Unlike RESRAD-ECORISK, the CRCIA model does not have a sensitivity analysis built into the code. The model is presently site specific; therefore modification of receptors is required for use with other sites. Because the model is in an Excel spreadsheet, modification can be accomplished easily. However, it is important that during the modification process to maintain all spreadsheet links. A Fortran version is under development, but the model is not presently available in an integrated software package for general use. The model's screening assessment to estimate exposure of aquatic and terrestrial plants is based on equilibrium partitioning, which does not accurately represent processes such as sorption and oxidation-reduction (PNNL, 1998). The CRCIA model required estimation of numerous exposure parameters, causing it to be susceptible to uncertainty errors. These errors arise from two sources: 1) propagation of errors and 2) "varying levels of confidence in the data used to parameterize the model" (PNNL, 1998).

5.4.6 Summary

Overall, the terrestrial and aquatic plants within the study area were at potential risk from all of the contaminants of concern. Terrestrial plant results indicated that hexavalent chromium presents a greater potential risk than tantalum (vanadium as surrogate) with molybdenum demonstrating the least risk. Aquatic plant exposure to hexavalent chromium and molybdenum result in potential risk, and are significantly greater than exposure to tantalum (vanadium as surrogate) and vanadium.

Only three terrestrial animals were found to be at potential risk, which is most likely attributed to foraging habits that do not place most of them in direct contact with contaminants on a continuous basis. Also, these metal contaminants, tantalum, chromium, molybdenum, and vanadium are not volatile which reduces inhalation exposure significantly. When compared to terrestrial animals, aquatic animals are at significantly more potential risk. This result may be attributed to their aqueous habitat, where they are continually in contact with the dissolved contaminant via absorption, ingestion, and respiration. Furthermore, benthic organisms (i.e., mussels) appear to be at greater risk than organisms that live primarily in the water column (i.e., salmon). This result may be attributed to the sediment, which is not only a benthic organism's primary habitat but is also a primary sink for metal contaminant accumulation.

As presented in the benchmark and toxicity data section of this thesis, toxicity studies were conducted on a variety of analytes. Because some analytes are more soluble in water, the resulting EHQ may not accurately represent true contaminant behavior. The form of metal contaminant determines how well it will be absorbed and excreted. For example, organometalic compounds because of their lipid solubility have a tendency to remain in the body longer than inorganic compounds.

One benefit of this code is that it identifies whether a receptor is at potential risk based on its diet and behavior. The ecological risk component of the code is based on many algorithms and therefore many (estimated) parameters, which increases uncertainty. Yet the model addresses all routes of exposure to aquatic and terrestrial organisms by accounting for dermal (absorption) and inhalation routes of exposure. The model is in a format that can be easily modified to site specific receptors and contaminants. Recommended tools for improvement include, but are not limited to, developing a program-based code applicable for use in a PC environment with the ability to integrate databases such as toxicity. Including a sensitivity analysis function to compare the influence of various parameters. Also, the model should be linked to a transport code to account for contaminant mobility.

CHAPTER 6

CONCLUSIONS, RECOMMENDATIONS, AND FUTURE WORK

6.1 Conclusion

To accomplish this preliminary ecological risk assessment, surrogate use was essential. Simply, a surrogate should not only have similar physical and chemical properties to the species of interest, but they should also behave alike. In other words, the surrogate should have similar speciation and stability. In the case of tantalum, using vanadium pentoxide as a surrogate resulted in risks greater than those of chromium. Furthermore, toxicity data for receptors specific to the selected ecological habitat were not all available; in which case a surrogate receptor was substituted to extrapolate contaminant effects to the species of interest. Benchmark data for the case study were gathered; if data for a receptor was unavailable, a surrogate was selected based on taxonomy, life style, and/or toxicological response similarity (PNNL, 1998).

An evaluation was completed of the CHEMS-1 model that ranks and scores contaminant toxicity and exposure potential. Results indicated that the vanadium compounds, in particular vanadium pentoxide, presented the greatest hazard, with hexavalent chromium following. An approximate ranking was accomplished and based on the data gathered, **tantalum posed less of a hazard than hexavalent** chromium to the terrestrial and aquatic animal. However, only two animals are used in this ranking model to assess ecosystem toxicity. Furthermore, due to the multiple toxicity data and therefore the consequential uncertainty, many of the hazard values overlapped. Overall, the model is qualitative and cursory at best, and is not recommended as a tool for ecological risk assessment.

In the RESRAD-ECORISK code, a transport model is linked to the ecological risk for soil contamination. This model is limited to five receptors: American robin, mallard, white-tailed deer, white-footed mouse, and the eastern cottontail. However, a code problem currently being addressed by the developers prevented risk assessment of the mallard. Risks are categorized into four groups ranging from potential to an extreme adverse risk. Results from applying this model revealed risks posed to receptors were found to be greatest for the American robin, where all metals resulted in extreme adverse effect risk characterization. While extreme risks were found for the eastern cottontail and white-footed mouse from exposure to vanadium, moderately high risks were observed from exposure to Cr(VI). On the other hand, the White-tailed deer received the least amount of risk from these contaminants, where all risk resulted as "potential". Based on these surrogates, tantalum and molybdenum contaminated soil presented a limited risk to the deer, while tantalum contaminated soil posed a greater risk to the rabbit and mouse than molybdenum contamination.

The third model, the CRCIA, included the most comprehensive ecological habitat of the models evaluated. In this model, a site requires further assessment when a potential risk exists, which was the case for terrestrial and aquatic plants when exposed to any contaminants. Generally, risks were greater from hexavalent chromium than tantalum (with vanadium as the surrogate) and molybdenum. In addition, for aquatic plants, potential risks from hexavalent chromium and molybdenum were greater than risks from tantalum (again vanadium was the surrogate) and vanadium. As demonstrated, numerous aquatic animal receptors were at risk from the contaminants. For the most part, potential risks resulted from exposure to hexavalent chromium and vanadium. While overall risks posed by the metals followed the order of Cr > V > Ta > Mo. Only three (of the twenty) terrestrial animals were at risk; the muskrat and raccoon were at potential risk from vanadium and tantalum, and the American coot was at risk from hexavalent chromium. Therefore, because of the multiple receptors at potential risk, CRCIA protocol deems further assessment of the contaminated site applying stochastic risk assessment methods.

This work only addresses the potential affect chromium and tantlum may have on an ecosystem. It does not address how (chemical) processes within their respective life-cycles will effect ecology. For example, mining and refining are used to process raw ore for both metals. Refining processes require organic solvents and strong acids and bases. To achieve a better understanding of the overall environmental impact of replacing chromium with tantalum, future work should address ecological impact and risk during processing of tantalum and chromium. In addition, LC_{xx} of LD_{xx} data were used to derive LOAELs following EPA and DOE (Cheng, 1998; PNNL, 1998) protocol, and only address receptor mortality. Because death is an unacceptable endpoint, a more conservative and comprehensive endpoint would be EC_{xx} data that accounts for infertility, genetic defects, and related impacts. Once these are understood, NOAELs can then be determined from laboratory studies.

6.2 Recommendations

Based on this preliminary assessment and model evaluation, it is recommended that future ecological risk models incorporate the following: 1. Using transient models (i.e., applied daily doses) for aquatic and terrestrial animal receptors; 2. Including terrestrial and aquatic plant receptors; 3. Comprehensively characterizing the ecological habitat; 4. Accessing and linking toxicity data into the ecological model; 5. Considering dermal, ingestion, and inhalation pathways for exposure; 6. Linking the ecological risk model with a transport code; and 7. applying NOAEL endpoints as benchmarks. Furthermore, combining a preliminary ecological risk assessment with a life-cycle approach will take into account the overall cradle-to-grave perspective for sustainable-development projects. The next phase of this research should include formulating an ecological framework, which must support military operations.

6.3 Future Work

The next phase of this research should include a comprehensive evaluation of the DoD location that is currently evaluating and testing chromium and tantalum coated artillery. This evaluation needs to include site characteristics, receptors, and associated toxicity data. Subsequently, the existing computer codes should be modified or a new code developed to include components identified within the recommendation section of this thesis. Upon completion of this task the code should be applied to the existing site to conduct a computer simulated ecological risk assessment.

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