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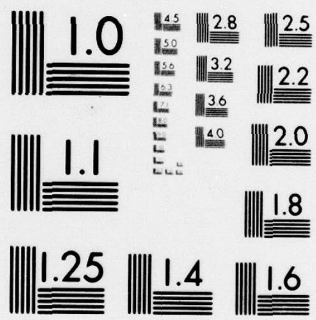

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LEAD: PRELIMINARY POLLUTANT LIMIT VALUE FOR LEAD COMPOUNDS IN SOIL

TECHNICAL REPORT

by

DAVID R. COGLEY

MAY 1979

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ENVIRONMENTAL PROTECTION RESEARCH DIVISION
US ARMY MEDICAL BIOENGINEERING RESEARCH
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Fort Detrick, Frederick, MD 21701

Supported by

US ARMY MEDICAL RESEARCH AND DEVELOPMENT COMMAND
Fort Detrick, Frederick, MD 21701

and

US ARMY TOXIC AND HAZARDOUS MATERIALS AGENCY
Aberdeen Proving Ground, MD 21010

Contract No. DAMD17-77-C-7050

WALDEN DIVISION OF ABCOR, INC.
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Wilmington, MA 01887

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SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE

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1. REPORT NUMBER

2. GOVT ACCESSION NO.

3. RECIPIENT'S CATALOG NUMBER

4. TITLE (and Subtitle)
LEAD: PRELIMINARY POLLUTANT LIMIT VALUE FOR LEAD COMPOUNDS IN SOIL.

5. TYPE OF REPORT & PERIOD COVERED
Technical Rep[redacted]t.
Feb[redacted]-May [redacted]79

6. PERFORMING ORG. REPORT NUMBER

7. AUTHOR(s)
DAVID R. COGLEY, Ph.D.

8. CONTRACT OR GRANT NUMBER(s)
DAMD17-77-C-7050

9. PERFORMING ORGANIZATION NAME AND ADDRESS
Walden Division of Abcor, Inc.
350 Main Street
Wilmington, MA 01887

10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS

11. CONTROLLING OFFICE NAME AND ADDRESS
US Army Medical Research & Development Command
ATTN: SGRD-AJ
Fort Detrick, Frederick, MD 21701

12. REPORT DATE
May [redacted]79

13. NUMBER OF PAGES
14

14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)
US Army Medical Bioengineering Research and Development Laboratory, ATTN: SGRD-UBG
Fort Detrick, Frederick, MD 21701

15. SECURITY CLASS. (of this report)
UNCLASSIFIED

15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

Approved for Public Release; Distribution Unlimited.

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Lead azide	Lead salicylate
Lead chromate	Soil pollution
Lead styphnate	Health hazard
Lead ethylhexanoate	

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

A preliminary pollutant limit value (PPLV) of 42 mg-Pb/kg-soil has been calculated for lead compounds in soil. The solubilities of two compounds of interest to the Army, lead azide, and lead chromate, exceed the 1979 proposed water quality criterion for lead; these compounds could produce toxic effects in humans at soil concentrations which exceed the PPLV.

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EXECUTIVE SUMMARY

A preliminary pollutant limit value (PPLV) of 42 mg-Pb/kg-soil has been calculated for lead compounds in soil. This PPLV is based on the 1979 proposed water quality criterion for human health effects, which is 0.05 mg-Pb/kg-water. The solubilities of two compounds of interest to the Army, lead azide and lead chromate, exceed the water quality criterion and could thus produce toxic effects in humans at concentrations in soil which exceed the PPLV. Solubility data were not available for lead ethylhexanoate, lead styphnate or lead salicylate. In the environment, the solubility of lead compounds increases at low pH.

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INTRODUCTION

Army operations have involved the use of lead compounds in munitions manufacture. The compounds of interest in the present study are:

- lead azide
- lead chromate
- lead ethylhexanoate
- lead salicylate
- lead styphnate

It is possible that certain of these compounds may be present in soil at various locations and at concentrations which could result in adverse human health effects. To assess this possibility, a preliminary pollutant limit value (PPLV) has been calculated for lead compounds in soil. The PPLV is an estimate of the no-effect concentration of each particular compound in soil, based on lifetime exposure. PPLVs are meant to be target values for assessment of alternative restoration scenarios.

The PPLV methodology is explained in detail in several of the documents cited in references 1-3. Briefly, a no-effect dose to humans is chosen from published data and a quantitative assessment of environmental pathways is used to calculate the lead concentration in soil which would result in the intake of this no-effect dose each day.

Calculations have been performed assuming that the solubility of all five compounds is sufficient to produce toxic effects at the calculated PPLV. Preliminary data indicate this is valid for lead azide and lead chromate. No solubility data are available for the other three lead compounds. However, the derived PPLV is assumed to be applicable to all five compounds.

SELECTION OF A NO-EFFECT DOSE FOR LEAD

A no-effect dose (D_T), 0.00143 mg/kg-body weight per day, based on the proposed water quality criterion for lead, 0.05 mg/L (4), has been selected as the basis for a PPLV calculation.* The water quality criterion

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$$* \quad D_T = \frac{C_W \times W_W}{BW} = \frac{0.05 \text{ mg/L} \times 2\text{L}}{70 \text{ kg}} = 0.00143 \text{ mg/kg}$$

was arrived at after careful consideration of published literature available to the end of 1978. The criterion allows for the protection of the health of the most sensitive unit of the United States population, young children. It quantitatively accounts for lead intake from several sources including: air, water, food and pica. (Pica is a craving for unnatural foods and includes the ingestion of chips of lead-based paint by children.)

INITIAL PPLV CALCULATIONS

Calculations are based on the methodology detailed in references 1-3. Five pathways are considered all of which begin with lead in soil and end with humans: water, root crops, feed animals raised on root crops, river sediment via fish flesh, and inhalation of particulates.

1. Limit value for soil via water.

$$C_{s1} = \frac{BW \times D_T}{K_{sw} \times W_w} = 35\ D_T = 0.05 \text{ mg Pb/kg-soil}$$

2. Limit value for soil used to grow crops for human consumption (root crops).

$$C_{s2} \leq 1111\ D_T = 1.6 \text{ mg-Pb/kg-soil}$$

3. Limit value for soil used to grow feed for food animals consumed by humans:

$$C_{s3} = \frac{C_{s2}}{k_{pa}} = \frac{1.6}{5} = 0.32 \text{ mg/Pb/kg-soil}$$

only for animals subsisting on root crops.

4. Limit values for river sediment via fish flesh.

From Nriagu p. 325 + text (5).

Bioconcentration factor, $\frac{\text{Fish}}{\text{sediment}} \leq 1$.

If fish intake = 0.63 kg/day

$$C_{s4} = \frac{D_T \times BW}{\text{Weight-Fish*}} = \frac{0.00143 \text{ mg} \times 70 \text{ kg}}{\text{kg-day} \quad 0.63 \text{ kg/day}} = 0.16 \text{ mg/kg-soil}$$

5. Soil containing the pollutant, inhaled as a particulate, respired by humans:

$$C_{s5} = 6.3 \times 10^7 D_T = 90{,}000 \text{ mg/kg}$$

However, it should be noted that the National Ambient Air Quality Standard for Pb is 1.5 μg Pb/m^3 (6), which yields:

$$C_{s5} = \frac{1.5 \text{ μg Pb/m}^3}{\text{m}^3} \times \frac{\text{m}^3}{0.06 \text{ mg soil}} = \frac{25 \text{ μg}}{\text{mg}} = \frac{25{,}000 \text{ mg}}{\text{kg}}$$

6. Normalization

$$C_{sf} = \frac{1}{\frac{1}{0.05} \times \frac{1}{1.6} \times \frac{1}{0.32} \times \frac{1}{0.16} \times \frac{1}{25{,}000}} = 0.033 \text{ mg/kg}$$

FACTORS AFFECTING PPLV RESULTS

Detailed consideration of environmental factors is beyond the scope of the present effort. However, brief consideration is given to the effects of the following factors on the validity of the PPLV:

- solubility of military-unique lead compounds
- solubility of possible environmental transformation products
- attenuation capacity of soils
- natural complexing agents in soils
- pH changes
- refinement of bioconcentration factors
- background concentrations

---

* Weight of soil.

The solubility of the five military-unique lead compounds and of the environmental transformation products is important. If lead, once dispersed, were always to form very insoluble compounds, it might, in effect, be inactivated and pose a health problem only when ingested as a solid particulate from air, water, or food. This is not the case. As detailed in Appendix B, the solubility of lead azide and chromate exceed the water quality criteria. The same applied for $Pb(OH)_2$ at all pH values; $PbCl_2$ at all pH values; $PbSO_4$ for sulfate <4 g/l; PbS under aerobic conditions; and $PbCO_3$ in equilibrium with atmospheric CO_2 at pH <6.5.

Soil adsorptive capacity for lead is high for most soils at neutral or basic pH values. As reported on pages 95-96 of Lead in the Environment (7), addition of soluble lead salts at levels up to 3000 mg/kg resulted in fixation of 99+ percent of the lead. That is, less than 1 percent of the lead could be leached from the soil with water. However, addition of humic acid extracts (0.1 percent solution) resulted in solubilization of the lead. Thus, naturally occurring complexing agents, e.g., humic acids, can solubilize lead in soil. Humic acids are apparently present at higher concentrations under acid conditions. Thus, acidification of soil could directly and indirectly result in solubilization of lead compounds.

Refinement of bioconcentration factors could result in a change in the lead PPLV value. However, since the single path PPLVs for food pathways are 3 to 30 times greater than the water pathway, increase of at least this much in bioconcentration factors would be required to produce a significant change in the PPLV.

In plants, lead seems to be immobilized by formation of insoluble phosphate compounds in the roots (Boggess, et al., pp. 101-103) (7). This seems to indicate that as long as phosphate levels are adequate there need be no concern over accumulation of lead in plant parts above the soil line.

For aquatic biota, a further assessment of bioconcentration of lead might be helpful.

Background concentrations of lead in soil vary widely. The accepted average value for the lead content of the earth's crust is 15 mg/kg (Boggess, et al., p. 93) (7) which is approximately 500 times the PPLV. A range of 0.8 to 500 mg/kg has been reported for arable soils. Soils of sedimentary or alluvial origin often have as little as 0.04 mg/kg.

REFINEMENT OF PPLV

Initial PPLV calculations were performed with default values for many of the distribution coefficients. These default values are applicable to cases of extreme pollutant-environment interaction but not necessarily to lead. For example, the soil-water distribution coefficient default value assumed for pathway one was unity. This is applicable only to compounds of high solubility or to soils of very low sorptive capacity. Such conservative estimates provide margins of safety for extreme environmental conditions (e.g., soluble lead in acidic, sandy soils) but they can also grossly overestimate the problems for more likely situations (e.g., agricultural soils with typical nutrient capacities, typical alkalinity, and neutral pH.) We discuss briefly some of the less conservative assumptions which may well apply to specific sites.

1. Limit value to soil via water. Data from <u>Lead in the Environment</u>, p. 95 (7), quoting from Brewer's work shows that of 3000 mg/kg soluble lead added to soil, 3 days later only 3 mg/kg were soluble. From this we calculate $K_{sw} = 0.001$. The corresponding PPLV is:

$$C_{s1} = \frac{BW \times D_T}{K_{sw} \times W_w} = \frac{70 \times 0.00143}{0.001 \times 2} = 50 \text{ mg-Pb/kg-soil}$$

2. Limit value for soil used to grow crops for human consumption (root crops). The full equation for the single path PPLV is:

$$C_{s2} = \frac{BW \times D_T}{K_{sw} \times K_{wp} \times f \times DFI}$$

and the following default values were assumed:

$BW = 70$ kg,

$D_T = 0.00143$ mg/kg-day,

$K_{sw} = 1$

$K_{wp} = 1$

$f = 0.1$

$DFI = 0.63$ kg/day

Assuming $K_{sw} = 0.001$ leads to:

$C_{s2} = 1600$ mg-Pb/kg-soil

3. Limit value for soil used to grow feed for food animals consumed by humans. Assuming, again, that an extreme case may apply, e.g., beef cattle raised on sugar beet pulp, and assuming that cattle retain all of the dietary lead in their edible tissues:

$$C_{s3} = \frac{C_{s2}}{K_{pa}} = \frac{1600}{5} = 320 \text{ mg/Pb/kg soil}$$

4. Limit values for river sediment via fish flesh. From Nriagu pp. 321-324 (5), bioconcentration factor,

$$\frac{\text{Pb-fish}}{\text{Pb-sediment}} = 0.001 \text{ to } 1$$

If fish intake = 0.63 kg/day

$$C_{s4} = \frac{BW \times D_T}{\text{Weight-fish}}$$

ranges from 0.16 mg-Pb/kg-soil to 160 mg-Pb/kg-soil. Pathway 5 is the same, C_{s5} = 25,000 mg-Pb/kg-soil.

5. Normalization for pathways other than fish ingestion.

$$C_{sf} = \frac{1}{\frac{1}{50} \times \frac{1}{1600} \times \frac{1}{320} \times \frac{1}{25,000}} = 42 \text{ mg-Pb/kg-soil}$$

In cases where the above assumptions apply, one obtains:

For soil, PPLV = 42 mg-Pb/kg-soil.

For river bottom sediment on soils which may erode and deposit in rivers, PPLV = 0.16 to 160 mg-Pb/kg-sediment depending on the sediment to fish distribution coefficients.

CONCLUSIONS

A very conservative approach yields a lead PPLV (0.033 mg-Pb/kg-soil) 500-fold below typical background lead concentrations. More realistic assumptions yield a lead PPLV (42 mg-Pb/kg-soil) which is somewhat higher than typical background values and which applies to soils other than sediments. For sediments, the available data allow only for a calculation of a range within which the appropriate PPLV lies, 0.16 to 160 mg-Pb/kg-sediment.

It is clear from the foregoing discussion that specification of a lead PPLV for any particular site will require careful consideration of site-specific factors. A particularly sensitive parameter in PPLV calculations is the soil-water distribution coefficient, and it is important that the parameter be experimentally determined for the major soil types at each facility under study.

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GLOSSARY OF TERMS

BW = body weight

C_s = limiting pollutant level in soil for human health effects, $mg\ kg^{-1}$

C_{sf} = final C_s value

C_w = limiting pollutant level in water, for human health effects, $mg\ kg^{-1}$

DFI = daily food intake, $kg\ day^{-1}$

D_T = acceptable daily dose of a toxicant, $mg\ kg^{-1}\ day^{-1}$

f = fraction of total diet represented by food of a given type

K_{pa} = concentration in a food animal/concentration in a crop plant

K_{sw} = concentration in water/concentration in soil, i.e., partition coefficient between soil and water

K_{wp} = concentration in a crop plant/concentration in water

W_w = daily water intake, $kg\ day^{-1}$

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