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May 30, 1995

95-RF-04715

Kurt Muenchow
Environmental Restoration Division
DOE, RFFO

OPERABLE UNIT 5 (OU5) WOMAN CREEK PRIORITY DRAINAGE: HUMAN HEALTH RISK ASSESSMENT - CAB-051-95

Action: Transmit the attached information to the Environmental Protection Agency (EPA) and the Colorado Department of Public Health and Environment (CDPHE) and request approval

The discussion on the development of the chemical-specific matrix effects for OU5 is attached for transmittal to the EPA and CDPHE for their review and approval before submittal of the baseline risk assessment.

Attachment #1 is the discussion of chemical-specific matrix effects for OU5 chemicals of concern (COCs) in soil and sediments. This discussion was prepared in response to one of the comments received from EPA on the OU5 Exposure Assessment Technical Memorandum (EATM) #12 and will be incorporated into the risk assessment section of the OU5 RFI/RI Report. The EPA stated that, "the chemical specific matrix effect parameters must be formally transmitted in a separate letter to EPA and CDPHE for their approval before submittal of the baseline risk assessment." It was further agreed that this will avoid potential problems with the draft RFI/RI Report.

Please transmit this attachment to the EPA and the CDPHE and request their approval. Contact me at 966-9100 with any additional questions regarding this transmittal.

C. A. BICHER ✓✓
M. L. HOEG ✓✓
E. C. MAST ✓
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IN REPLY TO RFP CC NO: N/A

ACTION ITEM STATUS:
PARTIAL/OPEN
N/A CLOSED

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CAB CB

Carol A. Bicher

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Operable Unit No. 5 Closure
Environmental Restoration Program Division

CAB:cb

Attachment:
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ATTACHMENT 1: CHEMICAL-SPECIFIC MATRIX EFFECTS

This attachment discusses the development of chemical-specific matrix effects for Rocky Flats Environmental Technology Site (RFETS) Operable Unit No. 5 (OU5) chemicals of concern (COCs) in soil and sediment samples. The attachment begins with its purpose and the OU5 matrix effect. This is followed by a discussion of how the matrix effect was determined by describing chemical-specific matrix factors for both inorganic and organic chemicals.

Purpose

This attachment is a presentation of the chemical-specific matrices for OU5 COCs for which toxicity factors were derived from studies in which the agent was administered in solution. The matrix effect is used to account for decreased bioavailability relative to drinking water or other solutions such as corn oil, where information on matrices are limited or do not exist.

As indicated in U.S. Environmental Protection Agency (EPA) guidance for risk assessment, adjustments of bioavailability may be necessary if the "medium of exposure in the site exposure assessment differs from the medium of exposure assumed by the toxicity value" (EPA 1989). The guidance further states that "a substance might be more completely absorbed following exposure to contaminated drinking water than following exposure to contaminated food or soil (e.g., if the substance does not desorb from soil in the gastrointestinal tract)." Although these matrix effect values were initially developed for the soil ingestion pathway, they also apply to other media where significant binding of compounds to a solid matrix may occur (e.g., compounds ingested from sediments or compounds ingested in homegrown produce).

Derived Matrix Factor

For RFETS OU5 COCs in soil and sediment whose toxicity factors were derived from studies in which the agent was administered in solution, a matrix factor of 0.5 was used to calculate intake for human health risk assessment (HHRA). Chemical-specific matrix effects for OU5 COCs in soil are listed in Table 1. The matrix effect of 0.5 is a conservative value derived from a review of literature summarized in Table 2. This value is based in part on:

- EPA-derived relative bioavailability factors for cadmium in food (0.5) and lead in soil (0.6) (EPA 1995)

- A literature-derived relative bioavailability factor of 0.47 for arsenic in soil (Freeman et al 1993)
- The evidence supporting a 50 percent relative bioavailability of semivolatile organic compounds (SVOCs) in soil (Goon et al. 1991, Ney 1990).

Note that several studies discussed in the section discussing the derivation of the chemical-specific matrix effects indicate that the decrease in bioavailability from the matrix effects of food and soil can be substantially greater than 50 percent (as much as 99 percent), indicating that a matrix effect of 0.5 is conservative (Freeman et al. 1992; Cox et al. 1975; Sunagawa 1981; Heard and Chamberlain 1982; Sunderland et al. 1989; EPA 1995).

Table 1 shows that the following OU5 COCs in surface and subsurface soil or sediments had toxicity values which were derived from studies using drinking water or other solutions and, therefore should be evaluated using a matrix effect of 0.5:

- Antimony
- Aroclor-1254
- Beryllium
- Fluoranthene
- Pyrene.

Where the critical toxicity study was dietary but no vehicle was indicated in IRIS, a default matrix effect of 1 will be used. This was the case for benzo(a)pyrene (BaP) and copper. Other polyaromatic hydrocarbon (PAH) COCs that had toxicity equivalency factors (TEFs) based on BaP [benzo(a)-anthracene, benzo(b)fluoranthene, dibenzo(a,h)anthracene, and indeno(1,2,3-cd)pyrene] (EPA 1994a) were assigned a default matrix effect of 1 by analogy to BaP. For COCs where the chemical was injected directly into the receptor (e.x., intraperitoneal or intravenous), it was not necessary to apply a matrix effect. This was the case for mercury and silver. Cadmium, molybdenum, and nickel were mixed directly into the diet and therefore a default matrix effect of 1 will be used.

For radionuclides, slope factors were derived mostly from epidemiological studies (EPA 1994b). Slope factor calculations assume that each radionuclide is ingested in a soluble form in food or water and that it would, therefore, be appropriate to consider possible retardation of intake if the radionuclide is bound within a soil matrix. The reduction in potential intake and toxic effects cannot be quantified by multiplying the slope factor by a soil matrix effect because the

adjustment must account for differential effects on different target organs. Therefore, a matrix effect of 1 has been adopted for radionuclides in the present HHRA, even though this factor probably overestimates the effects of radionuclides ingested in soil and sediment.

Derivation of the Chemical-Specific Matrix Effect

The derivation of the 0.5 matrix effect was completed from the literature for several chemicals. Matrix effects for each of these chemicals are listed in Table 2 and the literature values for matrix effects shown in Table 2 are discussed in the following paragraphs, organized by inorganic and organic chemicals. Various studies are cited (some that used OU5 COCs and some that did not) that provide the rationale to use the matrix effects that are identified in Table 1.

Inorganic Chemicals

Six examples of EPA precedence for assuming decreased bioavailability of inorganics from food and soil, compared to that in water are presented in the following discussion. Following these paragraphs are examples of decreased bioavailability of inorganics in soil versus solution from the available toxicological literature.

Cadmium (an OU5 COC) and manganese (not a COC in soil or sediment) each have two EPA-derived oral reference doses (RfDs), one for ingestion in food and one for ingestion in water. In deriving media-specific RfDs for cadmium, EPA assumed that 5 percent of cadmium ingested in water is bioavailable (RfD = 5.0E-04 mg/kg-d), compared to 2.5 percent for cadmium ingested in food (RfD = 1.0E-03 mg/kg-d) (EPA 1995). Cadmium has an oral RfD for ingestion from food ingestion as seen in Table 1. Therefore, there is no need for a matrix effect for cadmium and the default matrix effect of 1 was used for cadmium.

The RfD for manganese ingested in water (5.0E-03 mg/kg-d) is 28 times less than the RfD for manganese ingested in food (1.4E-01 mg/kg-d) (EPA 1995). Although relative bioavailability of manganese in food and water is not discussed in the Integrated Risk Information System (IRIS), one explanation for a 28-fold decrease in toxicity of manganese ingested in food is a matrix effect resulting in greatly decreased bioavailability.

Another example of media-specific differences in toxicity of inorganics is suggested by EPA's RfD for cyanide. In deriving the RfD for cyanide, based on a dietary study in rats, EPA included a safety factor of 5 to protect for an expected increase in toxicity of cyanide ingested in

water (EPA 1995). The use of this safety factor implies that cyanide ingested in food is 0.2 times as toxic as cyanide ingested in water, corresponding to a matrix effect of 0.2. This matrix effect is less than the conservative 0.5 matrix effect used for those chemicals whose toxicity values were derived from studies in which the agent was administered in solution (Table 1).

EPA does not discuss the matrix effect of beryllium (an OU5 COC) in IRIS (EPA 1995). The IRIS file, however, presents an unpublished investigation by Cox et al. (1975) which indicates a much higher no-observed-effect-level (NOEL) of 25 mg/kg-d in the diet than that in the rat drinking water study used to derive the RfD of 5.0E-03 mg/kg-d (NOEL of 0.54 mg/kg bw/day) (Schroeder and Mitchner 1975). The corresponding matrix effect for beryllium is 0.02. This matrix effect is much less than the conservative 0.5 matrix effect used for those chemicals whose toxicity values were derived from studies in which the agent was administered in solution (Table 1).

Antimony, another OU5 COC, has a RfD of 4.0E-04 mg/kg-d that was derived using a lowest-observed-adverse-effect-level (LOAEL) of 0.35 mg/kg bw-day from a chronic drinking water study with rats (Schroeder et al. 1970). A LOAEL of 500 mg/kg was reported for rats fed metallic antimony for 24 weeks (Sunagawa 1981). The resulting matrix effect for antimony is 0.0007. This matrix effect is much smaller than the conservative 0.5 matrix effect used for those chemicals whose toxicity values were derived from studies in which the agent was administered in solution (Table 1).

EPA's Integrated Exposure Uptake Biokinetic Model (IEUBK) for lead in children assumes that the bioavailability for lead ingested in soil is 30 percent, compared to 50 percent bioavailability for lead ingested in water. The corresponding soil matrix value is 0.6 (EPA 1994c).

Evidence in the available toxicological literature indicates that absolute absorption of inorganics ingested in food is less than that from water. Sixty percent of radiolabeled lead chloride administered to adult humans in water was bioavailable, compared to 3 percent for lead chloride ingested in food (Heard and Chamberlain 1982). Similarly, nickel chloride administered to adult humans in food was much less bioavailable (0.7 percent) than nickel chloride administered in water (28 percent) (Sunderland et al. 1989). Increased blood levels of manganese were observed in humans ingesting high doses in water. When similar doses of manganese were ingested with food (Bales et al. 1987), blood levels of manganese were not increased.

Available toxicological literature also indicates that the absolute absorption of inorganics ingested in soil is also less than that from water. This is expected because inorganics only partially desorb from soil. In rats, the bioavailability of lead acetate ingested in soil was 8 percent of that for lead acetate ingested in water (Freeman et al. 1992). Arsenic administered in soil to rabbits was much less bioavailable (28 percent) than arsenic administered in water to rabbits (59 percent), corresponding to a soil matrix of 0.47 (Freeman et al. 1993).

Organic Chemicals

Several studies show that organic chemicals, including pesticides, also bind tightly to soil, reducing their bioavailability through both oral and dermal exposure. Clays and organic colloids have a large surface area and cation exchange capacity, which permits significant adsorption of virtually all classes of pesticides. Furthermore, the adsorbed fraction desorbs slowly and is effectively a bound fraction that increases over time as the soil-pesticide bond "ages" (Calderbank 1989). The bound fraction is estimated to be about 20 to 70 percent of the total amount of organic chemical applied to the soil.

McConnell et al. (1984) showed, using soil containing 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD) from the Minker Stout site, that 3 $\mu\text{g}/\text{kg}$ -bw TCDD in corn oil resulted in the death of all six treated guinea pigs and 13.3 ppb TCDD was detected in the animals' livers. In the same study, 3.3 $\mu\text{g}/\text{kg}$ -bw TCDD from soil caused only 2 deaths of 6 treated animals with 1.4 ppb detected in the liver. This study indicates about 10 percent relative bioavailability of TCDD from the soil. Shu et al. (1988) conducted further studies on TCDD and found an average 43 percent (range of 25 to 50 percent) bioavailability of TCDD in rats receiving soils from Times Beach, Missouri.

Goon et al. (1991) showed that BaP aged 6 months in soil was only 34 to 51 percent orally bioavailable for clayey and sandy soils, compared to BaP administered alone to rats. Polychlorinated biphenyls (PCBs) and pesticides like dichlorodiphenyltrichloroethane (DDT), chlordane, and heptachlor, may be expected to adsorb strongly to soil similarly to BaP (Ney 1990). This PCB and pesticide absorption characteristic results in reduced bioavailability due to this matrix effect. These studies support a conservative estimate of 50 percent relative bioavailability of SVOCs in soil compared to those in solution.

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Table 1
REETS OU5 Soil Matrix Effects

Type of Critical Study^a			Matrix Effect^b
Chemical of Concern	Oral Reference Dose	Oral Slope Factor	
Antimony	Drinking water (rats)		0.5
Aroclor-1254	Glycerol and corn oil vehicle (monkeys)	By analogy to Aroclor-1260 (corn oil vehicle, stirred in food, rats)	0.5
Benzo(a)anthracene		By analogy to benzo(a)pyrene	1
Benzo(a)pyrene ^c		Dietary; vehicle not specified (rats)	1
Benzo(b)fluoranthene		By analogy to benzo(a)pyrene	1
Beryllium	Drinking water (rats)	Drinking water (rats)	0.5
Cadmium	Dietary (humans)		1
Copper	Oral dose; vehicle not specified (humans)		1
Dibenzo(a,h)anthracene		By analogy to benzo(a)pyrene	1
Fluoranthene	Gavage (mice)		0.5
Indeno(1,2,3-cd)pyrene		By analogy to benzo(a)pyrene	1
Mercury	Intraperitoneal HgCl ₂ (rats)		N/A
Molybdenum	Dietary (humans)		1
Nickel	Dietary (rats)		1
Pyrene	Gavage (mice)		0.5
Silver	Intravenous injection (humans)		N/A

Table 1 (continued).

Chemical of Concern	Type of Critical Study ^a		Matrix Effect ^b
	Oral Reference Dose	Oral Slope Factor	
Americium-241		Epidemiological studies (humans)	1
Plutonium-239/240		Epidemiological studies (humans)	1
Uranium-233/234		Epidemiological studies (humans)	1
Uranium-235		Epidemiological studies (humans)	1
Uranium-238		Epidemiological studies (humans)	1

N/A Not applicable, chemical was administered directly into the receptor via injection.

a. Source: IRIS, unless otherwise noted.

b. A soil matrix effect of 0.5 supported by literature for COCs with toxicity values based on solution vehicles. All other soil matrices are 1. See text and Table 2.

c. Adopted for all carcinogenic PAHs in soil.

Table 2
Derivation of RFETS OU5 0.5 Soil Matrix Effect

Chemical/Species	Fraction Absorbed from Food/Soil (Fm)	Fraction Absorbed from Water (Fw)	Matrix Effect	Source
Cadmium (human adults)	0.025	0.05	0.50 ^a	EPA (1995)
Manganese (human adults)	NA	NA	0.04 ^b	EPA (1995)
Cyanide (rats)	NA	NA	0.20 ^c	EPA (1995)
Beryllium (rats)	NA	NA	0.02 ^d	EPA (1995)
Antimony (rats)	NA	NA	0.0007 ^e	EPA (1995)
Lead (human adults)	0.03	0.6	0.05 ^a	Heard and Chamberlain (1982)
Nickel (human adults)	0.007	0.28	0.03 ^a	Sunderland et al. (1989)
Lead (human children)	0.3	0.5	0.60 ^a	EPA (1994)
Lead (rats)	NA	NA	0.08 - 0.20 ^f	Freeman et al. (1992)
Arsenic (rabbits)	0.28	0.59	0.47 ^a	Freeman et al. (1993)
TCDD (guinea pigs)	NA	NA	0.10 ^g	McConnell et al. (1984)
Benzo(a)pyrene (rats)	NA	NA	0.34 - 0.51 ^h	Goon et al. (1991)

NA Not available from the data.

a. Based on Fm/Fw.

b. Based on relative toxicity of manganese in water vs. food (RfD in water = 5.0E-03 mg/kg-d; RfD in food = 1.4E-01 mg/kg-d; ratio = 0.04).

c. Based on expected increase in toxicity of cyanide ingested in water.

d. Based on relative toxicity of beryllium in water vs. food (NOEL in water = 0.54 mg/kg bw/day; NOEL in food = 25 mg/kg-d).

e. Based on relative toxicity of antimony in water vs. food (LOAEL in water = 0.53 mg/kg bw/day; LOAEL in food = 500 mg/kg-d).

f. Based on relative retention of lead in blood, bone, and liver from EPA's IEUBK lead model.

g. Based on relative retention of TCDD in the liver.

h. Based on relative bioavailability of benzo(a)pyrene from soil compared to water.