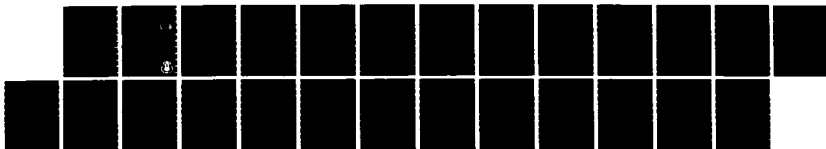AD-A169 179   CONTAMINATED SOIL CLEANUP OBJECTIVES FOR CORNHUSKER   1/1
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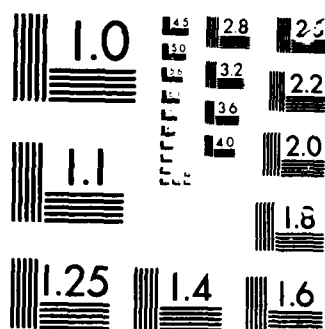   RESEARCH AND DEVELOPMENT LAB FORT..   D H ROSENBLATT
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TECHNICAL REPORT 8603

CONTAMINATED SOIL CLEANUP OBJECTIVES
FOR CORNHUSKER ARMY AMMUNITION PLANT

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DAVID H. ROSENBLATT, Ph.D.

Prepared for
U.S. Army Toxic and Hazardous Materials Agency
Aberdeen Proving Ground, MD 21010-5401
Mr. Robert Turkeltaub, Project Coordinator

by

U S ARMY MEDICAL BIOENGINEERING RESEARCH & DEVELOPMENT LABORATORY

Fort Detrick

Frederick, Maryland 21701

MAY 1986

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NOTICE

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Cleanup	2,6-Dinitrotoluene	Pollutant limit values
Cornhusker AAP	DNT	RDX
Cyclotrimethylenetrinitramine	Explosives	Soil contaminants
2,4-Dinitrotoluene	Groundwater	TNB

20. ABSTRACT *(Continue on reverse side if necessary and identify by block number)*
A method has been developed to determine soil cleanup objectives for small chemically contaminated source areas located within a large installation. The purpose of such cleanup is to reduce the sources of groundwater pollution, so that levels of the contaminants in the aquifer would eventually not exceed applicable drinking water criteria. The method has been applied to derive site-specific soil concentration limits for Cornhusker Army Ammunition Plant. The numbers so derived, not to be used elsewhere, are as

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19. Key Words Continued

TNT
1,3,5-Trinitrobenzene
2,4,6-Trinitrotoluene

20. Abstract Continued

.follows: TNT, 5 ppm; RDX, 10 ppm; 1,3,5-trinitrobenzene (TNB), 15 ppm.
Numbers were also derived for 2,4-DNT and 2,6-DNT; but removal of soil
excessively contaminated with TNT should be sufficient to assure adequate
removal of the two DNTs at this site. Thus, analysis for the latter compounds
on a regular basis need not be required.

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INTRODUCTION AND SITE BACKGROUND

Remedial actions to control groundwater contamination by explosives and related compounds are required at the Cornhusker Army Ammunition Plant (CAAP), Grand Island, Hall County, Nebraska. CAAP is an inactive U.S. Army Armament, Munitions and Chemical Command facility that had a primary mission to load, assemble and pack conventional munitions and provide associated support functions. The facility is located 2 miles west of the city of Grand Island and occupies 4,845 hectares (18.7 square miles). CAAP consists of five major load-line production areas where LAP (load, assembly and pack) activities were conducted, an ammonium nitrate area where fertilizer was produced immediately following World War II, associated storage facilities located north and south of the load lines, a sanitary landfill, and a burning ground for open burning of explosives contaminated material.[1]

Cornhusker Army Ammunition Plant was constructed in 1942 for production of conventional munitions used in World War II. The operations were directed by the Quaker Oats Ordnance Corporation, a subsidiary of the Quaker Oats Company, which produced bombs, shells, boosters and supplementary charges. The plant was put in standby status on 1 September 1945 until 1 February 1950. In 1950, Mason & Hanger Silas Mason Company, Inc., rehabilitated the plant for operation to produce artillery shells and rockets for the Korean conflict. The plant was again placed on standby status in 1957 until 1965 when operations were conducted for the Vietnam Conflict. On 12 October 1973, operations were stopped and the plant was put in standby status, the present status of the installation. The plant is Government-owned, and contractor-operated.[1]

Present activities of the plant are limited to maintenance operations, leasing of property for agriculture and livestock grazing, storage building leasing and wildlife management.[1]

Extensive groundwater contamination by RDX (hexahydro-1,3,5-trinitro-1,3,5-triazine or cyclotrimethylenetrinitramine) and by 2,4,6-TNT (2,4,6-trinitrotoluene) and associated impurities/degradation products, i.e., 2,4-DNT (2,4-dinitrotoluene), 2,6-DNT (2,6-dinitrotoluene) and 1,3,5-TNB (1,3,5-trinitrobenzene) has resulted from the disposal of explosives wastewater into 56 earthen impoundments (cesspools and leaching pits) located within the five load lines of the plant. Groundwater contamination originating from these impoundments has affected approximately 186 individual residential water supplies.[1]

The Army intends to remove major pockets of soil contamination from 56 surface impoundments in order to prevent additional groundwater contamination. This soil will be incinerated in a transportable rotary kiln to decompose the explosives and related organic compounds. Incineration operations will begin in 1986, with completion scheduled for 1987. The treated soils will be backfilled into the excavations. Routine chemical analysis will be used to monitor performance of the incineration system, residual explosives concentration in the incineration ash, and undisturbed soil not excavated from the impoundments.[1]

The purpose of the present study was to define soil concentration limits for the five contaminants shown above. It should not be necessary to disturb

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soil containing concentrations of the contaminants below the concentration limits. The technical approach used in this report to derive soil cleanup objectives represents an extension of the preliminary pollutant limit value (PPLV) methodology employed in previous reports that derived site-specific pollutant limits or evaluated the seriousness of residual contamination for the US Army Toxic and Hazardous Materials Agency (USATHAMA).[2-8]

APPROACH TO THE DEVELOPMENT OF SOIL POLLUTANT LIMIT VALUES

Because the area of CAAP is 18.7 square miles, it should be assumed from the outset that only certain portions—relatively small areas—are contaminated at all. To assume that the entire area has become contaminated would mean that the highest allowable concentrations in soil (C_s) would be levels for which water in equilibrium with the soil contains the permissible drinking water level (C_w). Thus, the equilibrium constant for the ratio of contamination in soil and water, K_d, would be used as follows:

$$C_s = C_w K_d$$

Values of C_s derived by this equation from C_w values (Table 1) and estimates of K_d (developed below, see Table 5) would be so low that analysis, and perhaps cleanup costs would be intolerably high.* Instead, the following line of reasoning should be considered:

● For each of the five contaminants, assume that the area of residual contamination after cleanup is equal to four times the areas of those leaching pits and cesspools known to be presently contaminated with the compound.[12,13] (This is a working hypothesis, wherein the radius of contamination is assumed to be twice the radius of the impoundment.) Since only four out of 11 leaching pits and four out of 45 cesspools were actually sampled for pollutant analysis, the proportion of those sampled that showed the presence of a contaminant was pro-rated to the entire number (considering leaching pits and cesspools separately).**

● Assume that the groundwater stream subject to contamination (Fig. 1) is one mile wide, i.e., W.

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* For example, for TNT one calculates: C_s = 0.044 mg/L x 1.069 L/kg = 0.047 mg/kg. Thus, if TNT at this "highest allowable concentration" were assumed to be uniformly distributed in the soil, the calculated TNT concentration in leachate reaching the aquifer throughout CAAP would be 0.044 mg/L. The amounts of TNT recovered for analysis at this level would be extremely variable, and the analyses—if at all feasible—would be very time-consuming and expensive.

** The presence of contaminants in French drain and sack sump samples has been omitted from consideration.

TABLE 1.   PERMISSIBLE DRINKING WATER CONCENTRATIONS, C_w,
FOR FIVE SOIL/WATER CONTAMINANTS FOUND AT CORNHUSKER AAP

Compound	Drinking Water Criterion, C_w (mg/L)	Source of Information
2,4,6-TNT	0.044	Letter, OTSG, 1983[a]
RDX	0.035	Letter, OTSG, 1983[a]
1,3,5-TNB	0.20	Unofficial, Rosenblatt, 1981[b]
2,4-DNT	0.0011[c]	EPA, 1980[d]
2,6-DNT	0.00022	Unofficial, ESE, 1985[e]

a. Reference 9
b. Reference 5.
c. For 10^{-5} cancer risk.
d. Based on Reference 10.
e. Based on Reference 11.

● Imagine, separately for each contaminant, that all the contaminated areas were moved into a strip straddling the groundwater stream. This contaminated strip is the shaded area of Figure 1; the aggregate contaminated area is L x W. It is as if the stream became contaminated in the course of traveling a distance L beneath contaminated soil.

● When soil removal for incineration has been completed, assume that the residual concentration of each contaminant throughout the remaining original volume of contamination beneath the shaded area of Figure 1 will be uniform and at the limit value that will be calculated below. Moreover, the pure leachate concentration for each contaminant will be equal to residual concentration/K_d.

ALTERNATIVE APPROACH #1

● Assume an aquifer porosity of 20%.

● Estimate a groundwater flow rate, R, of 1.5 feet per day, based on travel of 4 1/4 miles in 42 years.[14]

● Assume that groundwater recharge due to rainfall is equal to 20% of the annual rainfall, i.e., about 5 inches, or 12.5 cm. This assumption is confirmed (order-of-magnitude) by data from Fulton and Spaulding[15] (Fig. 8 and Fig. 2 of Ref. 15). The distance from sampling well NW 8 to the nearest leaching pit in load line 1 (identified in reference 12) is 2.39 miles. At the flow rate of 1.5 feet per day, groundwater would have taken 23 years to travel between the two points. In this time, the center of the contaminated layer of groundwater was overlain by about 34 1/2 feet of clean water, i.e., at a rate of 1.5 feet per year. With the assumed aquifer porosity of 20%, this equals 3.6 inches of rain per year.
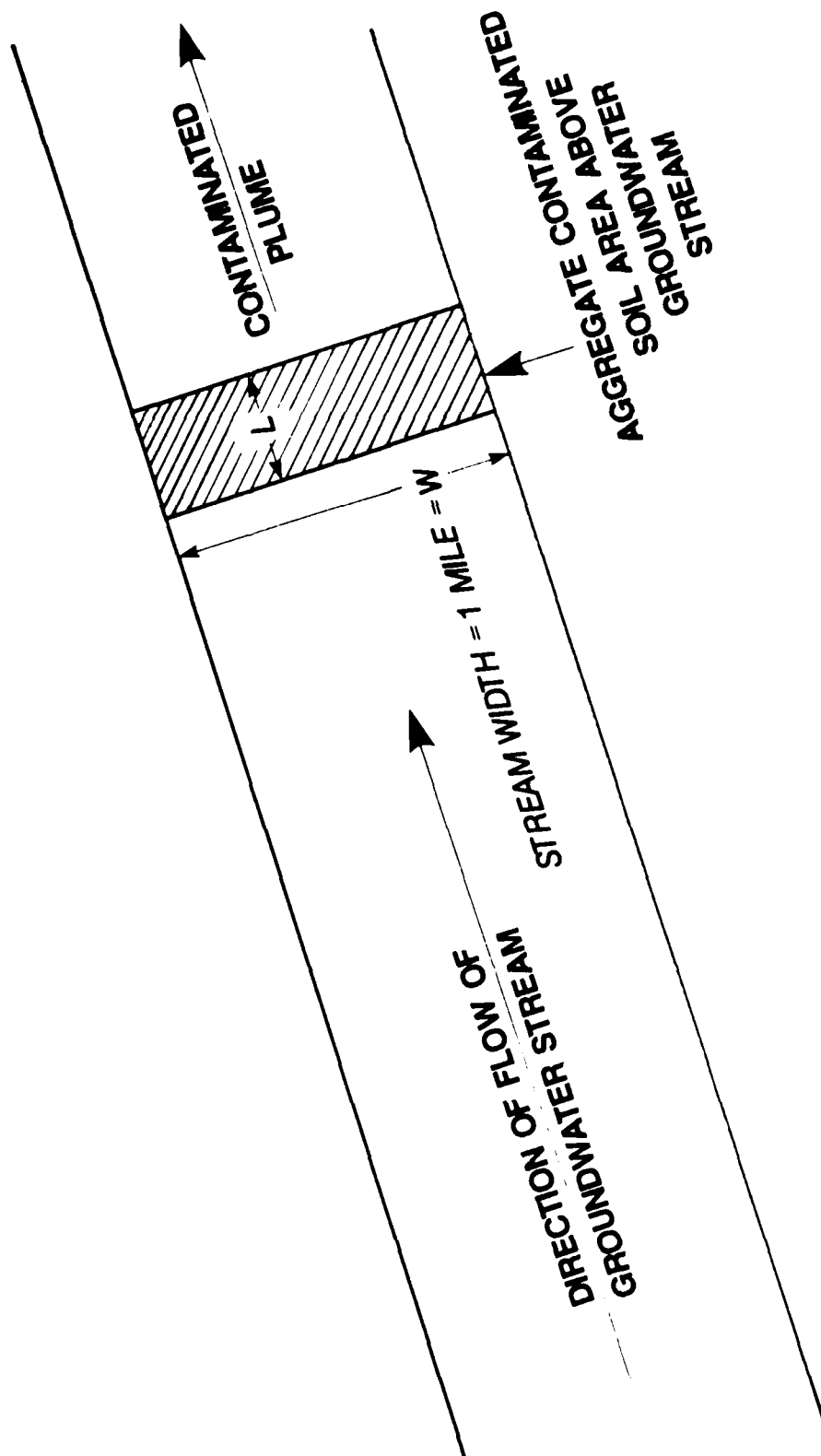
Figure 1. Hypothetical Contaminated Soil Area for Groundwater
Contamination Model, Value of "L" Varying with
the Compound.

● Based on the aquifer porosity of 20%, estimate that 12.5 cm of recharge water over a year would occupy an aquifer thickness, T_o, of 62.5 cm per year.

● Use information furnished by USATHAMA to the effect that a monitoring well samples an aquifer thickness of 15 feet, i.e., 457 cm.[15]

● Assume that some monitoring wells will draw water samples that include the water from a contaminated layer of the aquifer (which has a thickness T cm as will be defined below) plus dilution water from clean layers above and below the contaminated layer. In that case, one may calculate a dilution factor, $F_d = T/457$. The allowable residual soil concentration for a particular compound is then $C_s{}' = C_s/F_d$.

To estimate contaminated areas, one must have available (1) the total areas of leaching pits and cesspools times 4 (Table 2), (2) listing of leaching pits and of cesspools contaminated by each contaminant (Table 3), and (3) the estimated proportions (by area) of the leaching pit and cesspool areas that are contaminated (Table 4).

Values of K_d for TNT and RDX in Louisiana Army Ammunition Plant (LAAP) sand have been measured[16] and are believed by USATHAMA[17] to typify what should be applicable to Cornhusker AAP. (Concerning RDX, Tsai et al.[17] quoted USATHAMA, without attribution to the actual authors, a draft ESE report[16] on the determination of K_d values for TNT, RDX, and tetryl in LAAP soils.) One problem with these values is that the organic carbon content of the sand (f_{oc}) was not measured. Thus one cannot compare the measured values of K_d with values of K_{oc} determined elsewhere* (using the relationship $K_d = K_{oc} f_{oc}$). Moreover, the basic assumption that sorption is attributable overwhelmingly to the organic matter in sands or clays is probably invalid for sands with very low organic content, where sorption on mineral surfaces might dominate. As a reasonably conservative approach in the present instance, the following procedure was adopted (see Table 5):

(1) Observed K_d values for RDX and 2,4,6-TNT from the ESE study[16] were used.

(2) K_d values for 1,3,5-TNB, 2,4-DNT, and 2,6-DNT were derived (Table 5) as follows:

$$K_d = \frac{K_{oc} \text{ for compound}}{K_{oc} \text{ for } 2,4,6\text{-TNT}} \times K_d \text{ for TNT}$$

Note: TNT is judged to be more similar to the other three nitroaromatic compounds than is RDX.

(3) K_{oc}s (Table 5) were taken from Spanggord[19] and from studies by ESE;[20] values have been selected (somewhat arbitrarily) from within the ranges of values given.

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* $K_{oc} = \dfrac{\text{concentration of contaminant in organic fraction of soil}}{\text{concentration of contaminant}}$

TABLE 2. AREAS X 4 OF MUNITIONS COMPOUND-CONTAMINATED
LEACHING PITS AND CESSPOOLS AT CORNHUSKER AAP[12]

| Location No. | Areas x 4 (Square Feet) | |
	Leaching Pit	Cesspool
1	12,000	--
2	25,000	--
3	--	452
4	8,000	--
5	17,600	--
6	--	113
7	--	201
8	22,000	--
9	11,700	--
10	--	201
11	33,000	--
12	8,000	--
13	--	314
14	5,600	--
15	4,800	--
Sum	147,700	1,281
Adjusted Sum[a]	162,470	11,529

a. Data were found[12] for 10 leaching pits, but the
total number of leaching pits is supposedly 11; the
total leaching pit area was therefore multiplied by
10/11. Data were found[12] for five cesspools out of
45; the total cesspool area was therefore multiplied
by 45/5.

TABLE 3. MAXIMUM CONCENTRATIONS OF CONTAMINANTS FOUND IN CORE SAMPLES AT LEACHING PITS AND CESSPOOLS AT CORNHUSKER AAP[13]

Location No.	Site Type[a]	Maximum Concentration (ppm) Found in Sample Cores[b]					Maximum Nonsurface[c] Ratios of DNT:TNT in Particular samples	
		$2,4,6$-TNT	RDX	$1,3,5$-TNB	$2,4$-DNT	$2,6$-DNT	$2,4$-DNT	$2,6$-DNT
2	LP	30,000	2	100	None	None	--	--
3	C	300	4	30	3	4	0.01[d]	0.01[e]
7	C	8	2	2	1	2	f	g
8	LP	70	None	4	None	None	--	--
10	C	30	2	None	None	None	--	--
12	LP	30,000	40	100	None	None	--	--
13	C	3	0.7	1	None	None	--	--
14	LP	3,000	2	8	2	None	0.0007	--

a. LP = leaching pit; C = cesspool.
b. French drain and sack sump analyses are not relevant. "Less than" analyses were all considered negative.
c. Because of photochemical reactions at the surface, the proportion of DNTs found might be unrealistically high; further, the surface soil will be removed. A ratio always refers to coexisting concentrations in a specific sample.
d. Surface occurrence, ratio 0.03.
e. Surface occurrence, ratio 0.04.
f. Surface occurrence, ratio 0.125.
g. Surface occurrence, ratio 0.25.

TABLE 4. ESTIMATION OF 4X CONTAMINATED AREAS AT CORNHUSKER AAP

Location No.	Areas of Contamination (ft^2)				
	2,4,6-TNT	RDX	1,3,5-TNB	2,4-DNT	2,6-DNT
A. Leaching Pits					
2	25,000	25,000	25,000	--	--
8	22,000	--	22,000	--	--
12	8,000	8,000	8,000	--	--
14	5,600	5,600	5,600	5,600	--
Total positive areas	60,600	38,600	60,600	5,600	0
% of tested areas	100	63.7	100	9.2	0
Estimated total area[a]	162,470	103,493	162,470	14,947	0
B. Cesspools					
3	452	452	452	452	452
7	201	201	201	201	201
10	201	201	--	--	--
13	314	314	314	--	--
Total positive areas	1,168	1,168	967	653	653
% of tested areas	100	100	82.8	55.9	55.9
Estimated total area[b]	11,529	11,529	9,545	6,445	6,445
C. Total					
	173,999	115,022	172,015	21,392	6,445

a. % x 162,470.
b. % x 11,529.

TABLE 5. VALUES OF SOIL/WATER PARTITION COEFFICIENTS, K_d, FOR CORNHUSKER AAP MUNITIONS-RELATED COMPOUNDS

| | K_{oc} | | | | | | Sand K_d |
| | Predicted Values | | | Based on Measurements | | | |
Compound	Spanggord, et al. (1980a)[a]	Spanggord, et al. (1980b)[b]	Tucker, et al. 1985[c]	Spanggord, et al. (1980b)[d]	Tucker, et al. 1985[c]	Chosen Value	
2,4,6-TNT	--	130	300	1536 (1060-2545)	178[e] 534[f]	530	1.069[g]
RDX	--	270	538	96 (42-167)	71[e] 136[f]	100	1.588[g]
1,3,5-TNB	520	--	177	--	--	300	0.605[h]
2,4-DNT	87	63	201	240 (118-364)	--	250	0.504[h]
2,6-DNT	100	--	249	--	--	250	0.504[h]

a. Reference 18, based on log K_{oc} = -0.27 - 0.782 (log solubility, molar)
b. Reference 19.
c. Reference 20.
d. Reference 19, with measurements on soil with 3.3% organic carbon content.
e. Measurements on "1% organic soil."
f. Measurements on various soils.
g. References 16 and (for RDX only) 17.
h. Estimated as described in text.

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For a derivation of the thickness of the contaminated groundwater layer at the CAAP boundary, the following approach was employed:

Compute L = aggregate contaminated area for a given compound $\div$ W, where W = 5280 feet.

Compute t_1 = days for groundwater stream to travel the distance L under the contaminated area (shaded area in Figure 1) = L (feet)/1.5 (feet/day).

Compute the thickness, T cm, of the contaminated aquifer layer as the fraction (t_1/t_2) of the annual recharge layer thickness (T_o = 62.5 cm/yr) that would be contaminated due to flow under the contaminated area, where t_2 = 365 days/year, i.e.,

$$T = t_1 \times T_o/t_2$$

From the above,

$$C_s{}' = C_s/F_d = C_w \times K_d \times 457 \times t_2/(t_1 \times T_o)$$

$$= C_w \times K_d \times 457 \times 365 \times 1.5/(L \times 62.5)$$

$$= 4000\ C_w K_d/L\ \text{(feet) in mg/kg}$$

This approach to the estimate of dilution resulting from vertical mixing addresses only the mixing that occurs in the monitor well during sampling. It does not attempt to account for any dilution that might occur by the vertical mixing of leachate with uncontaminated water within the aquifer during transport from the source to the monitor wells.

ALTERNATIVE APPROACH #2

● Assume that the groundwater plume flows a total of 3.7 miles (2×10^4 feet) from the beginning of the contaminated area to the eastern boundary of CAAP.

● Assume that all recharge water, clean and contaminated, is commingled. Consider that portion of the groundwater stream contributed by on-site recharge. The volume ratio of contaminated recharge water (i.e., leachate) to total recharge water will be the distance L traveled beneath contaminated soil divided by the total distance (3.7 miles) traversed by the groundwater stream from the western boundary to the eastern boundary. The raw leachate of concentration C_w will thus be diluted by a factor of $L/(2 \times 10^4)$ (actually $(L/(2 \times 10^4-L))$. The average groundwater concentration of a contaminant will be C_w / dilution factor, and the value of $C_s{}'$ will be $2 \times 10^4 \times K_d \times C_w/L$.

This calculation has the advantage of avoiding an estimate of the groundwater recharge rate. It has the disadvantage of ignoring the layering effect, which could cause a particular well, tapping into the most contaminated layer of groundwater, to show contaminant levels in excess of those that are predicted by this approach. There is some theoretical evidence to suggest that the assumptions of Alternative Approach #2 are realistic at the Cornhusker site (Appendix A).

RESULTS AND DISCUSSION

ALTERNATIVE APPROACH #1

Values calculated for permissible soil residual concentrations of the five pollutants are provided in Table 6. These values take into account the fact that 2,4,6-TNT appeared in cores at every sampled site, sometimes in very high concentration. The other contaminants appeared at lower concentrations and with considerably less frequency.[13] Of particular significance is the fact that no nonsurface core sample contained a concentration of 2,4-DNT or 2,6-DNT of more than 1 percent of the associated 2,4,6-TNT. This suggests that removal of 2,4,6-TNT to the C_s' level of 5.7 ppm would lead to a proportionate decrease in DNTs, so that the nonsurface DNT isomer concentrations would be no more than 0.057 ppm, vs. a C_s' value of 0.54 ppm for 2,4-DNT and 0.37 ppm for 2.6-DNT. The proportionate decrease is to be expected since TNT and the DNTs should have similar migration tendencies, and since rather low levels of the DNTs occur in TNT as it is shipped to LAPs. The higher ratios of DNTs to TNT in two surface samples (see locations 3 and 7 of Table 3) may have resulted from photochemical loss of TNT.

TABLE 6. CALCULATION OF PERMISSIBLE SOIL RESIDUES, C_s',
FOR FIVE MUNITIONS-RELATED COMPOUNDS AT CORNHUSKER AAP
LEACHING PIT AND CESSPOOL SITES

Compound	Coverage (ft^2)	L^a (ft)	C_w (mg/L)	K_d	$C_s'^b$ (mg/kg) Approach #1[c]	Approach #2
2,4,6-TNT	173,999	33	0.044	1.069	5.7	28.5
RDX	115,022	22	0.035	1.588	10.1	50.5
1,3,5-TNB	172,015	33	0.20	0.605	14.7	73.3
2,4-DNT	21,392	4.1	0.0011	0.504	0.54	2.70
2,6-DNT	6,445	1.2	0.00022	0.504	0.37	1.85

a. L = Coverage/5280.
b. These numbers cannot be applied to any other installation because they were derived on a site-specific basis.
c. Approach #1 is preferred over Approach #2 (see text).

ALTERNATIVE APPROACH #2

As for Approach #1, values calculated for permissible residual concentrations of the five pollutants according to Approach #2 are provided in Table 6. These are five times the results of the first approach. Since the results are less conservative than those of the first approach, they should probably not be adopted.

GENERAL STATEMENT

Owing to vertical diffusion, a "true" model for the behavior of soil contaminants uniformly dispersed under the areas of the leaching pits and cesspools (multiplied by 4) would predict a value of C_s' somewhere between those obtained by the two alternative approaches. It is to be expected that most of the residual soil under these areas will be less contaminated than C_s' after remedial action, so that removal to the level of C_s' should quite effectively eliminate the source of groundwater contamination—provided no significant pockets of contamination have been missed.

CONCLUSION

Site-specific cleanup target levels of the leaching pit- and cesspool-associated areas of CAAP can be established as follows:

2,4,6-TNT - 5 ppm

RDX - 10 ppm (a level that was actually exceeded in only one sample)

1,3,5-TNB - 15 ppm

Similarly, samples showing more than 0.5 ppm of 2,4-DNT or more than 0.4 ppm of 2,6-DNT should be removed; however, it may not be necessary to analyze for them, since it is highly likely that removal of TNT to 5 ppm would reduce the level of these compounds to less than 0.4 ppm (which is also less than the detection level).

Caution: The foregoing cleanup target levels are pertinent only to the CAAP site, even though the general method is applicable at other installations.

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APPENDIX A

The following theoretical analysis[1] sheds some light on the tendency for contaminants to disperse vertically in unconsolidated deposits.

For any Fickian diffusion process (see, for example, Csanady[2]) the spread of contaminants can be characterized by the standard deviation, σ, of a Gaussian distribution:

$$\sigma = \sqrt{2Dt}$$

where D = the dispersion coefficient (ft^2/day), and

t = is the time of travel (day).

In flow-through porous media[3]:

$$D = \alpha V$$

where α = the dispersivity (ft), and

V = the average linear velocity of groundwater.

Gelhar et al.,[3] based on review of a large number of field scale dispersion experiments, conclude that the vertical dispersivity, α_v, in unconsolidated aquifer materials may be estimated as:

$$\alpha_v = bd$$

where d = the distance traveled (ft), and

b = may range from 0.00016 to 0.0033 with an average value of 0.00025.

Using the average value,

$$\alpha_v = 0.00025 \, d$$

The time of travel is

$$t = \frac{d}{V}$$

Substituting in the equation for σ,

$$\sigma = \sqrt{2 \, (0.00025) \, d \, V \, \frac{d}{V}}$$

or $\sigma = 0.022 \, d$

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In a Gaussian distribution, approximately 95 percent of the contaminant mass will be contained within 2 σ of either side of the plume's center of mass, implying a vertical spread of 4 σ = 0.088 d.

If the shortest source to receptor (boundary) distance, d, is approximately 4,000 ft,[4] then the plume could spread 350 ft. The spread would ultimately be limited by the aquifer thickness of about 60 ft. At distances more than 700 ft downgradient from source areas, the aquifer is expected, by this analysis, to be vertically well mixed, and the assumptions of Alternative Approach No. 2 would be more realistic than those of Alternative Approach No. 1. This theoretical treatment is not borne out by the facts, according to analytical data for off-site wells, dated 31 May 1985;[4] complete vertical mixing does not take place by the time the plume has left CAAP; it would appear that there is partial vertical mixing.

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