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JANUARY 1995

Metals Criteria for Land Management of Exploration and Production Wastes:

**Technical Support Document for
API Recommended Guidance
Values**



**American
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Technical Support Document for API Recommended Guidance Values

**Health and Environmental Sciences Department
Exploration and Production Department**

API PUBLICATION NUMBER 4600

PREPARED BY:

AMERICAN PETROLEUM INSTITUTE
PRODUCTION WASTE ISSUE GROUP
METALS MANAGEMENT WORKGROUP

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ABSTRACT

This document provides the technical support for recommended maximum concentrations for 12 metals of environmental concern in land-managed exploration and production waste. The guidance values for arsenic, cadmium, chromium, copper, lead, mercury, molybdenum, nickel, selenium, and zinc were adopted directly from the EPA's regulations for the land application of sewage sludge. EPA's risk-based approach was used to calculate values for barium and boron which were not addressed by the sewage sludge regulations. General guidelines for sampling and analysis of metals are also provided. Also, formulae for calculating the application rate for exploration and production (E&P) wastes containing metals are included. A comparison of these guidance values with metals concentrations from three E&P waste databases indicated that E&P wastes do not generally have levels of metals that are of environmental concern.

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EXECUTIVE SUMMARY

In 1992, the American Petroleum Institute (API) initiated a study to develop guidelines for land-management of exploration and production (E&P) waste containing metals. This report documents the scientific basis for the API-recommended metal concentration limits for soils to which E&P waste has been applied.

In February 1993, the United States Environmental Protection Agency (EPA) completed an update of its 1980 study on land treatment technology for sewage sludge. The EPA employed exposure assessment models for 14 possible exposure pathways to develop risk-based numerical pollutant limits for sewage sludge application to land. Specifically, the 1993 update recommended maximum metals concentration limits for sewage sludge application which were protective of human health and the environment.

With respect to metal constituents, the land application of E&P waste is very similar to the land application of sewage sludge. Therefore, EPA's scientifically valid application guidelines for metals can be used for E&P wastes. Where the EPA study had not addressed a metal contained in E&P waste, the EPA methodology was used to establish a guidance value.

Specific numerical guidance has been established for 12 metals of potential environmental concern for E&P operations. These guidance values are shown in Table 4. It should be noted that these values are general guidance and will not necessarily be appropriate in all situations. In general, due to the nature of the EPA approach, these numbers should be considered conservatively low. Site-specific factors such as current and future land use, background soil concentrations, native vegetation, etc., may allow for different levels of metals to be applied to land and still be protective of human health and the environment. Specific numerical guidance was not established for tin, which may be found in E&P wastes. Technical evaluation indicated that tin is not of environmental concern in the form and concentrations in which it occurs in E&P wastes.

The level of environmental concern for a given total metal concentration is dependent on the physical and chemical state of the metal and its surroundings, which dictates the metal's form (species) and mobility. With the exception of boron, the metals levels included in this report are based on the total metals concentration as determined by various low pH extraction methods. This generally leads to a conservatively low guidance level since much of the total metals content of a given waste is not in a dissolved or bioavailable form and therefore is not available to cause toxic effects. The overwhelming current regulatory practice is to regulate the total metals content and not to consider the forms and fate of the metal in the environment where it is found. If regulatory agencies begin to regulate based on dissolved or bioavailable metals content, API will consider modifying these proposed metals levels.

INTRODUCTION

BACKGROUND

The petroleum industry generates approximately 21 billion barrels per year of waste from the exploration and production (E&P) of oil and natural gas. The vast majority of this waste (98% by volume) is water produced in conjunction with the oil and gas and is typically disposed via re-injection. The balance of E&P wastes is made up of wastes from the drilling and completion of wells (< 2%) and other wastes associated with the production of petroleum hydrocarbons (0.1%) (ERT, 1987).

Drilling wastes and these “associated” wastes (e.g., crude oil-impacted soil and tank bottoms) are disposed of in a variety of ways. Often, the most economically attractive method for their disposal is on-site land application in the form of land treating (e.g., land farming, land spreading, or composting). If these types of cost-effective land application methods are to continue, it is important to understand the nature of these wastes and the potential environmental impact from any constituents contained in them.

Organic compounds, salts and metals are constituents of possible environmental concern in drilling and associated wastes. API recommends that soil pH be maintained between 6 and 9, soil conductivity be less than 4 mmho/cm, and oil and grease content be less than one percent in the final soil-waste mixture (SAS, 1993, 1995). In 1992, API initiated this study to address the environmental concern associated with metals found in these wastes. The level of environmental concern for a given total metal concentration is dependent on the physical and chemical state of the metal and its surroundings, which dictates the metal's form (species) and mobility. The fate and impact of metals in the environment is a complex subject and, although there has been a significant body of work completed on this subject, the focus of previous studies has not been on E&P wastes.

OBJECTIVES

Practical experience has shown that many E&P wastes which contain metals can be successfully managed on-site in ways that are protective of human health and the environment. The objective of this report is to provide the scientific basis for API-recommended metal concentration limits for land-managed waste/soil mixtures. A secondary objective is to identify any knowledge gaps that may require further study to refine the suggested concentration limits.

METALS IN E&P WASTE

METALS - DEFINITION

Metals are a class of elements which may be of concern if present in a medium (such as, soil or groundwater) in a form and concentration considered to pose a risk to some receptor. Metals are defined as those elements with atomic numbers between 21 and 92 with the exception of the halogens (atomic numbers 35, 53, and 85), the noble gases (atomic numbers 36, 54, and 86), non-metals (atomic numbers 34 and 52), and a semi-metal (arsenic, atomic number 33). Although they are not defined as metals, beryllium, boron, aluminum, arsenic, selenium, and tellurium are included in this study due to their environmental importance. The resulting 67 naturally occurring metals included in this broad definition are shown on Figure 1.

Metals, as with all natural chemical elements, are ubiquitous in the environment. Any water, soil, or waste sample, if examined to a sufficient degree, will be found to contain these elements. Therefore, a measurable concentration of a metal is not, by itself, justification for concern.

PRESENCE OF METALS IN E&P WASTES

Metals content of drilling wastes and associated wastes have been analyzed by EPA (1987) and API (ERT, 1987). Together, they analyzed for 59 separate elements and identified 24 metals within drilling waste. The remaining 35 metals tested for by the EPA were not detected as they are rare elements not normally found in most geological formations at detectable levels. Table 1 lists the concentration range for each metal found in drilling wastes. Also listed is the normal range of metal concentrations typical for soils of the United States.

METALS OF CONCERN

Of the metals found in E&P wastes, the following are not considered to limit the disposal of drilling or associated wastes because of their presence at typical or low concentrations, and/or their non-toxic/non-accumulative nature: aluminum, antimony, silver, beryllium, cobalt, iron, manganese, strontium, titanium, vanadium, and yttrium. Guidance values for these metals were not developed in this study. Tin was initially of concern, but a risk evaluation indicated that a guidance value was not needed (see Appendices C & D)

The remaining metals are considered to be of potential environmental concern and guidance values were developed in this study. These metals are:

arsenic (As)	cadmium (Cd)	lead (Pb)	nickel (Ni)
barium (Ba)	chromium (Cr)	mercury (Hg)	selenium (Se)
boron (B)	copper (Cu)	molybdenum (Mo)	zinc (Zn)

1 H																	2 He		
3 Li	4 Be													5 B	6 C	7 N	8 O	9 F	10 Ne
11 Na	12 Mg													13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr		
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe		
55 Cs	56 Ba	57 La	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn		
87 Fr	88 Ra	89 Ac																	
			58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu			
			90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr			

Atomic Number

21
Sc

Symbol

Metals

Metals Requiring Soil Criteria

Atomic
Number21
Sc

Symbol

Metals

Metals Requiring
Soil Criteria

Figure 1: Periodic Table showing naturally occurring elements defined as “metals” and having soil criteria developed in this document for E&P waste.

Table 1

Metals in Drilling Waste and Soils

Metal	Drilling Waste (EPA, 1987)			Drilling Waste (ERT, 1987)			Soil (Lindsay, 1979)	
	Detections per 21 samples	Mean (mg/kg)	Maximum (mg/kg)	Detections per 19 samples	Mean (mg/kg)	Maximum (mg/kg)	Average (mg/kg)	Range (mg/kg)
Al	21	9,153	20,900	19	7,860	20,800	71,000	10,000 - 300,000
Ag	6	< 0.1	9.1	0			0.05	0.01 - 5
As	11	5.3	29	19	10	27.9	5	1 - 50
B	18	83.3	290	19	18.4	73.6	10	2 - 100
Ba	21	7,190	56,200	19	6,440	24,500	430	100 - 3,000
Be	3	0.2	3	10	0.4	1.5	6	0.1 - 40
Cd	12	2.5	14	3	0.2	1.5	0.06	0.01 - 0.7
Co	5	3.4	17	19	8.7	20.3	8	1 - 40
Cr	20	42.9	368	19	28.5	145	100	1 - 1,000
Cu	18	23.5	82	19	22.5	124	30	2 - 100
Fe	21	22,100	56,800	19	17,200	46,100	38,000	7,000 - 550,000
Hg	3	< 0.130	2.1	3	0.1	1.1	0.03	0.01 - 0.3
Mn	21	352	940	19	296	495	600	20 - 3,000
Mo	2	1.4	16	13	4.1	9	2	0.2 - 5
Ni	15	19.6	61	19	17.9	40.6	40	5 - 500
Pb	12	60.9	446	19	71.5	302	10	2 - 200
Sb	0			2	1.97	23.6	0.66	< 1 - 8.8
Se	0			1	0.03	0.58	0.3	0.1 - 2
Sn	8	16.5	101	2	3.8	60.3	10	2 - 200
Sr	8	180	1,090	19	282	885	200	50 - 1,000
Ti	21	167	554	19	110	318	4,000	1,000 - 10,000
V	15	17	74	19	19.2	37.3	100	20 - 500
Y	2	0.952	12	0			50	25 - 250
Zn	21	209	823	19	131	413	50	10 - 300

METHOD FOR DETERMINING METALS GUIDELINES FOR LAND APPLICATION OF E&P WASTES

The only specific regulatory guidelines for the land application of metals in E&P wastes are those established by the State of Louisiana Statewide Order 29-B. These guidelines, suggested by Freeman and Deuel (1984), are based on a 1980 EPA study on land treatment technology for sewage sludge and hazardous waste (EPA, 1980). The EPA has recently updated its study using a more technical, risk-based approach (EPA, 1993b). It selected an approach based on risk to *highly exposed individuals* (HEIs) and consideration of health protection for higher risk populations (i.e., an aggregate risk assessment). This is more realistic than the worst-case *most exposed individual* (MEI) approach used in the past in many regulatory studies. The EPA set new standards based not only on cancer risk but on a series of other health and environmental effects. The EPA employed exposure assessment models to develop risk-based numerical pollutant limits for sewage sludge when it is applied to land.

With respect to metal constituents, the land application of E&P waste is equivalent to the land application of sewage sludge. Metals are found predominately in both types of wastes in either an unavailable form (e.g., insoluble metals) or a potentially available form (e.g., adsorbed metals, metal carbonates, metal sulfides), and therefore, environmental criteria for metals applicable to sewage sludge are also applicable to E&P wastes.

In setting these new limits, EPA conducted risk assessments for 14 exposure pathways from sewage sludge applied to agricultural land (see Table 2). These pathways address specific concerns about land application of waste. Toxic constituents from land applied wastes can (i) interfere with plant growth, (ii) move up the food chain from plants to humans or animals (including soil organisms and soil organism predators) and from plants to animals to human, (iii) leach from the recipient soils to contaminate surface and ground waters, (iv) generate contaminated airborne dust or airborne volatile pollutants that can be inhaled by humans, and (v) leave behind contaminated soils that can be ingested either by children directly or by animals that are subsequently ingested, or whose products are ingested, by humans.

The EPA initially selected 31 pollutants for consideration, 13 inorganic and 18 organic constituents. In the end, it concluded that numerical pollutant limits for all of the organic constituents and for three of the inorganic constituents were not required. The ten inorganic or metal constituents that the EPA set numerical pollutant limits for are As, Cd, Cr, Cu, Pb, Hg, Mo, Ni, Se, and Zn. EPA calculated the cumulative allowable application rate of a pollutant for each exposure pathway and the lowest application rate calculated was chosen as the regulatory limit (EPA, 1992). The results of EPA's risk evaluation are listed by pathway in Table 3.

Table 2

**Environmental Pathways of Concern Identified for
Land Application of Sewage Sludge (EPA, 1993b)**

Pathway	Description of Highly Exposed Individual
1. Sewage Sludge→Soil→Plant→Human	Human ingesting plants grown in sewage sludge-amended soil.
2. Sewage Sludge→Soil→Plant→Human	Residential home gardener.
3. Sewage Sludge→Human	Children ingesting sewage sludge
4. Sewage Sludge→Soil→Plant→Animal →Human	Farm households producing a major portion of the animal products they consume. It is assumed that the animals eat plants grown in soil amended with sewage sludge.
5. Sewage Sludge→Soil→Animal→Human	Farm households consuming livestock that ingest sewage sludge while grazing.
6. Sewage Sludge→Soil→Plant→Animal	Livestock ingesting crops grown on sewage sludge-amended soil.
7. Sewage Sludge→Soil→Animal	Grazing livestock ingesting sewage sludge.
8. Sewage Sludge→Soil→Plant	Plants grown in sewage sludge-amended soil.
9. Sewage Sludge→Soil→Soil Organism	Soil organisms living in sewage sludge-amended soil.
10. Sewage Sludge→Soil→Soil Organism→Soil Organism Predator	Animals eating soil organisms living in sewage sludge-amended soil.
11. Sewage Sludge→Soil→Airborne Dust→Human	Tractor operator exposed to dust while plowing large areas of sewage sludge-amended soil.
12. Sewage Sludge→Soil→Surface Water→Human	Water Quality Criteria for the receiving water for a person who consumes 0.04 kg/day of fish and 2 liters/day of water.
13. Sewage Sludge→Soil→Air→Human	Human breathing volatile pollutants from sewage sludge.
14. Sewage Sludge→Soil→Ground Water→Human	Human drinking water from wells contaminated with pollutants leaching from sewage sludge-amended soil to ground water.

Table 3

**Limiting Results for Each Pathway for Metals,
Reported as Reference Cumulative Application Rate of Metal (kg/ha)**

Pollutant	Exposure Pathway													
	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Arsenic	6,700	930	41			1,600	3,100				400	66,000		1,200
Cadmium	610	120	39	1,600	68,000	140	650			53	8,000	63,000		unlimited
Chromium			79,000				190,000	3,000			5,000	unlimited		12,000
Copper			10,000			3,700	2,000	1,500	2,900			unlimited		unlimited
Lead			300			11,000	1,200			5,000	10,000	unlimited		unlimited
Mercury	180	370	17	1,500	24,000						10,000	1,100		unlimited
Molybdenum			400			18*	530							
Nickel	63,000	10,000	820			1,800	5,400	420			3,000	unlimited		13,000
Selenium	14,000	1,200	100	15,000	13,000	790	130							
Zinc	16,000	3,600	16,000	150,000	2,200,000	12,000	36,000	2,800						

Notes: Definitions and descriptions of each pathway are given in Table 2. All results are rounded down to two significant figures.

"Unlimited" is defined as no concentration limit for the particular metal in soils for the specific pathway.

A blank cell indicates that the metal was not of concern for that exposure pathway and a risk analysis was not performed.

*On February 25, 1994 (59 FR 9050), EPA rescinded this result due to technical errors and has not yet re-established a limit for this pathway.

Reference: EPA, 1992. Technical Support Document for Land Application of Sewage Sludge: Volume I. EPA 822/R-93-001a.

Three metals identified in E&P waste (ERT, 1987; EPA, 1987) that were not included in the EPA sewage sludge risk evaluation are barium, boron, and tin. The risk associated with the land application of wastes containing these metals was evaluated using the same methodology. Summaries of environmental chemistry for each metal may be found in Appendices A-C, respectively. Risk evaluation calculations are contained in Appendix D. The evaluation for tin indicated very low risk; therefore, a guidance value is not warranted.

CALCULATION OF E&P WASTE / SOIL CONCENTRATION LIMITS

Using the results and methods from EPA's risk assessment for sewage sludge, guidelines for metals concentrations in waste/soil mixtures of land-managed E&P waste can be calculated. The results in Table 3 are expressed as reference cumulative application rates of pollutant in units of kilograms per hectare. These values are converted to a post-application maximum soil concentration by the following equation (p. 5-40, EPA, 1992):

$$MSC = \frac{CPLR}{2}$$

where:

MSC = maximum soil concentration (mg/kg)

CPLR = cumulative pollutant loading rate from Table 3 (kg/ha)

The conversion factor of 2 is based on the assumption that the soil in which the sewage sludge is incorporated weighs 2,000 metric tons dry weight per hectare based on an assumed bulk density of 1.33 g/cm³ and a soil incorporation depth of 15 cm.

However, for exposure pathways 3, 5, and 7, the risk was associated with the ingestion of whole (undiluted) sewage sludge. For these pathways, the maximum soil concentration is equivalent to the maximum waste concentration as calculated by the following equation (derived from Equation 1, EPA, 1993b):

$$MSC = MWC = \left(\frac{CPLR}{MWAR} \right) \times CF$$

where:

MWC = maximum waste concentration (mg/kg)

MWAR = maximum waste application rate (metric tons/ha) = 1000

CF = a conversion factor ((mg/kg)/(kg/metric tons)) = 1000

The API guidance for the twelve E&P metals of concern is listed in Table 4. The methodology for determining the limiting pathway and maximum soil concentration for barium and boron is discussed in Appendix D.