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TECHNICAL REPORT 8807

RESIDUAL EXPLOSIVES CRITERIA FOR TREATMENT OF
OF AREA P SOIL, LOUISIANA
ARMY AMMUNITION PLANT (U)

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From about 1950 to 1980, the Louisiana Army Ammunition Plant, near Shreveport, discharged wastewater from it's explosives load, assembly, and pack activities into a complex of leaching pits known as Area P. The groundwater under Area P has been found to contain the explosives TNT, RDX, and HMX as well as related compounds. The Army plans to incinerate soil that has been excavated from this area to a limited depth. An assessment of this plan from a health effects viewpoint was requested, details of which are documented in this report. Three situations were addressed, those of potable groundwater, safety of surface water for aquatic life, and future construction activities.

State regulations require the uppermost aquifer to be addressed as a potential water supply; at Area P, the uppermost aquifer is the Alluvial aquifer. The assessment concluded that current levels of explosive contamination in groundwater probably exceed acceptable levels of drinking water quality. Thus, an evaluation was done to determine

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residual soil target levels for treated and untreated soil at Area P that would provide acceptable levels of drinking water quality. For most explosives involved, the soil target levels are of the order of 0.1 to 1 mg/kg. Based on existing information about soil contamination, the treatment prescribed by the plan would not, by itself, provide a clean enough residual soil level to avert further contamination of the aquifer.

A second evaluation led to a set of soil levels that should prevent adverse aquatic effects in the nearest surface water. TNT and RDX levels in surface soil and drainage-ditch soil samples are in excess of these. Thus, the proposed removal and treatment of the top foot of soil in Area P should be undertaken.

A third evaluation addressed exposure of workers in future operations where Area P might be a construction site (not to be confused with exposure of workers in the clean-up of Area P). Based on exposure by particulate inhalation and ingestion, and inhalation of vapors diffusing from soil surfaces, a third set of soil levels was developed. In terms of documented TNT and RDX contamination, performance of the treatment plan should suffice to prevent any significant health hazard from TNT and RDX during such future activities.

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1.0 INTRODUCTION

The Louisiana Army Ammunition Plant (LAAP) is a shell manufacturing and explosives load, assembly, and pack (LAP) facility located about 20 miles east of Shreveport, LA. From about 1951 to 1980, wastewaters were trucked to and discharged into a series of artificial leaching pits at a site known as "Area P." The sediments and the underlying soils in the pits have become highly contaminated with explosive residues, as has topsoil at the site. Moreover, explosives and related chemicals have been detected in groundwater below this area. Area P is shown relative to LAAP in Figure 1. The water surface area of the pits covers about 375,000 ft^2 (about 8.6 acres or 3.5 ha); the entire Area P, as indicated by the outline in Figure 1, amounts to 18 acres[1].

The Army plans to treat contaminated soil and sediments from Area P by incineration. The pits will then be filled in and the entire area graded to conform with undisturbed surroundings. A formal plan to this effect[1] was initially prepared in conformance with the Louisiana Hazardous Waste Management Plan[2] by the U.S. Army Toxic and Hazardous Materials Agency (USATHAMA). The plan called for removal of up to the top five feet of soil under the pits proper and the top foot of soil in the surrounding portions of Area P. Moreover, as the excavation proceeded, soil samples would be taken to determine whether excavation of pit soil to the planned five foot depth was required. In 1987, USATHAMA requested an evaluation of this plan with respect to health effects. The present report documents this evaluation.

2.0 SITE SPECIFIC INFORMATION

The groundwater and soils at LAAP have been studied several times; Wirth[1] reviewed studies since 1979. A remedial investigation of selected disposal and burning sites at LAAP[3] focused upon groundwater contamination and aquifer flow patterns. From these reports, the following can be concluded:

o The groundwater contaminants involved are, in terms of common-use acronym and chemical names:

RDX	Cyclotrimethylene trinitramine
HMX	Cyclotetramethylene tetranitramine
TNT	2,4,6-Trinitrotoluene
TNB	1,3,5-Trinitrobenzene
DNB	1,3-Dinitrobenzene
NB	Nitrobenzene
2,4-DNT	2,4-Dinitrotoluene
2,6-DNT	2,6-Dinitrotoluene
Tetryl	N-Methyl-N,2,4,6-tetranitroaniline

o Soil beneath the pits has been assayed only for the explosives RDX and TNT. A plot of RDX and TNT concentrations versus depth, which the author believes represents the contamination situation in the pits, is shown in Figure 2. Such information must be

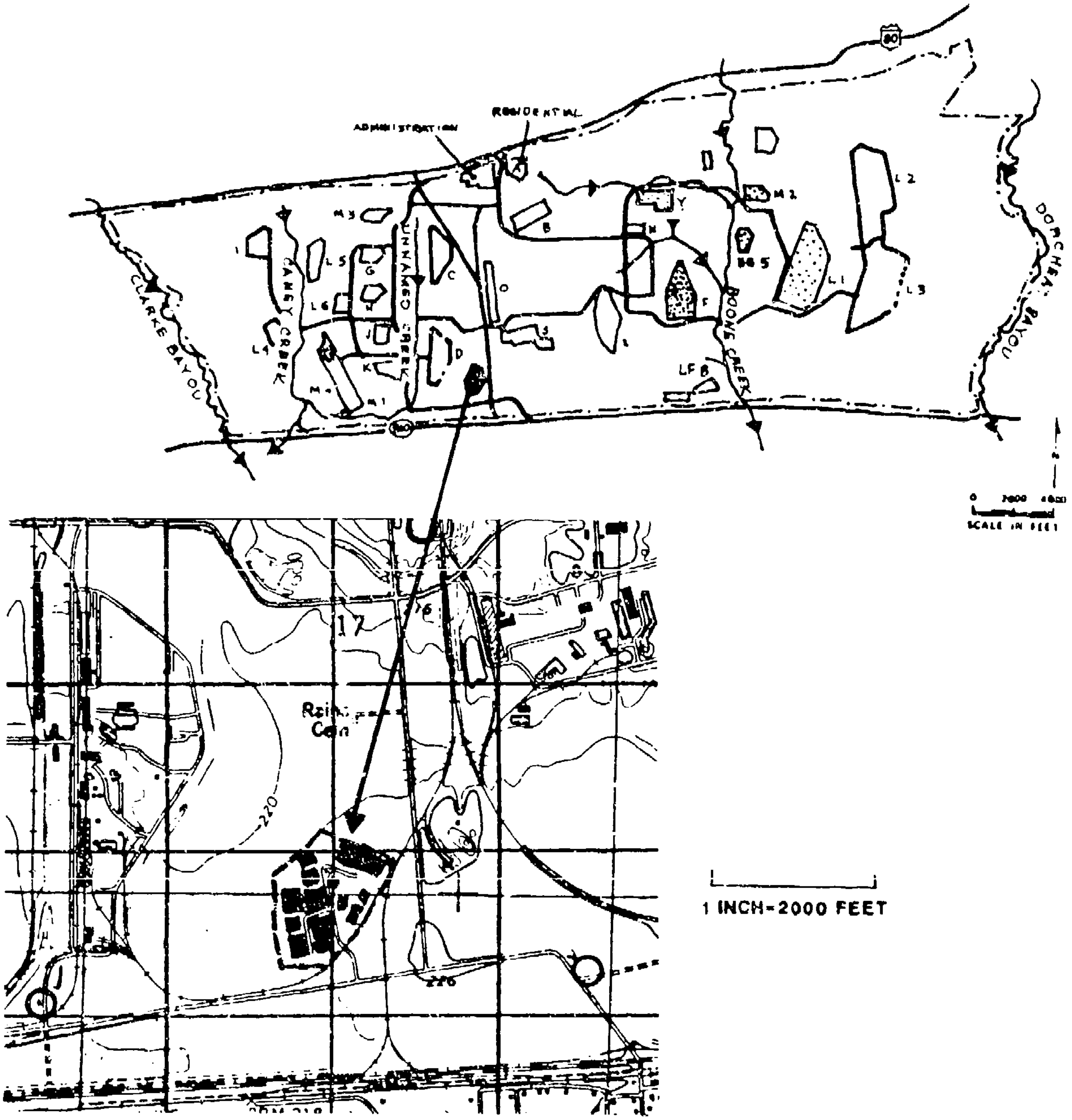

Figure 1 Louisiana Army Ammunition Plant With Detail of Area P in Inset

viewed with caution, since the uppermost sediment "soil" may contain particulate TNT and RDX, analysis of which might overstate the actual concentrations of explosives intimately mixed in soil. Moreover, the assays were performed on grab samples, which for some depths below grade, were obtained at one pit. Soil contamination could extend to the water table, which is about 6 m deep vs. the 1.5 m maximum depth from which soil was sampled.

o Several aquifers lie below the pits. The uppermost is called the Alluvial aquifer. It is relatively shallow, and may be regionally discontinuous. Below the Alluvial aquifer is the Sparta Sand aquifer. This is a recognized regional aquifer to the east of LAAP, but its extent below LAAP is conjectural. Its identification at Area P is based upon the similarity of soil cores to known Sparta Sand aquifer descriptions. Groundwater in these aquifers contains the substances listed above; see Appendix A for assays. Below them is the Wilcox aquifer. LAAP and the near-by town of Doyline use the Wilcox aquifer for their water supplies, and the substances listed above have not contaminated it[4]. The Wilcox aquifer is shielded from the other aquifers by an effective (100-200 feet thick) clay layer[3].

o To the extent that regions of contaminated groundwater (plumes) can be defined, groundwater beneath the pits is contaminated with several explosives. The local groundwater flow appears to be directing plumes towards the west in the Alluvial aquifer and to the southwest in the Sparta Sand aquifer. The average flow rate in the Alluvial aquifer was estimated to be 32 feet/year; in the Sparta Sand aquifer, 12 feet/year[3]. The flow fields beyond the LAAP border are not well-defined.

o Surface waters from Area P are directed to ditches, which in turn, discharge to the "Unnamed Creek" in Figure 1. The soils in these ditches contain TNT and RDX, as do surface soils in the vicinity of the pits. Assay data supporting these assertions appear in Appendix A.

The assessments below relate to a planned remedial action at an active ammunition plant. The action is subject to State of Louisiana regulations[2] related to the Resource Conservation and Recovery Act. These rules mandate that, in addition to any land renovation plans, certain groundwater surveillance and treatment procedures will be required[*]; the extent of these will have to be

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[*] From section 23.34 of the Louisiana Plan[2], "The owner...must implement a groundwater monitoring program capable of determining the facility's impact on the quality of groundwater in the uppermost aquifer underlaying the facility..." Further, from section 23.45, "Post-Closure care must continue for 30 years after the date of completing closure..."

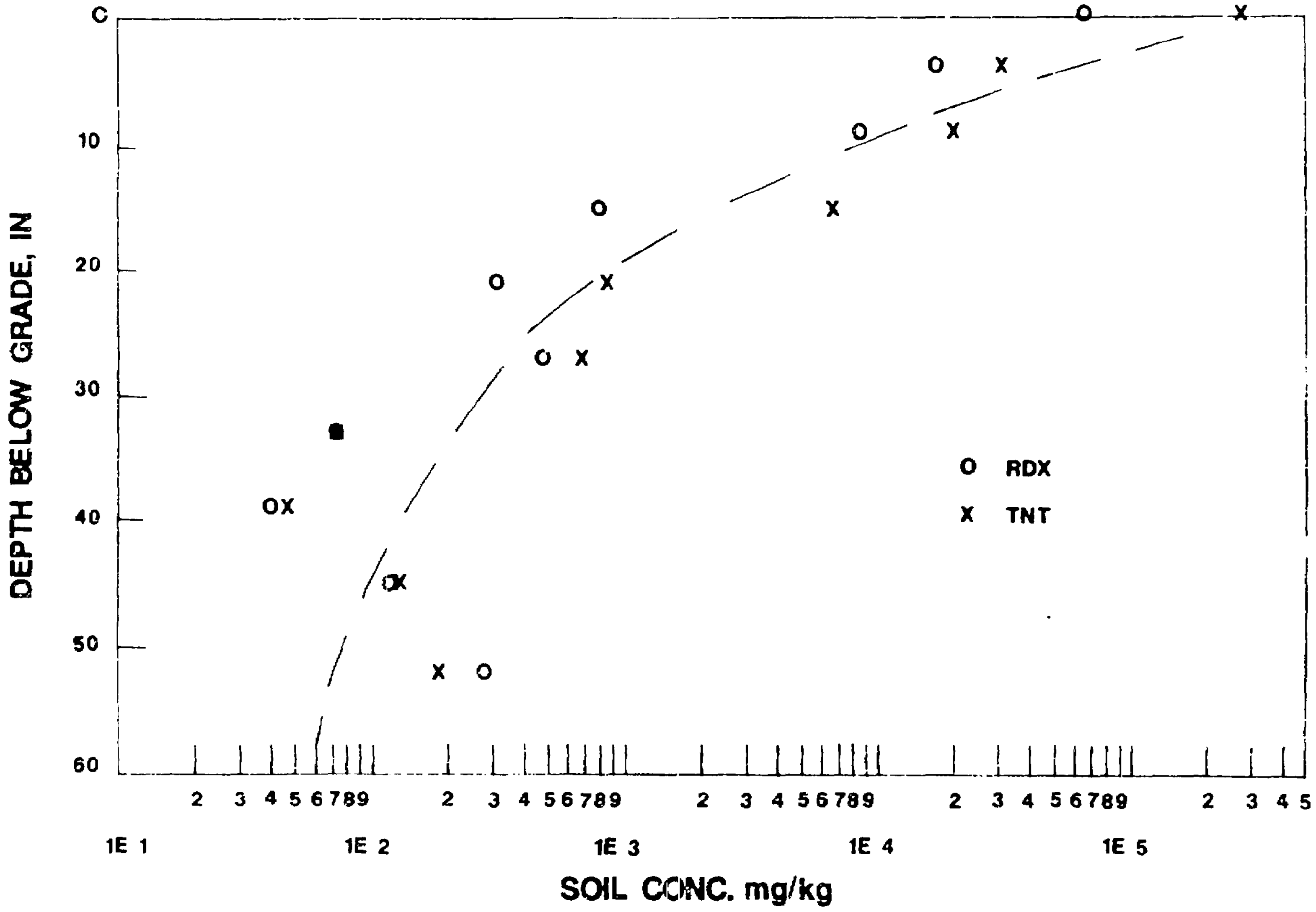

Figure 2 Composite Sludge/Soil Assays for RDX and TNT in Area P Pits (From Data in Reference 3).

negotiated between LAAP and the State of Louisiana. The Commander, LAAP is responsible for the plan within the context of his mission; USATHAMA has a consultative role. Other projects may have to be undertaken to minimize hazards from Area P to health and the environment during and after pit closure. A detailed discussion of these is outside the scope of this report.

3.0 CONCEPTUAL APPROACH

Three scenarios were evaluated from either a health or an environmental effects viewpoint: groundwater as a drinking water supply; aquatic life maintenance in streams; and construction activities at Area P. For each scenario and each explosive, a soil limit was sought that would prevent deleterious effects. These limits could then be compared to recent data on soil contamination to determine whether remedial efforts were needed, and when practical, the extent of such efforts.

The drinking water scenario posed a problem, since the sources of contamination were expected to be at depths lower than those planned for excavation. Thus, the strategy undertaken was to determine a soil limit for each contaminant, one that would permit use of any portion of groundwater in the Alluvial aquifer as a drinking water source (called a DCSL). If the contaminant level in soil continued to decrease with increasing soil depth as suggested in Figure 2, DCSLs would indicate the limit to which excavation was necessary. With respect to replacement soil that had been treated, DCSLs would indicate an allowable residual level. The approach undertaken to determine DCSLs is summarized in Section 5.0.

In a like manner, an aquatic life safety-related contaminated soil limit (ACSL) was sought for each compound, to avoid toxic effects to aquatic biota in "Unnamed Creek" from Area P run-off. The limits would pertain to the surface soils either currently at Area P (if the limits were higher than explosive concentrations in such soils, the soils could be left undisturbed) or to replacement soil. The approach used and ACSLs obtained are in Section 6.0.

The last scenario was evaluated to determine a set of limits (CCSLs) to protect future construction workers should development occur at Area P. These would apply to the soil strata above the Alluvial aquifer, since one consequence of construction would be to expose sub-surface soil to the atmosphere and allow contaminants in this soil to vaporize into the ambient air, which would be inhaled by workers. The approach taken and CCSLs developed are summarized in Section 7.0.

4.0 TOXICOLOGICAL INPUTS

Table 1 shows limits for human intake and aquatic safety. The reference doses (RD) presented are based on lifetime exposure to contaminants. With the exception of 2,4- and 2,6-DNT, RD values are predicated on the avoidance of adverse toxic effects. The values for RDX and TNT differ from those in the recent study concerning Cornhusker Army Ammunition Plant[5]. The documentation and explanation for these limits appears in Appendix B.

The 2,4-DNT RDs are based on Environmental Protection Agency (EPA) developed values for carcinogenic potency[6], derived from two-year bioassays with rodent species. More recent work (see Appendix B) suggests that 2,6-DNT, which was an impurity in the 2,4-DNT, is an even more potent potential carcinogen. The values given in Table 1 for 2,6-DNT are tentative. The EPA considers carcinogencity an adverse effect for which there is no threshold; avoidance would be attained only by the absence of the carcinogen in drinking water. A more practical approach has been to pre-specify acceptable risk levels (ARL). These correspond to an expected additional risk for incidence of cancer within a 70-year lifetime to a person exposed to a constant dose level. The EPA guidance is to evaluate remedial efforts in terms of providing ARLs from 10^{-7} to 10^{-4}[6].

With the exception of 2,4-DNT, no compounds in Table 1 have been formally evaluated by the EPA[6]. For toxicants, the RDs are based on toxicological information assessments similar to those that the EPA has employed in evaluating similar information, or when not possible, in a manner considered reasonably prudent. A drinking water limit (DWL) is based on an RD and the consumption of 2 L/day of water by a 70 kg adult.

Aquatic life safety-related water limits (ASWLs) are estimates of maximum allowable concentrations in water that preclude adverse toxic effects to aquatic species. With the exception of TNT, 2,4-DNT, and RDX, the background information (see Appendix B) is rather tenuous, and ASWLs are tentative.

5.0 SOIL LIMITS BASED ON GROUNDWATER POTABILITY

Groundwater quality has been locally degraded in the upper aquifers of LAAP. This is evident by comparing DWLs from Table 1 to sample data in Table A-1, Appendix A. Figure 3 shows the estimated RDX plume in the Alluvial aquifer based on the assays shown in Table A-1. The area in which RDX concentrations exceed 100 ug/L (about the RDX DWL) is shaded. If a well existed at the downgradient edge of this plume, drinking water quality could be impaired for decades. For example, the major axis of the 100 ug/L isopleth (assumed to be an ellipse) is about 600 m; passage of this portion of the plume at 10 m/year without dilution would take 60 years.

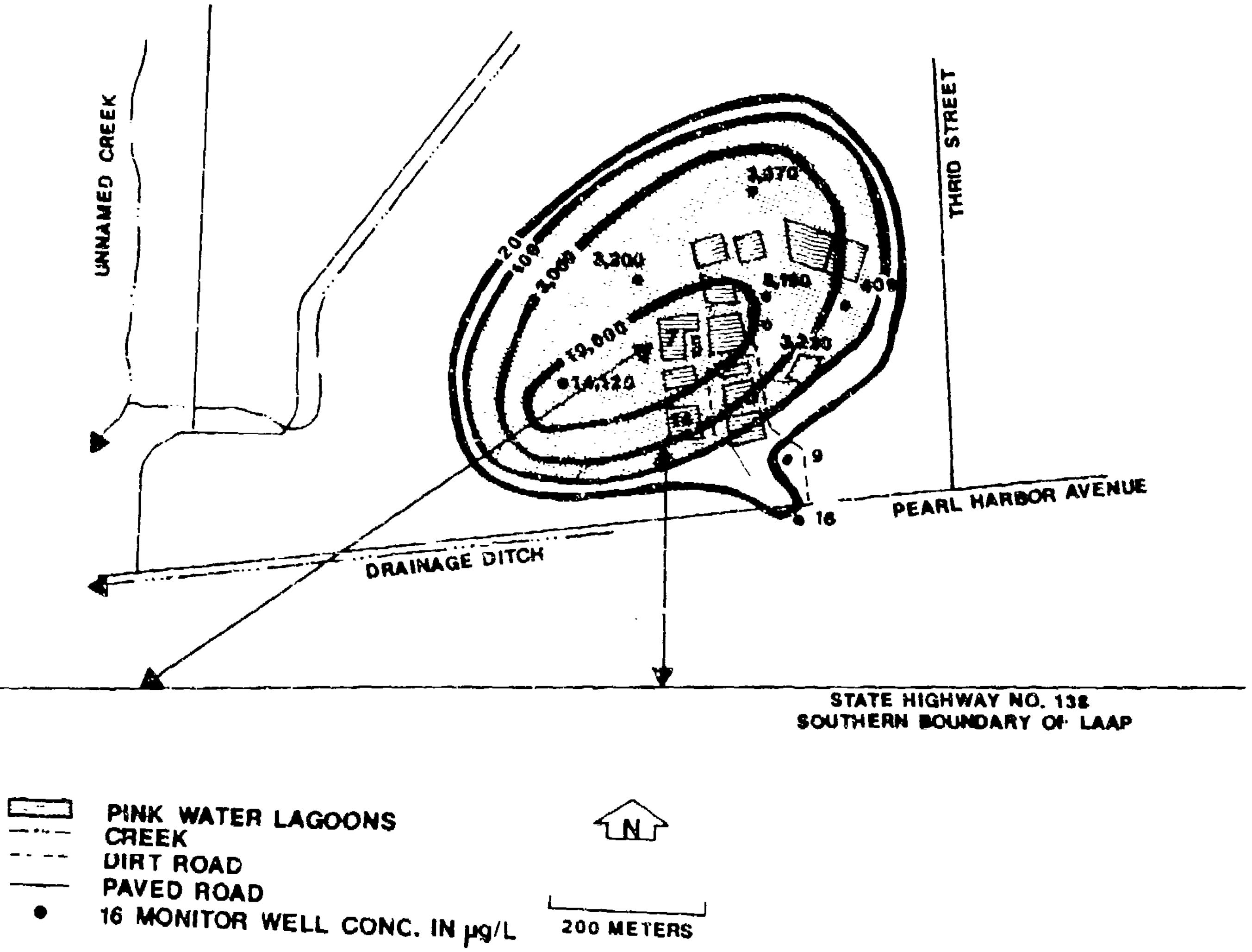

Figure 3 Estimated RDX Plume in Alluvial Aquifer. Isopleths in µg/L (Ref.3)

Table 1. Reference Doses and Maximum Allowable Concentrations in Water for Explosive Contaminants at LAAP.

Compound	RD µg/kg/day[a]	DWL µg/L[a]	ASWL µg/L
RDX	3.0	103	103
HMX	10	350	N/D
TNT	4.0	140	540
TNB	2.5	87	3
DNB	1.0	35	26
NB	5.0	175	430
2,4-DNT	3.1×10^{-4} (10^{-7} ARL)	0.011	200
	3.1×10^{-3} (10^{-6} ARL)	0.11	
	3.1×10^{-2} (10^{-5} ARL)	1.1	
	3.1×10^{-1} (10^{-4} ARL)	11	
2,6-DNT	5.2×10^{-5} (10^{-7} ARL)	0.0018	100
	5.2×10^{-4} (10^{-6} ARL)	0.018	
	5.2×10^{-3} (10^{-5} ARL)	0.18	
	5.2×10^{-2} (10^{-4} ARL)	1.8	
Tetryl	1.5	53	N/D

a. RD and DWLs correspond to acceptable risk level (ARL) shown for DNTs.

For purposes of evaluation, the line beyond which drinking water quality should be maintained was open to interpretation. Since the groundwater flow parameters are not well-defined, particularly with respect to direction, three different boundary situations were defined.

(1) A line 50 m west of the edge of pits 7 and 14 (see Figure 3). This would approximate the western (downgradient) edge of Area P.

(2) The LAAP boundary at closest approach to the Area P pits. Since LAAP will continue to operate for the foreseeable future, the Army can exercise control over groundwater use within its borders. Beyond its boundary, no such control could be maintained. This boundary could be of concern if the present direction of groundwater flow were altered, such as by removal of the pits as aquifer recharge. From Figure 3, the distance from the southern edge of Pit 14 to the LAAP boundary is about 350 m.

(3) The LAAP boundary based on continuation of plume movement in the current direction at current speed. Figure 3 shows the estimated extent of the RDX contamination plume in excess of 20 ug/L in the Alluvial aquifer. As shown in this figure, the distance along a line drawn through the apparent major axis of this plume from the western edge of the pits to the intersection with the property boundary is about 800 m.

A two-step simulation model was developed to link DWLs to DCSLs. The model applies to a post-remediated area. First, the introduction of pollutant to groundwater under the portion of Area A now occupied by pits is simulated; the geometry of the simulation appears in Figure 4. Initially, the soil in the unsaturated soil column that would occupy the area of the pits has a uniform concentration of 1 mg of pollutant per kg of soil. The pollutant is leached from the lower portion of the unsaturated soil column (LPUSC) to groundwater as a result of seasonal changes in the Alluvial aquifer water table. The pollutant also transfers from the upper portion of the unsaturated soil column (UPUSC) to the LPUSC by infiltration, which partially replenishes LPUSC contamination levels. The end product of the simulation is a concentration-time profile of the pollutant in groundwater exiting Area P. The details are discussed in Appendix C.

The second step of the model simulates mass transport in groundwater from the leaching processes discussed above to more distant points. Diffusion and advection effects are involved. The end result of this step is a time-concentration profile of a contaminant at a boundary point. A 70-year period within this profile is chosen to determine a lifetime-averaged concentration (LAC). The LAC corresponds to an initial 1 mg/kg contaminant level in soil. The ratio of DWL to LAC is the DCSL, since the LAC is based on an initial unit soil content of contaminant.

The partition coefficient between soil and water, Kd, governs the leaching of explosive compounds from soil in the pits. The Kd values used in this analysis are shown in Table 2; their sources or derivations appear in Appendix C. The explosives in soil and in the aquifer are treated conservatively; none is chemically transformed.

The computed DCSLs appear in Table 3. They are a function of distance to a boundary, advection, and diffusion effects. The DCSLs for the major explosives RDX and TNT approach detection limits only for the 800 m boundary case. Moreover, the DCSLs are considerably below soil concentrations indicated in Figure 2. Since the DCSLs presume an initial uniform concentration profile in soil, one concludes that planned removal of the top five feet of soil in the pits won't remove the effective source of groundwater contamination; other measures would have to be employed to treat the groundwater to provide a potable supply at the boundary.

A sensitivity analysis was performed to gauge how the DCSL for TNT at the 350m boundary would vary with reasonable alternate values of different input parameters. The results are summarized in Table 4. Generally, the replacement of a model input by an alternate value within the ranges shown alters DCSLs by less than 50 percent, which is not considered a very wide range. The analysis was not extended to multiple variate alternatives.

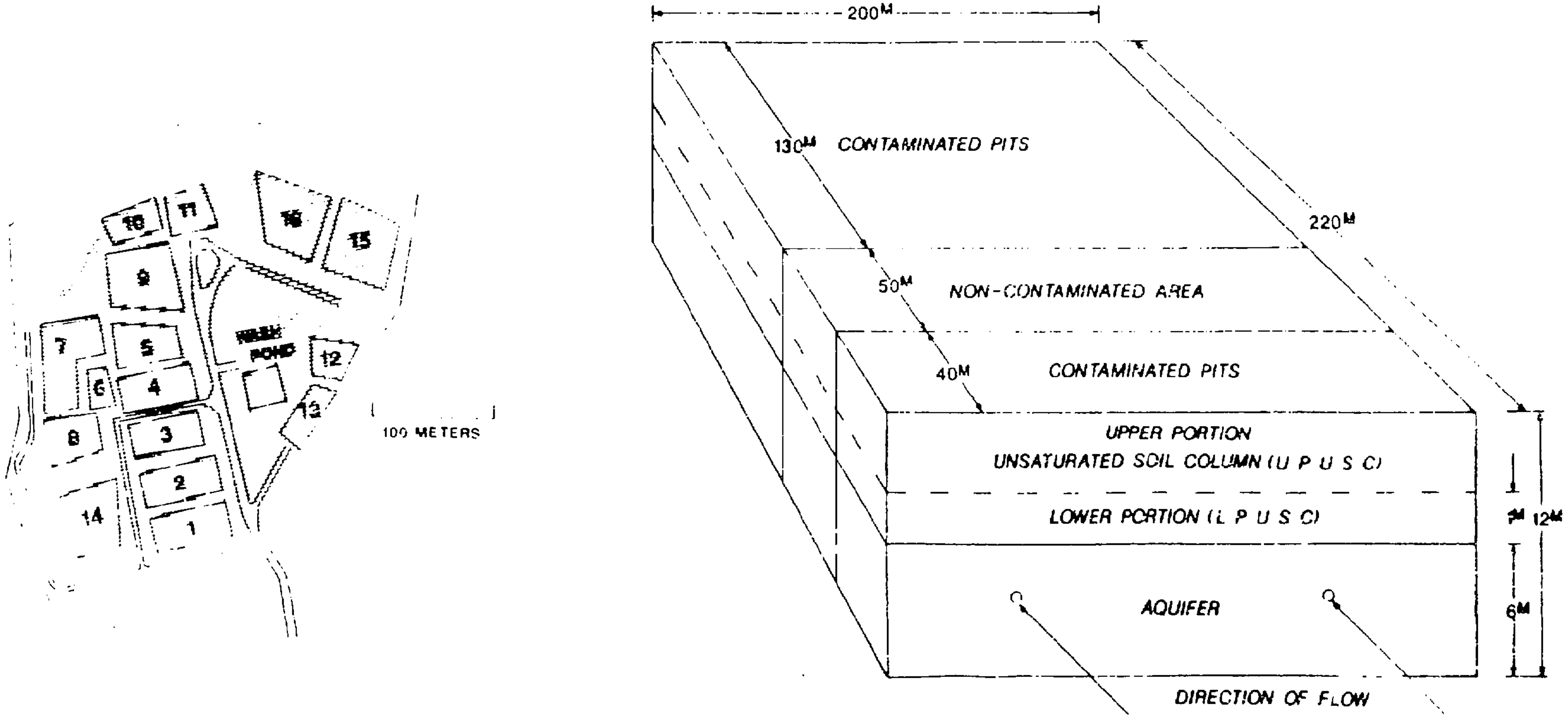

Figure 4 Modeled Portion of Area P (left) and Model Representation (right)

Table 2. Soil Detection Limits and Kd Factor for Explosives

Compound	Detection Limit, mg/kg soil[3]	Kd, L/kg
RDX	0.8	1.58
HMX	1.4	2.42
TNT	1.0	1.069
TNB	0.6	0.605
DNB	0.6	0.225
NB	0.6	0.53
2,4-DNT	0.6	0.504
2,6-DNT	0.6	0.504
Tetryl	0.8	0.637

Table 3. Drinking Water Quality-Related Contaminated Soil Limits

Compound	DCSL, mg/kg		
	50 m	350 m	800 m
RDX	0.38	0.52	0.73
HMX	1.6	2.2	3.1
TNT	0.43	0.58	0.82
TNB	0.20	0.27	0.38
DNB	0.047	0.064	0.091
NB	0.38	0.51	0.71
2,4-DNT (10^{-7} ARL)	2.3×10^{-5}	3.1×10^{-5}	4.4×10^{-5}
(10^{-6} ARL)	2.3×10^{-4}	3.1×10^{-4}	4.4×10^{-4}
(10^{-5} ARL)	2.3×10^{-3}	3.1×10^{-3}	4.4×10^{-3}
(10^{-4} ARL)	0.023	0.031	0.044
2,6-DNT (10^{-7} ARL)	4.0×10^{-6}	5.4×10^{-6}	7.6×10^{-6}
(10^{-6} ARL)	4.0×10^{-5}	5.4×10^{-5}	7.6×10^{-5}
(10^{-5} ARL)	4.0×10^{-4}	5.4×10^{-4}	7.6×10^{-4}
(10^{-4} ARL)	4.0×10^{-3}	5.4×10^{-3}	7.6×10^{-3}
Tetryl	0.13	0.17	0.24

6.0. SOIL LIMITS BASED ON AQUATIC LIFE PROTECTION

In this analysis, Area P is viewed as part of the Unnamed Creek watershed. This creek is taken as the waterway of concern; it was found to have fish life in the early 1970s[7] when the pits were in active use. Moreover, discharge permits have been issued for point discharges[8] to Unnamed Creek.

The relationship used to estimate an ACSL is

$$ACSL = ASWL * Kd / fw$$

Table 4. Sensitivity Analysis Summary for TNT at the 350 m Boundary

Changed variable	Model value	Alternate value range	Alternate DCSL range, mg/kg[a]
None			0.58
Kd	1.069	0.504 - 2.42	0.39 - 0.87
Infiltration	2 cm/year	0.1 - 7	0.88 - 0.32
Water table rise/fall	1 m	0.5 - 1.5	0.79 - 0.46
Dispersivities	9, 30 m[b]	3,10 - 20,100	0.43 - 0.74

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a. Values correspond to range limits in order shown.
b. Transverse and axial dispersivities in order

where fw is the fraction of the Unnamed Creek watershed area occupied by Area P. This relationship assumes that: (1) there are no other sources of pollutant in the watershed; (2) mixing of run-off flow from Area P and of creek water is rapid; (3) the run-off per surface area of Area P will be the same as in other parts of the watershed.

The Kd values listed in Table 2 are used in calculations. These Kd values are based on either direct measurements in or extrapolations from measurements in sandy soils. Existing surface soils at LAAP generally are silty or clayey, and Kd determinations in these soils are higher than in sandy LAAP soil[9]. However, the soil types at the surface after treatment may not necessarily be those existing now. Thus, selection of the sandy soil Kd as a basis for ACSLs is a safe-sided measure.

The factor fw was determined from an analysis of contour lines on a 1:24000 topographic map of LAAP to identify the Unnamed Creek watershed area above the intersection of flow from Area P to the creek and the portion of this watershed occupied by Area P. Figure 5 indicates both these areas; fw is estimated to be 0.044.

Table 5 provides the calculated ACSLs. Wirth[1] presents some surface soil (0 to a maximum of 24 inch deep samples) assay data of TNT and RDX in Area P; see Table A-2 in Appendix A. Generally, then-existing contamination levels exceeded these ACSLs. Thus, if aquatic species safety were a clean-up criterion, considerable clean-up of surface soils at Area P would be required. The plan had provided for removal and treatment of the top foot of soil in portions of Area P outside the pits proper. The ACSL analysis indicates that this should be done. Soil contamination in excess of ACSLs below a one-foot depth is not expected to be deleterious to aquatic life, since the provision of ground cover (which is also part of the plan) should limit leaching from this soil to

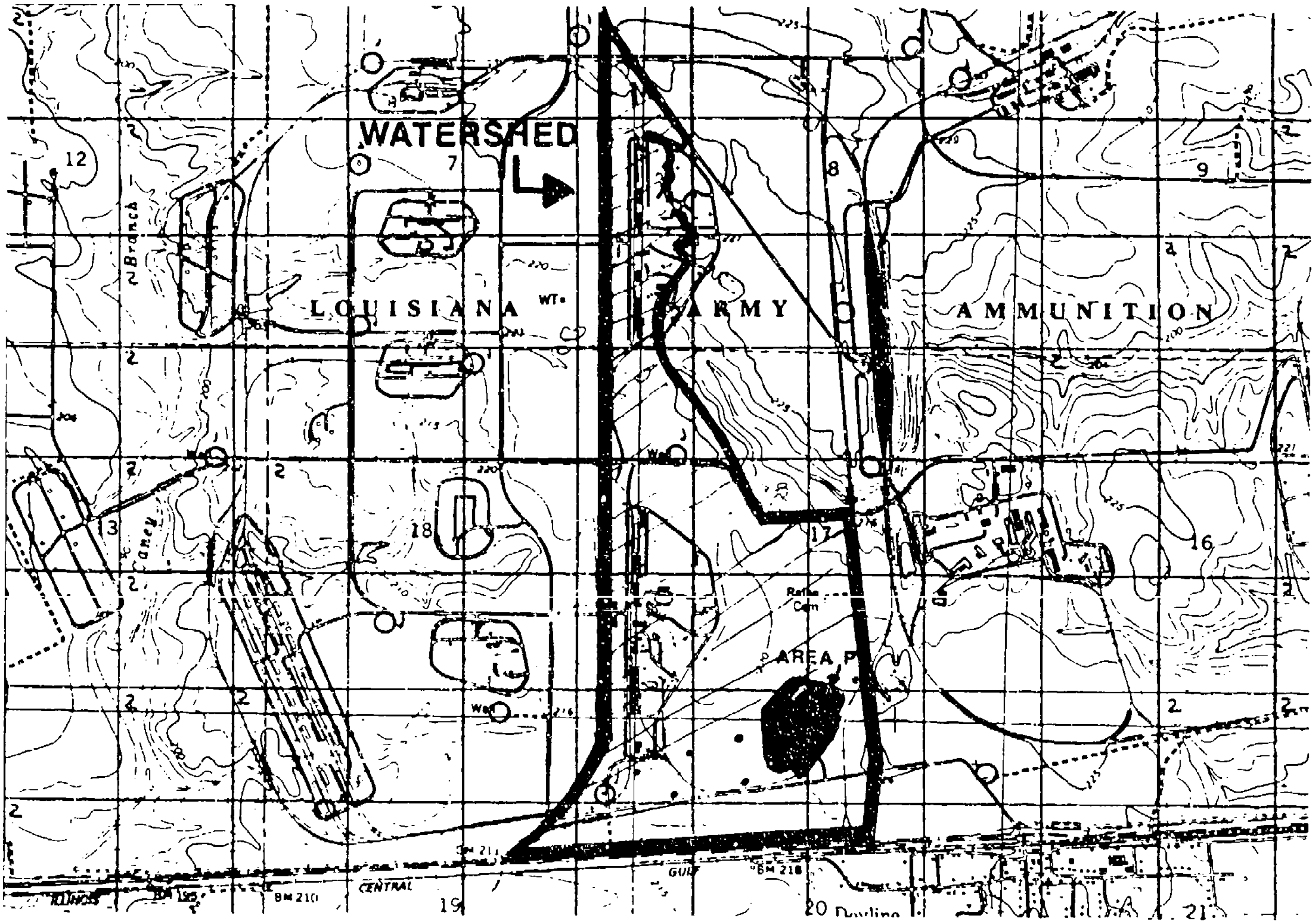

Figure 5. Unnamed Creek Watershed To Intersection With Area P Drainage Ditch

run-off. The ACSLs for TNB and DNB are less than detection limits. Moreover, the levels of these substances in surficial soil has not been determined. A surrogate analyte might be developed, but soil assays would be required to validate it.

7.0 SOIL LIMITS BASED ON PROTECTION OF CONSTRUCTION WORKERS AT AREA P

This scenario deals with hypothetical excavation and construction at Area P, after clean-up and restoration has been completed. On-site workers can inhale explosive-containing dust disseminated by these activities, particularly during dry periods of weather. Moreover, they can ingest particulates incidentally (by eating, smoking or involuntary tongue movement). Although most of the contaminants at Area P are not particularly volatile, sufficient concentrations in breathable air might be attained as a result of diffusion from soil. CCSLs were desired to avoid adverse effects from such exposures.

The CCSLs were based on several high exposure condition assumptions, considered conservative in that they would be expected to lead to lower allowable soil levels than alternative conditions. Workers would ingest or inhale, on a time-averaged basis, 207 mg of particulate matter. About two-thirds of this would be inhaled, the rest ingested. Moreover, they would be located in the center of an area approximately the size of one Area P pit. This locale would be excavated so that a new layer of soil would be exposed daily, and vapors diffusing from the soil could be inhaled. The workers would be exposed to such conditions for 15 months. The details of the assumptions and the computation involved are discussed in Appendix D. The CCSLs estimated are shown in Table 6.

Table 5. Aquatic Life Safety-Related Contaminated Soil Limits

Compound	ACSL, mg/kg
RDX	4.1
HMX	Not determined
TNT	13
TNB	0.041
DNB	0.13
NB	5.2
2,4-DNT	2.3
2,6-DNT	1.1
Tetryl	Not determined

Table 6. Construction Worker Health-Related Contaminated Soil Limits

Compound	CCSL, mg/kg
RDX	1010
HMX	3380
TNT	1080
TNB	550
DNB	34
NB	97
2,4-DNT	6.8[a]
2,6-DNT	0.63[a]
Tetryl	510

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a. CCSL corresponds to ARL of 10^{-6}.

These CCSLs are generally less restrictive than for the other scenarios, which illustrates the need to carefully consider the modes of exposure proposed in assessments. Based on soil TNT and RDX assays presented in Wirth[1], these CCSLs could be attained with excavation and treatment of soils in the pits proper to a depth of about two feet, and probably of drainage ditches and surface "hot spots" elsewhere. With the exception of 2,6-DNT, these CCSLs are well above detection limits. It should be kept in mind that the information used in their derivation is rather "soft".

8.0 SUMMARY AND CONCLUSIONS

A plan has been[1] proposed to remove and treat the uppermost levels of soil at Area P of LAAP. This report examines the question as to whether the plan's implementation would leave contamination in Area P that would be detrimental to: possible use of the Alluvial aquifer below Area P as a drinking water source; aquatic life in Unnamed Creek, to which run-off from Area P drains; and the health of future construction workers at Area P, who could be harmed by residual levels of explosives. The report also attempts to determine whether a less extensive excavation effort might suffice to meet health and environmental concerns.

Baseline estimates of the contaminated groundwater plume size and extent for each substance of concern had been developed in a remedial investigation[3]. In terms of health effects, water in these plumes would not be safe to drink. A DCSL was determined for each substance of concern, an initial level of soil contamination beneath the pits that should prevent groundwater from being unduly contaminated. These DCSLs are in Table 3. Contamination at the five-foot depth, and probably at lower depths, based on projections from contamination profiles in soil beneath the pits (Figure 2), exceeds these DCSLs. Area P may continue to be a source of contamination to the extent that Alluvial aquifer groundwater could not be used without treatment as a drinking water source.

ACSLs were developed on the premise that contaminated surface run-off from Area P would mix with clean run-off from the rest of the watershed of Unnamed Creek, and that aquatic life below this juncture would be protected from adverse effects of the contamination. The resulting ACSLs, Table 5, are criteria for possible removal of surface contamination in unexcavated portions of Area P. On the basis of available information for RDX and TNT, treatment of the surface soil as planned should suffice.

CCSLs were developed for a hypothetical construction project judged to lead to higher exposure levels to worker than would realistically occur. The CCSLs in Table 6, at least on the basis of TNT and RDX soil assays, indicate that the plan would leave an Area P that would not pose a health hazard to construction workers.

9.0 SUBSEQUENT DEVELOPMENTS

Reference 24 (see Appendix B) was issued as a final report in August 1987. Therein, a carcinogenic potency for 2,6-DNT was estimated to be 4.83 $(mg/kg/day)^{-1}$ based on studies reported by Popp and Leonard[22] (see Appendix B). This would indicate a potency about 2.5 times higher than that used in the report, with corresponding reductions in the 2,6-DNT DCSL and CCSL by a factor of 2.5. While the evidence points to 2,6-DNT being the prime agent in tests that indicated that 2,4-DNT was a potential carcinogen, this is not an accepted position, and 2,4-DNT is still considered a potential carcinogen.

A draft in-depth review of DNB (and other explosives) has been recently received (Layton, D., B. Mallon, W. Mitchell, L. Hall, R. Fish, L. Perry, G. Snyder, K. Bogen, W. Malloch, C. Ham, and P. Dowd. 1987. Data-Base Assessment of the Health and Environmental Effects of Conventional Weapons Demilitarization and Their Co-Contaminants. Lawrence Livermore National Laboratory, Livermore, CA). It details an oral ingestion study (Cody, T.E., S. Witherup, L. Hastings, K. Stemmer, and R.T. Christian. 1981. 1,3-Dinitrobenzene: toxic effects _in vivo_ and _in vitro_. _J. Toxicol. Environ. Health_ 7:829-847.) in which rats were given DNB in drinking water for 16 weeks. Male rats had increased spleen weight and wheel-running activity at the lowest dose (estimated at 0.4 mg/kg-day) while female rats showed increased ovary weight at the lowest dose (estimated at 0.5 mg/kg-day). The review uses these data to develop a RD of $6x10^{-4}$ mg/kg-day. Toxicology studies are being programmed for DNB and TNB that will include a 90-day feeding test.

The State of Louisiana has accepted the USATHAMA plan[1] as an interim measure. The plan calls, after soil treatment, for grading and placement of a seeded clay soil cover over Area P. This cover should minimize infiltration of surface water to the aquifers. Future construction projects at Area P are expected to involve a minimum of excavation, so as not to disrupt this cover. Such projects should take less than the estimated 15 months to complete. The allowable doses set herein should be acceptable for shorter-term projects.

APPENDIX A. GROUNDWATER AND SURFACE SOIL ASSAYS AT LAAP

Table A-1 provides groundwater assays at monitor wells at Area P. The information is taken from Table 5-3 of the remedial investigation[3]. Figure A-1 shows the well location relative to the Area P surface features.

Table A-2 provides surface soil and surface drainage sediment assays taken in non-excavated areas of Area P. The information is from the Area P plan[1]. Figure A-2 shows the sample locations. It should be stressed that the results are from assays taken between 5 and 10 years ago; the documentation is confusing as to when the analysis was performed. Moreover, analytical detection limits appear to be higher than those cited in Table 2, main text.

Table A-1. Groundwater Assays at LAAP for TNT and RDX-related Contaminants[3]

Alluvial Aquifer Wells

	Concentration, µg/L of Cited Analyte								
Well	HMX	RDX	TNT	TNB	DNB	NB	2,4-DNT	2,6-DNT	Tetryl
G009	34	409	134	85	BDL*	BDL	BDL	BDL	BDL
G010	3.2	9.0	BDL	BDL	BDL	BDL	BDL	1.6	BDL
G011	199	3200	1860	14	195	BDL	75	29	4.1
G012	86	3670	3060	242	64	BDL	89	18	6.2
G014	4.7	16	BDL	2.0	1.4	BDL	BDL	BDL	BDL
G034	BDL	BDL	BDL	0.8	1.1	BDL	BDL	2.4	BDL
G068	2200	8190	5670	206	7.6	BDL	48	2.1	53
G104	4200	14100	18400	7720	BDL	BDL	BDL	BDL	BDL
G111	BDL	BDL	BDL	3.1	BDL	BDL	BDL	BDL	BDL
Sparta Sand Wells									
G097	13	1.2	15	8.2	BDL	BDL	BDL	BDL	BDL
G100	5.2	24	4.1	3.4	1.2	BDL	2.4	4	1.4
G103	BDL	35	BDL	BDL	BDL	BDL	BDL	BDL	BDL
G105	BDL	BDL	BDL	2.2	2.5	BDL	BDL	4.6	BDL
G107	BDL	4.3	2.5	1.0	BDL	5.2	BDL	BDL	BDL
G108	76	184	1410	74	23	45	176	4.6	BDL
G109	1750	3230	BDL	21	BDL	BDL	16	BDL	1.5
G110	56	785	604	75	20	BDL	95	12	BDL
G112	BDL	5.1	BDL	1.7	BDL	BDL	5.3	10	BDL
G136	7.6	14	BDL	1.7	BDL	BDL	BDL	BDL	BDL
G137	BDL	7.3	BDL	4.1	BDL	BDL	BDL	BDL	BDL
G138	BDL	1.3	BDL	1.4	BDL	BDL	BDL	BDL	BDL
G139	3.1	8.6	BDL	BDL	BDL	BDL	BDL	BDL	BDL

---

* Below detectable limits

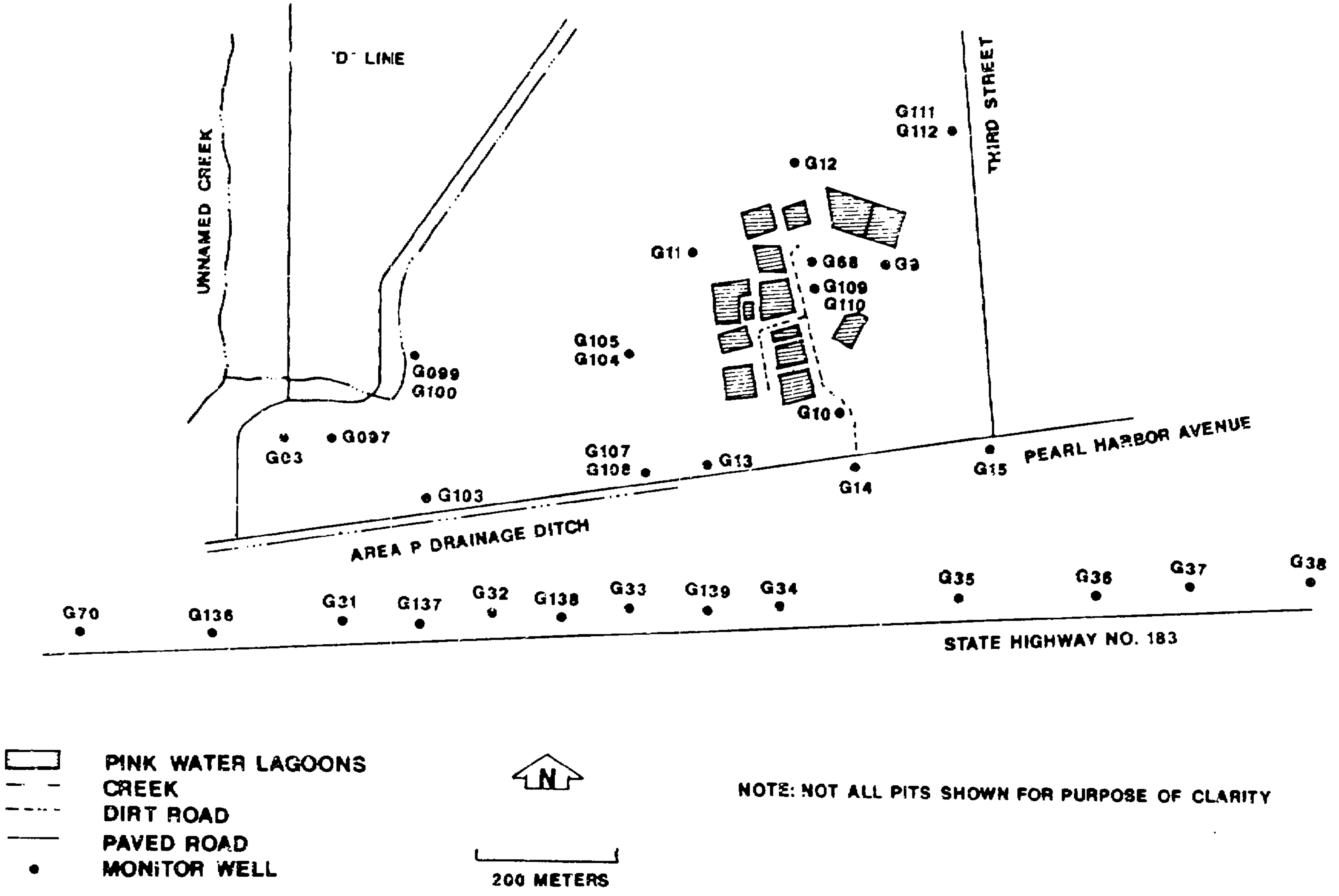

Figure A-1 Monitor Well Locations at Area P

Table A-2. Surface Soil and Drainage Sediment Assays at Area P.[1]

Sample	Concentration in mg/kg* TNT	 RDX
Site 1, 0 - 6 inch sample	3	30
6 -12 inch sample	92	19
Site 2, 0 - 6 inch sample	<10	<5
6 -12 inch sample	<10	<5
Site 3, 0 - 6 inch sample	12	15
Site 4, 0 - 6 inch sample	13	17
6 -12 inch sample	1033	602
12 -18 inch sample	51	20
Site 5, 0 - 2 inch sample	10	15
Site 6, 0 - 2 inch sample	45	55
Site 7, 0 - 2 inch sample	66	130
Site 8, 0 - 2 inch sample	no data	115
Site 9, 0 - 2 inch sample	76	86
Site 10,0 - 6 inch sample	7	23
6 -12 inch sample	5	3
Site 11,6 -12 inch sample	47	33
Site 13,0 - 6 inch sample	no data	15
Site 14,0 - 6 inch sample	12	27
Site 15,0 - 2 inch sample	15	23
Site 16,0 - 2 inch sample	no data	9
Site 17,0 - 2 inch sample	12	17
Site 18,0 - 2 inch sample	53	108
Site 19,0 - 2 inch sample	29	27
Ditch site 20, 0 - 6 inch sample**	101	23
6 -12 inch sample	171	218
12 -18 inch sample	19	17
Ditch site 21, 0 - 6 inch sample***	19	10
6 -12 inch sample	10	no data
12 -18 inch sample	9	5
18 -24 inch sample	96	92
Ditch site 22, 0 - 6 inch sample***	992	157
6 -12 inch sample	13	11

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* Reported in μg/L terms in reference

** Located approximately 140 m west of Area P along drainage ditch which parallels Pearl Harbor Avenue (see Figure A-1).

*** Located near intersection of same drainage ditch with Unnamed Creek.

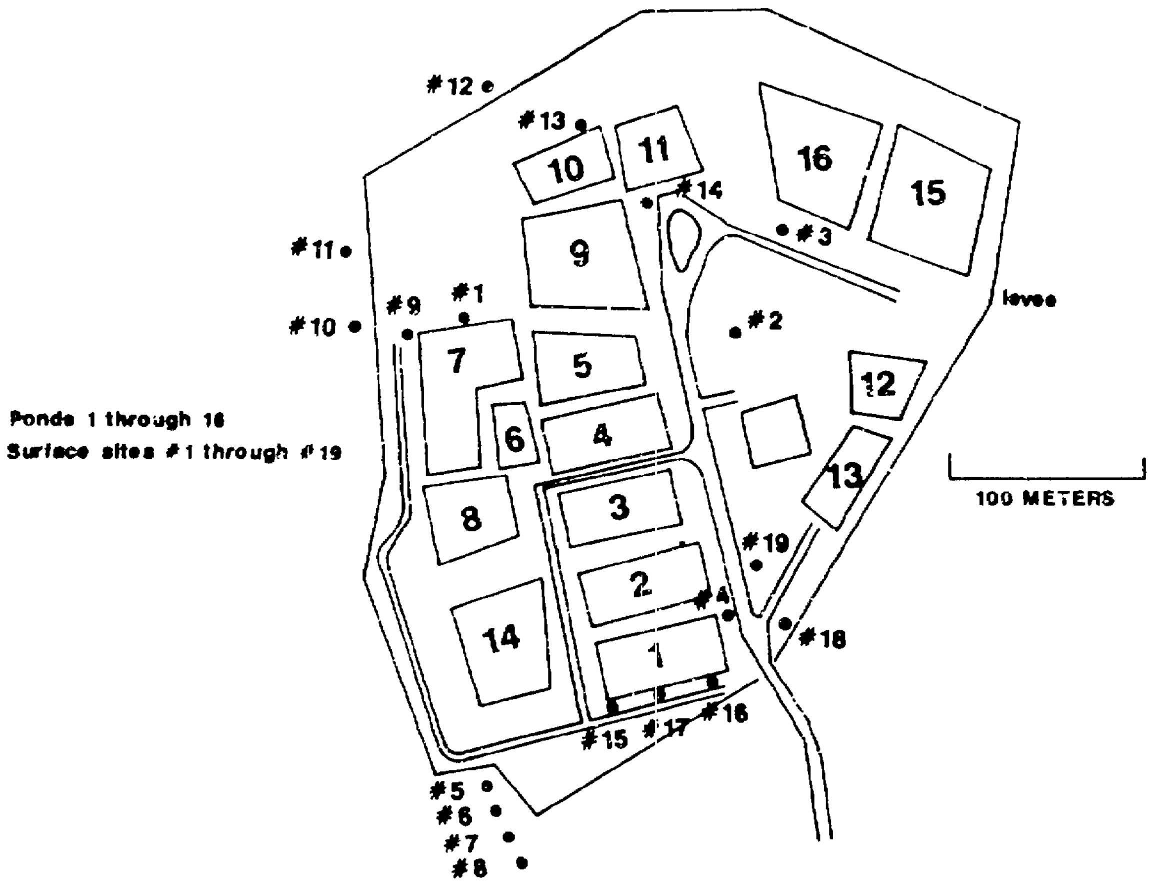

Figure A-2 Sampling Location of Area P Cited in Table A-2

APPENDIX B. DOCUMENTATION OF REFERENCE DOSES AND AQUATIC SAFETY WATER LIMITS

RDX: A water quality criteria document has been prepared by Etnier for this compound[10] in which the basis for a 103 μg/L drinking water limit is presented. This limit is three times the 35 μg/L interim criterion reported earlier[5]. The interim criterion was based on toxicological results from 90-day subchronic studies, while the revised criterion is based on a two-year study[10]. Aquatic toxicology results for RDX are not sufficient to derive criteria based upon EPA guidelines. Etnier considered the human limits sufficient for long-term safety of aquatic species[10]. Thus, the 103 μg/L value is used as the ASWL. This report, prepared under USABRDL sponsorship, has been submitted to the EPA.

HMX: Everett, et al.[11] studied the effects of HMX fed to Fischer 344 rats in their diet for 13 weeks. Daily dose levels were 0-4000 mg/kg in males and 0-1500 mg/kg in females. A no-observable effect level (NOEL) of 50 mg/kg/day for both sexes was indicated. Everett and Maddock[12] reported upon 13-week feeding studies with B6C3F1 mice. Daily dose levels were 0-200 mg/kg in males and 0-750 mg/kg in females. A 10 mg/kg NOEL for both sexes was indicated. The mouse NOEL value is divided by safety factor of 1000 to adjust for the length of the study to derive the RD. Aquatic studies with HMX are scant. Bentley et al.[13] failed to observe appreciable toxicity to fish or daphnia at 3 mg/L HMX in water.

TNT: Ryon has prepared a water quality criteria document for TNT[14], in which the basis for the DWL and ASWL of 140 and 540 μg/L respectively are presented. This report, prepared under USABRDL sponsorship, has been submitted to the EPA. Ryon's values for DWL and ASWL are higher than previously-developed interim criteria (44 and 60 μg/L respectively)[14]. As with RDX, the DWL is based on a more recent chronic feeding study; the previous value was based on 90-day mammalian feeding studies. Moreover, the ASWL is based on updated methodology and additional information that was not available when the 60 μg/L level was recommended.

TNB: Very little work has been done concerning the toxicity of this compound. An oral LD50 to rats of 505 mg/kg has been reported in an earlier assessment[15]. Layton et al.[16] presented approaches to estimating a conservative-sided human oral intake from an LD50. A conversion factor of LD50/200000 was recommended, and is the basis for the RD. Van der Schalie[17] has conducted chronic exposure tests of TNB with trout, daphnia, and algae. A no-effect level of 0.08 mg/L was observed for trout, but algal growth may have been diminished. The ASWL is based on this level divided by a safety factor of 30 to account for species that may be more sensitive than trout to TNB.

DNB: A Threshold Limit Value (TLV) of 1 mg/m^3 has been recommended[18]. While the studies upon which this is based are somewhat dated, it is the best information available. The EPA water quality criteria availability notice[19] included a method to convert a TLV to an estimate of acceptable human oral intake. If oral ingestion is assumed as effective as inhalation, and a safety factor of 100 is used*, the oral intake level in mg/kg/day is about TLV/1000. This is the RD used. Van der Schalie[17] also studied the effect of chronic DNB exposure to trout and algae, with no effect levels indicated at 0.26 to 0.44 mg/L. The ASWL used for DNB is the 0.26 mg/L level divided by 10 to account for potentially more sensitive species in the environment.

NB: A TLV of 5 mg/m^3 has been recommended[18]. While the studies upon which this is based are somewhat dated, it is the best information available. The RD for NB is developed as described above for DNB. Some acute toxicity data for NB have been reported by Spehar et al.[20] and Pickering et al.[21]; the most sensitive species was the bluegill, for which 50% mortality after 96 hours exposure is estimated in a 43 mg/L of NB solution. The ASWL is estimated to be 1/1000 of this concentration.

2,4- and 2,6-DNT: The estimated carcinogenic potency (q^*) of 2,4-DNT has been reported[6] as 0.31 $(mg/kg/day)^{-1}$. The EPA recommends that risk analyses with carcinogens be performed at acceptable risk levels (ARLs) from 10^{-7} to 10^{-4}. An ARL indicates an increased risk of cancer per person exposed to a constant dose for a 70-year lifetime. The corresponding constant dose is ARL/q^*, and this is used for an RD.

This q^* is now suspect since the test material used included 2,6-DNT as an impurity, and the percentage of 2,6-DNT was not precisely determined. A one-year study was conducted by Popp and Leonard[22], in which male Fischer-344 rats were fed diets including either technical grade DNT (76% 2,4-DNT and 19% 2,6-DNT), 99.9% pure 2,4-DNT, or 99.9% pure 2,6-DNT. The resulting incidence of hepatocellular carcinomas in these animals strongly indicated that the carcinogenicity observed in earlier tests could be attributed to 2,6-DNT as the principal carcinogenic chemical. Their work is being evaluated to determine if the potency estimates for 2,6-DNT can be derived and that of 2,4-DNT revised. As in a previous assessment by Finger et al.[23], the present report treats both 2,4- and 2,6-DNT as carcinogens, and the potency of 2,6-DNT has been estimated to be sixfold that estimated for 2,4-DNT.

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* TLVs are occupational standards, based on exposure of adult males. In some cases, they are not NOELs. The 100 factor accounts for the conversion to a potentially more sensitive population than adult males and the higher-than-NOEL effect a chemical may have at the TLV.

The ASWL for 2,4-DNT is taken directly from Etnier[24]. The 2,6-DNT aquatic biota value is half that for 2,4-DNT, and is a very rough estimate based on a comparable aquatic biota data for the two compounds. This document was prepared under USABRDL sponsorship, and when finalized, will be submitted to the EPA.

Tetryl: A TLV of 1.5 mg/m^3 has been recommended for this compound. The recommendation is based on skin sensitization by the explosive after distribution by air[18]. Systemic effects were not observed when tetryl levels in air were below the TLV. Extrapolation to an oral ingestion basis is coincided appropriate, as with the procedures used above for NB and DNB. The effect of tetryl on aquatic species apparently has not been studied.

APPENDIX C. GROUNDWATER MODEL TO DETERMINE CONTAMINATED SOIL LIMITS FOR DRINKING WATER QUALITY.

THE AREA P SIMULATION

The cleaned-up Area P is represented as a 200 m x 220 m rectangular plot with an unsaturated soil column depth of 6 m (see Figure 4, main text). This configuration corresponds roughly to the surface areas of known pits, intermediate non-pit areas, and their alignment relative to groundwater flow. As indicated in the figure, peripheral land areas, although geographically considered part of Area P, are not included. Groundwater flows to the west at 10 m/year, close to the estimated average flow computed[3] in the area of 32 feet/year (10 m = 32.8 feet). Thus, the simulated area can be considered as 22 contiguous compartments. The groundwater aquifer is assumed to be uniformly 6 m thick, which approximates the average thickness of the Alluvial aquifer.

The unsaturated soil column in the area now underlying the pits is assumed to be uniformly contaminated with 1 mg/kg of explosive. This is an assumption of convenience; it is easier to work forward from a soil condition to a water condition and scale results to a water criterion than to work in the reverse direction. Groundwater below Area P is initially clean. This ignores the contribution of the existing plume, but serves to separate this contribution from what may occur in the post-remedial environment. The main text demonstrated that some groundwater in the Alluvial aquifer is sufficiently contaminated that it would require treatment if were to constitute part of a potable water supply. The assumption made here would be reasonable if one intended to discontinue the treatment at some future time.

POLLUTION TRANSFERS FROM SOIL TO GROUNDWATER

The analytical model deals with each compartment of Area P as a discrete entity, and each year as a discrete entity. In a given year, two transfer events happen. First, the water table level rises into the LPUSC. Seasonal changes of 8 to 10 feet in the water table depth at LAAP have been reported[8]. For model purposes, a 1-m rise and fall in depth is assumed to occur once a year.

In the LPUSC, equilibrium is attained between contaminant adsorbed on soil and in groundwater. In a given compartment (here indexed as j), the available pollutant mass for allocation in the LPUSC is MASSMIX, where

$$\text{MASSMIX} = \text{CWIN}(j) * \text{VWCMIX} + \text{CSMIXIN}(j) * \text{MSCMIX}$$

CWIN(j) is the concentration of pollutant in groundwater in the j^{th} compartment at the start of this event, and VWCMIX is the volume of groundwater in the LPUSC of this compartment (these variables are used in the computer program described in this appendix). CSMIXIN(j) is the concentration of pollutant in the LPUSC at the start of this event, and MSCMIX is the soil mass in the LPUSC. The equilibrium process allocates a portion of MASSMIX to contaminate VWCMIX to a concentration level, XCW, given by:

$$XCW = MASSMIX / (VWCMIX + Kd * MSCMIX)$$

Kd is the partition coefficient for a pollutant which is in soil and water at equilibrium*, and has units of L/kg.

The second transfer event is infiltration of surface water through the UPUSC. The algorithm is similar to that used above, except that the volume of water involved (VFIN) is the product of infiltration rate*surface area of the compartment. The mass of pollutant transferred to the LPUSC is added after the groundwater leaching event. A somewhat more realistic approach would be that this event occurs first (groundwater level rises should be related to a period of heavy rain). The approach here simplifies the mathematics, and given the time frame of concern (decades), the ordering is not important.

Infiltration estimates are not available for LAAP. Layton, et al.[25] have estimated 3 - 7 cm/year infiltration rates for the regional Southeastern United States. This estimate includes contributions that would come from streams and lakes, and probably exceeds that which would occur at a cleaned-up Area P with the pits removed. A 2 cm/year infiltration rate was used in computation of DCSLs in Table 3, main text. The "Model Discussion" section of this Appendix deals with the impact of different rates.

After transfers, concentrations in soil and water are recomputed. After both events end, the contaminant concentration in the two portions of the soil column are determined; in each portion a uniform concentration profile is maintained. After the first transfer event, the groundwater in each compartment (that in the LPUSC and in the aquifer proper) is assumed to mix such that a uniform vertical concentration profile is established. The groundwater is then transferred to the next lower-numbered compartment as the water input for the next year's event. The contaminated groundwater exiting compartment 1 becomes the source for subsequent diffusion modeling.

---

* Kd (and subsequently Koc) is the ratio of the concentration of pollutant in soil (or soil organic carbon) and in water. Formally, the units are mg/kg per mg/L.

Data Inputs for the Leaching Process

Spatial dimensions, the infiltration rate, and initial concentrations have been specified. Two soil parameters are required, effective porosity and bulk density. An effective porosity of 0.25 has been estimated for the Alluvial aquifer[3]; here this value is also applied to the unsaturated soil column. A bulk soil density of 1400 kg/m^3 is assumed.

Each contaminant's ability to leach from soil is characterized by Kd. The Kd for TNT and RDX were experimentally determined in a sandy LAAP soil to be 1.069 and 1.588 L/kg, respectively[9]. Rosenblatt, in his analysis of Cornhusker Army Ammunition Plant[5], used these Kd values to develop estimates for TNB (Kd = 0.605 L/kg) and DNT (Kd= 0.504 L/kg). These four values are used in this analysis; Kd values for other compounds are discussed below:

HMX: The partition coefficients of HMX and RDX between the organic carbon portion of soil and water in equilibrium with the soil (Koc) were estimated in Layton et al.[25] as 93 and 61 L/kg respectively. The organic carbon portion of soil is assumed to be the only important portion of soil adsorbing these explosives; as a first approximation, Kd is proportional to Koc. Thus, the Kd for RDX can be used to estimate that of HMX; i.e., 1.588*(93/61) or 2.42 L/kg*.

Tetryl: Tetryl is considered similar enough to TNT for its Kd to be estimated from TNT just as the Kd for HMX was estimated from the Kd of RDX. Layton et. al.[25] estimated the Koc of tetryl and TNT to be 280 and 470 L/kg respectively. The calculated Kd is 1.069*(280/470) or 0.637 L/kg.

NB: Koc for NB is estimated through a relation given in Lyman, et al.[26]

$$\log \mathrm{Koc} = 1.377 + 0.544*\log \mathrm{Kow}$$

where Kow is the octanol-water partition coefficient. Hansch and Leo[27] report several estimates of log Kow from 1.79 to 1.85. A log Kow = 1.82 is used above, from which the NB Koc estimate is 233 L/kg. Scaling from the Kd for TNT as discussed above, Kd is estimated as 0.53 L/kg.

---

[*] RDX appears to be an exceptional compound, in that its solubility and Kd are quite different from what would be predicted from its octanol-water partition coefficient, the relative solubility of RDX in octanol and water when these solvents are in equilibrium. For example, the Koc of TNT is about 8 times that of RDX, yet RDX has a higher Kd. Thus, the Kd of RDX has been used to estimate the Kd of the closely-related HMX. For other compounds, TNT is used as the yardstick.

DNB: Koc for DNB is estimated from a relation given in Lyman et al.[26] for substances that are solids at 25 °C,

$$\log Koc = -0.83 * \log SOL - 0.01 * (MP-25) - 0.93.$$

In this equation, SOL is aqueous solubility in mole fraction, and MP is the melting point in °C. The solubility of DNB at 25 °C has been quoted as 470 mg/L[6], which corresponds to 5.0×10^{-5} mole fraction. The melting point of DNB is reported[18] as 89 °C. The relation then predicts Koc = 100 L/kg, and from comparison with TNT, Kd = 0.23 L/kg.

DISPERSION OF CONTAMINATED PLUMES DOWNGRADIENT OF AREA P

As the plume formed by contaminants leached from Area P soil moves downgradient, advective and dispersive effects come into play. Groundwater dispersion models are available; however, the variable profile pattern discussed above cannot be dealt with by models that provide a closed-form analog solution. Thus, a digital approximation was undertaken (see Figure C-1). The contaminant mass exiting the pits was viewed as discrete once-yearly "puffs". Each puff is generated from a very narrow "slit" source 6 m long (in the z-dimension). The contaminated groundwater "front" is simulated as 10 such sources spaced 20 m apart. Each source releases one-tenth the yearly mass of contaminant transported out of Area P.

The unsteady-state two-dimensional plume solution created by a "puff" from one source has been presented by Wilson and Miller[28]. The form shown here is for a unit mass release per unit length from a source. The normalized concentration within the plume relative to position and time, Q(x,y,t) is given by:

$$Q(x,y,t) = (1 \text{ mass/length})*R \,/\, (4\pi*\epsilon*t*V*[ax*ay]^{0.5})$$

$$\text{where } R = \exp-(\,[x-V*t]^2 / [4*ax*V*t] + y^2 / [4*ay*V*t]\,), \text{ and:}$$

ϵ = effective porosity in aquifer, unitless
t = time, years
ax = longitudinal dispersivity (downgradient), m
ay = transverse dispersivity (across gradient), m
V = Advective flow of substance in aquifer, m/year
x,y = Cartesian distances from source to receptor, m.

Q(x,y,t) has units of mass/volume per mass/length. This relation presumes that the groundwater field is uniform (same depth, flow rate, and porosity throughout) and infinite in the y-direction. Moreover, there are no water inputs or outputs, nor is there any mechanism to remove or destroy pollutant within the region modeled. There is no depth-related variation of the plume within the aquifer.

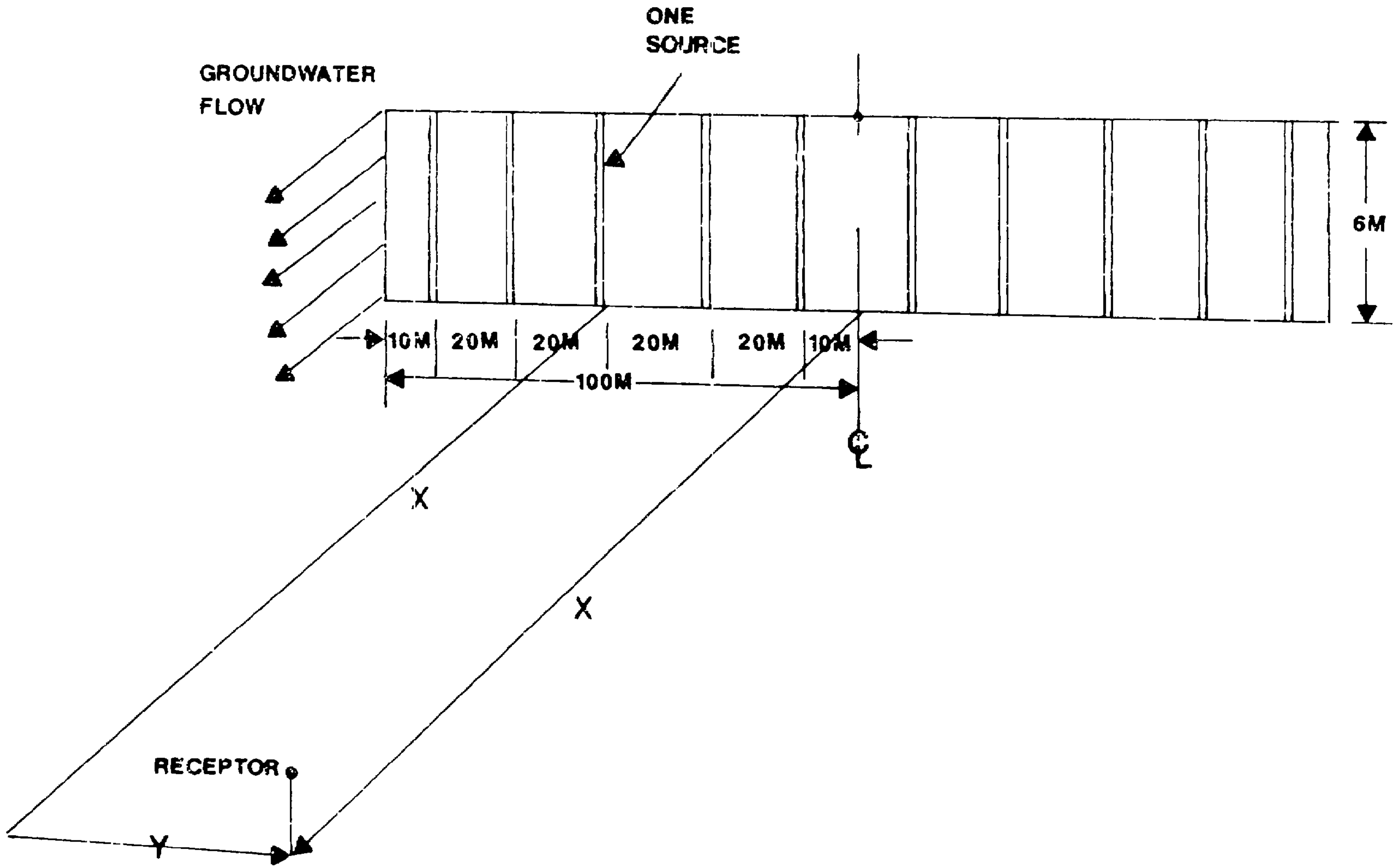

Figure C-1 Plume Generation Simulation Model Geometry

The receptor of interest is along the centerline downgradient of Area P, the most concentrated part of the plume. If the time of interest is the j^{th} year from "time zero" (the first release), the concentration at a receptor located x meters downgradient allocatable to the first puff, M0 (in mass/length units), is:

$$C(x,0) = M0 * \Sigma y \quad Q(x,y,j)$$

Here, the contribution from each source is determined and summed. The following year, another release occurs of magnitude M1. The concentration attributable to this release <u>at the same time as the previous release</u> is:

$$C(x,1) = M1 * \Sigma y \quad Q(x,y,j-1)$$

Conceptually, the impact of M0 is reflected by C(x,0) and that of M1 by C(x,1). At a given time, they add to each other. In general, for a release that occurs at year i, i <j,

$$C(x,i) = Mi * \Sigma y \quad Q(x,y,j-i)$$

The concentration at the receptor at year j, C(x) is given as:

$$C(x) = \Sigma i \ C(x,i).$$

Data Inputs for the Dispersion Model

The model releases emanate from ten sources. This is sufficiently accurate for the problem at hand; a comparison with releases from a twenty-source array resulted in less than 1% difference in the computed C(x). The groundwater velocity (10 m/year) and the effective porosity in the aquifer (0.25) have been previously developed. Dispersivities in the LAAP aquifers have not been estimated; dispersivities used to characterize the aquifer at Rocky Mountain Arsenal (ax = 30 m, ay = 9 m) are used here[29]. As a point of reference, values of 200 feet and 20 feet respectively were used to model the RDX plume in the sandy aquifer downgradient of Cornhusker Army Ammunition Plant[30]. The LAAP Alluvial aquifer is described as being a combination of silts and sands[3]. Silts generally have lower values of ax and ay associated with them than sands[31]; a rough dividing line set between the range of values for the two type aquifers is ax= 10 m and ay = 1 m. The effect of alternate values of ax and ay is discussed in the "Sensitivity Analysis" section.

COMPUTATIONAL DETAILS

Three BASIC programs were written to carry out the simulations described above. The first program, listed in Figure C-2, generates yearly values of the variable Σy Q(x,y,j), referred to in the program as the vector CONCSTD(YEAR), and writes the vector in a disk file. The first data element, MLOAD is 0.1 kg/m, but

```
10 REM this program computes a yearly concentration for a
20 REM "standard puff" based on 2-d model. distance is input.
22 DIM CONCSTD(255)
25 READ MLOAD,EP,AX,AY,VEL
26 DATA 1e8,0.25,30,9,10
30 DAY=365.25
32 INPUT "years to perform simulation";YER
34 LPRINT:LPRINT "SOLUTION OF "YER "YEARS OPERATION OF CONSTANT SOURCE PUFF"
40 VELD=VEL/DAY
50 DX=AX*VELD:DY=AY*VELD
60 COEFF=MLOAD/(4000*3.1416*EP*SQR(DX*DY))
65 REM 4000 includes conversion for meter cubed to liters.
70 PRINT COEFF
80 INPUT "input length,m";XL
90 LPRINT "solution for downgradient distance of " XL "meters":LPRINT
100 FOR YEAR=1 TO YER
105 YR=YEAR*DAY
110 XPARMN=(XL-VELD*YR)^2
115 XPARM=XPARMN/(4*DX*YR)
120 SUMYEAR=0
125 FOR YDEM=10 TO 90 STEP 20: YPARM=YDEM^2/ (4*DY*YR):ARGMT=XPARM+YPARM
130 CONYDEM=(COEFF/YR)*EXP(-ARGMT):SUMYEAR=SUMYEAR+2*CONYDEM
133 NEXT YDEM
140 PRINT YEAR,SUMYEAR:CONCSTD(YEAR)=SUMYEAR:NEXT YEAR
150 INPUT "enter file name (b:xxxxxxx) for storage";FIL$
160 OPEN FIL$ FOR OUTPUT AS # 1
170 FOR J=1 TO YER:WRITE #1,CONCSTD(J):NEXT J
180 CLOSE #1
190 END
```

Figure C-2. Program Listing for Simulation of Receptor Concentration-Time Profile from a Series of Puffs.

is expressed in µg/m, and refers to a single source. Thus, the model output indicates the concentration in µg/L at the selected downgradient receptor yearly after a 1 kg/m release from Area P's boundary at an initial time = 0 (see remark at line 65).

The second program, shown in Figure C-3, simulates the Area P leaching situation described earlier. The initial conditions for the area are specified at statement lines 100-140; soil concentrations at lines 120 and 140 are in µg/kg. The model configuration is entered by the "READ...DATA" statements lines 200-210. Kd for a given substance and the infiltration rate of surface water are input at line 220. The various volumes (in L) and compartmental soil masses (in kg) involved are computed at lines 260-310. At line 340, the option is presented to produce printouts of the compartmental concentration results at every 10th year of simulation. The simulation is performed for YRIN years, which is entered at line 375. The first transfer (due to rise and fall of the water table) is simulated at lines 390-410; the second transfer (infiltration effect) is simulated at lines 420-440. The year-end concentrations are computed at lines 450-490, and uniformity of concentration profiles is re-established. Lines 510-520 cause the optional printout if specified at line 340.

At line 550, the groundwater concentration from compartment 1, CWOUT(1), is converted to a mass term and entered into the OUTGO vector for the respective year (within the loop from line 380 to 620). OUTGO values represent "puff" masses. At lines 570-600, the soil column concentrations are recomputed for the next simulation year, and the indices assigned to groundwater compartments are decremented by 1 to simulate "flow" to the next downgradient soil compartment. At lines 650-670, the the applicable CONSTD vector is read from a stored file (name input at line 224); in this program it is called CONC(J). The yearly concentration computation is carried out at lines 680-720; the results are printed out for each year as line 730 is executed. In line 710 of this loop, OUTGO terms are divided by DCW to provide the proper mass/length term. The concentration vector corresponding to C(X), RSLT(YEAR), is written to a disk file (line 770), and the program terminates.

The final program (not listed) determines the 70-year segment upon which to base LAC. The algorithm used is that the endpoint concentration in any 70-year consecutive period cannot be higher than the starting concentration of the period. The LAC is then computed and printed out.

The yearly terms CWOUT(1) provide a digital approximation of concentration-time profile of pollutant exiting Area P. Figure C-4 shows two such profiles, one for DNB and one for TNT. The Kd of DNB is about one-fifth that of TNT, which indicates DNB is more leachable. Thus, the maximum concentration of the DNB

```
10 DEFSNG A-H,L-X
25 DIM CONC(255),RSLT(255)
30 DIM CWIN(23),CWOUT(23),CSTOPIN(22),CSTOPOUT(22),CSMIXIN(22),CSMIXOUT(22),OUTGO(255)
40 REM CWIN(j) is conc in groundwater entering compartment j
45 REM CWOUT(j) is conc in groundwater exiting compartment j
50 REM CSTOPIN(j) is conc in UPUSC of compartment j before infiltration.
55 REM CSTOPOUT(j) is conc in USUSC of compart. j after infiltration.
60 REM CSMIXIN(j) is conc in LPUSC of compart. j before gw contact.
65 REM CSMIXOUT(j) is conc in LPUSC of compart. j after gw contact.
70 REM OUTGO(year) is mass exiting in gw.from compartment 1 at any year.
75 REM CONC(year) reads normalized diffusion info.
80 REM RSLT(year) is name of conc-time profile exiting Area P written to file
90 REM First, all initial conditions are set.
100 FOR J=1 TO 22: CWIN(J)=0: CWOUT(J)=0 :NEXT J
120 FOR K=1 TO 13: CSTOPIN(K)=1000 :CSMIXIN(K)=1000: NEXT K
130 FOR K=14 TO 18: CSTOPIN(K)=0 :CSMIXIN(K)=0 : NEXT K
140 FOR K=19 TO 22: CSTOPIN(K)=1000 :CSMIXIN(K)=1000: NEXT K
160 REM LC=length of pits, WC=width of compartment, DCS= soil column depth
170 REM DCS=nominal gw depth, PSOIL=bulk soil density, EP=porosity
180 REM DMIX=depth of LPUSC
190 REM FIN=infiltration thru soil column. All in kg & meters
200 READ LC,WC,DCS,DCW,PSOIL,EP,DMIX
210 DATA 200,10,6,6,1.4e3,0.25,1
220 INPUT "enter Kd (L/kg) and depth of infiltrant, m" ;KD,FIN
222 INPUT "enter downgradient distance of analysis (meters)";METERS
224 INPUT "enter file number for puff diffusion(b:xxxxxx)";B$
230 REM compute mass of soil in each compartment(MSCTOT)and LPUSC(MSCMIX)
240 REM compute volume of water in each cmpt (VWCTOT), LPUSC (VWCMIX)
250 REM and mass of soil in UPUSC(MSCTOP) and volume water infil(VFIN)
260 MSCTOT= LC*WC*DCS*PSOIL
270 MSCMIX= LC*WC*DMIX*PSOIL
280 VWCTOT= LC*WC*DCW*1000!*EP
290 VWCMIX= LC*WC*DMIX*1000!*EP
300 MSCTOP= MSCTOT-MSCMIX: summass=0
310 VFIN= LC*WC*FIN*1000:MIXPARAM=VWCMIX+KD*MSCMIX:TOPPARAM=VFIN+KD*MSCTOP
320 WIDTH "lpt1:",120
322 LPRINT:LPRINT "MIGRATION ANALYSIS FROM LAAP AREA P PITS":LPRINT
324 LPRINT "Kd = " KD "INFILTRATION (cm/yr) = "FIN*100
326 LPRINT "MIGRATION DISTANCE (meters) ="METERS
328 LPRINT
330 REM MIXPARAM,TOPPARAM are partitioning "volumes" in LPUSC,UPUSC
340 INPUT "do you want any conc profile printouts? yes=1,no=0";PDEC
350 IF PDEC=0 THEN 370:LPRINT
360 LPRINT "    Time ";"   Cpmt ";" CW/mix ";" CS/mix ";" Cinf/top ";" CW/out ";" CSmixout
";" CStopout ":LPRINT
370 REM: start process (lines 390-410 for LPUSC; 420-440 for UPUSC)
375 INPUT "enter years (100 for 50m;150 for 350m;180 for 800m)";YRIN
380 FOR YEAR=1 TO YRIN
390 FOR J=1 TO 22: MASSMIX=CWIN(J)*VWCMIX+CSMIXIN(J)*MSCMIX
400 XCW=MASSMIX/MIXPARAM
410 XCS1=XCW*KD
```

Figure C-3. Listing of Program to Model Area P Soil Leaching to Groundwater and Compute Downgradient Profile (Page 1 of 2 pages)

```
420 MASSMIX2=MSCTOP*CSTOPIN(J)
430 XCS2=MASSMIX2/TOPPARAM
440 MCS2=VFIN*XCS2
450 CWOUT(J)=XCW*(DMIX/(DCW+DMIX))+(DCW/(DCW+DMIX))*CWIN(J)
460 MASSMIXOUT=MASSMIX-XCW*VWCMIX+MCS2
470 CSMIXOUT(J)=MASSMIXOUT/MSCMIX
480 MASSTOPOUT=MASSMIX2-MCS2
490 CSTOPOUT(J)=MASSTOPOUT/MSCTOP
500 IF PDEC=0 THEN 530
510 IF YEAR/10 <> INT(YEAR/10) THEN 530
520 LPRINT USING "#####.##";YEAR;J;XCW;XCS1;XCS2;CWOUT(J);CSMIXOUT(J);CSTOPOUT(J)
521 REM XCW=Groundwater conc. in portion in LPUSC after leaching.
522 REM XCS1=Soil conc. in portion of LPUSC after leaching.
523 REM XCS2=Conc in infiltration water leaving UPUSC after infiltration
524 REM MCS2= Mass of pollutant leaving UPUSC after infiltration
530 NEXT J
540 REM CWOUT(1) is moved out of Area P as yearly OUTGO
550 OUTGO(YEAR)=CWOUT(1)*((DCW+DMIX)/DCW)*VWCTOT
560 REM reset LPUSC and UPUSC concentrations for next year, move groundwater.
570 FOR J=1 TO 22
580 CSTOPIN(J)=CSTOPOUT(J):CSMIXIN(J)=CSMIXOUT(J)
590 CWIN(J)=CWOUT(J+1)
600 NEXT J
610 PRINT YEAR
620 NEXT YEAR
650 OPEN B$ FOR INPUT AS # 1
660 FOR J=1 TO YRIN:INPUT#1,CONC(J):NEXT J
670 CLOSE #1
675 LPRINT:LPRINT "year   ug/yr migrate  diffusion   ug/L":LPRINT
680 FOR YEAR= 1 TO YRIN: FOR J=1 TO YEAR
710 RSLT(YEAR)=RSLT(YEAR)+OUTGO(YEAR-J+1)*CONC(J)/DCW
720 NEXT J
730 LPRINT USING "##.###^^^^";YEAR,OUTGO(YEAR),CONC(YEAR),RSLT(YEAR)/1000000000#
735 summass=summass+outgo(year)
740 NEXT YEAR
745 lprint : lprint "total mass lost ug " summass:lprint
750 INPUT "enter file for conc profile in b:drive ";B$
760 OPEN B$ FOR OUTPUT AS #1
770 FOR J=1 TO YRIN:WRITE #1,RSLT(J):NEXT J
780 LPRINT:LPRINT "result vector written to  "B$
790 system
```

Figure C-3. Listing of Program to Model Area P Soil Leaching to Groundwater and Compute Downgradient Profile (Page 2 of 2 pages)

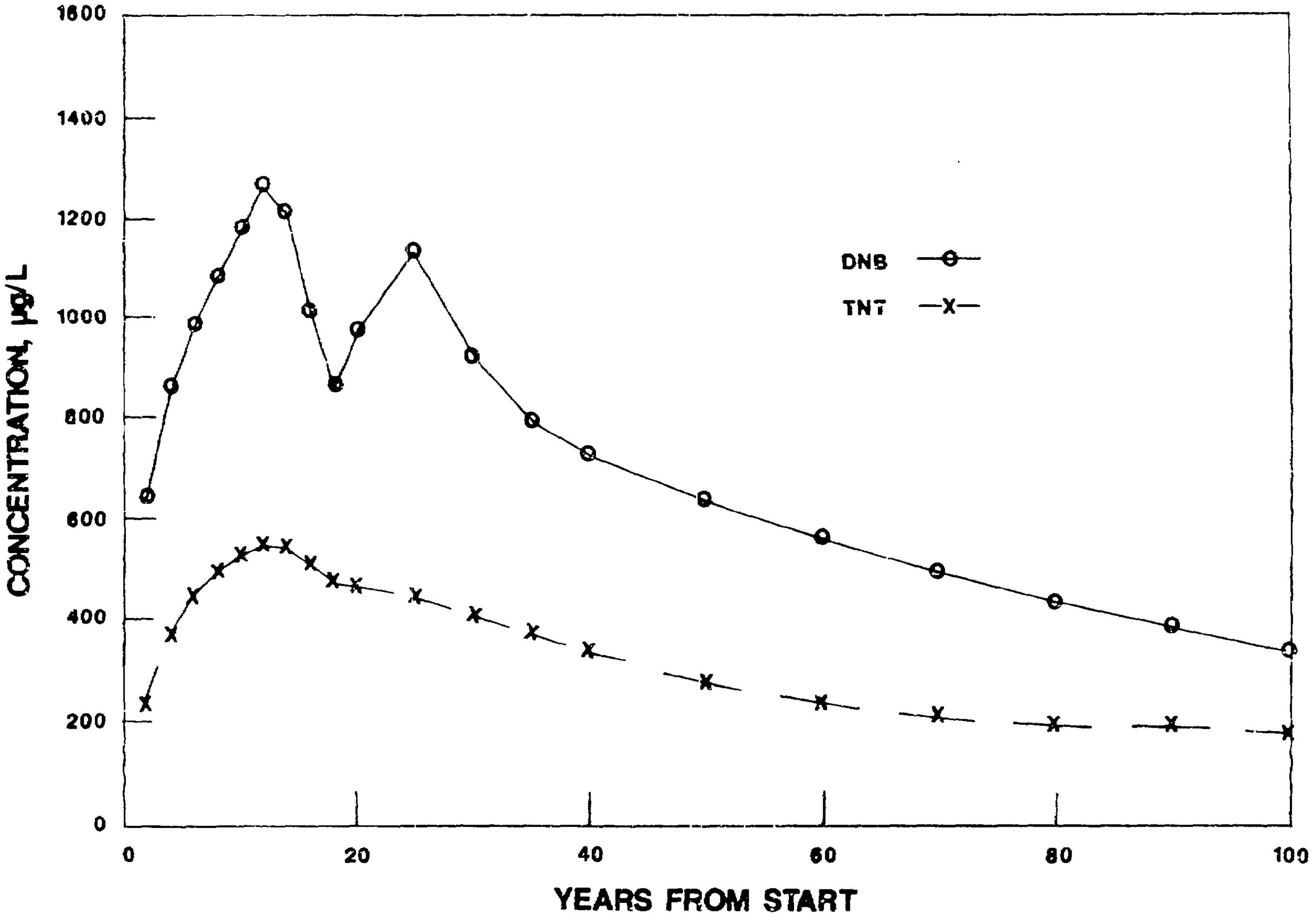

Figure C-4 Concentration-Time Profiles of TNT and DNB Leaching From Area P Pits profile is higher than that of TNT. Moreover, the DNB profile shows a sharper decline in the 12-20 year timeframe than does TNT, which reflects the effect of the intermediate non-contaminated area in Figure 4, main text. These profiles are normalized to an initial 1 mg/kg level of a contaminant in the unsaturated soil column, which corresponds to 286 kg of contaminant. In terms of percent removal from Area P, the 100-year DNB profile represents removal of 72% of initial material; for TNT, the profile represents removal of 32% of initial material.

Figure C-5 presents the TNT concentration profiles predicted for 50, 350, and 800 m downgradient. The profiles have lower maxima and "flatten out" as distance increases. Since the LAC is a 70-year averaged value, the changes in LAC at these downgradient receptors are somewhat less marked than might be inferred from maximum values alone.

MODEL DISCUSSION

The model assumes that a pollutant in groundwater is redistributed uniformly in the vertical direction within a year. The validity of this can be assessed in terms of the vertical dispersivity in the Alluvial aquifer. The puff dispersion equation, when viewed in the transverse direction (y-axis), describes a normal distribution. The corresponding dispersivity, ay, is related to the standard deviation, $\sigma(y,t)$, such that

$$\sigma(y,t) = (2*ay*V*t)^{0.5}$$

For V= 10m/year, ay=9m, and t=1 year, $\sigma(y,1)$ is about 13.5 m. In lieu of information to the contrary, aquifers are assumed to be isotropic, or the dispersivity in the vertical direction, az, is approximately equal to ay. Assuming this is so at LAAP, $\sigma(z,1)$ would be about 13.5 m. A characteristic of a normal distribution is that if the maximum value of the function is Qm (where $\sigma=0$, i.e., the mean), the ordinate corresponding to one standard deviation from the mean is 0.62*Qm. In relation to the current problem, suppose the aquifer were of infinite extent in depth and a puff occurred at some arbitrary depth Zd. One year later, at any downgradient location along the plane of Zd, the concentrations noted within 13.5 m above or below the plane would be 62% or greater of that which had occurred at the plane. Thus, the assumption of uniformity within 6 m thickness of aquifer appears reasonable.

The model described does not account for contamination of the Sparta Sand aquifer, which, if it were included, would lead to lower LAC in the Alluvial aquifer, and a higher DCSL. Based on the estimated extent of plumes and the similarity in depth of the two aquifers, inclusion of the Sparta Sand aquifer would alter the ASLs by less than two-fold. The model does not account for

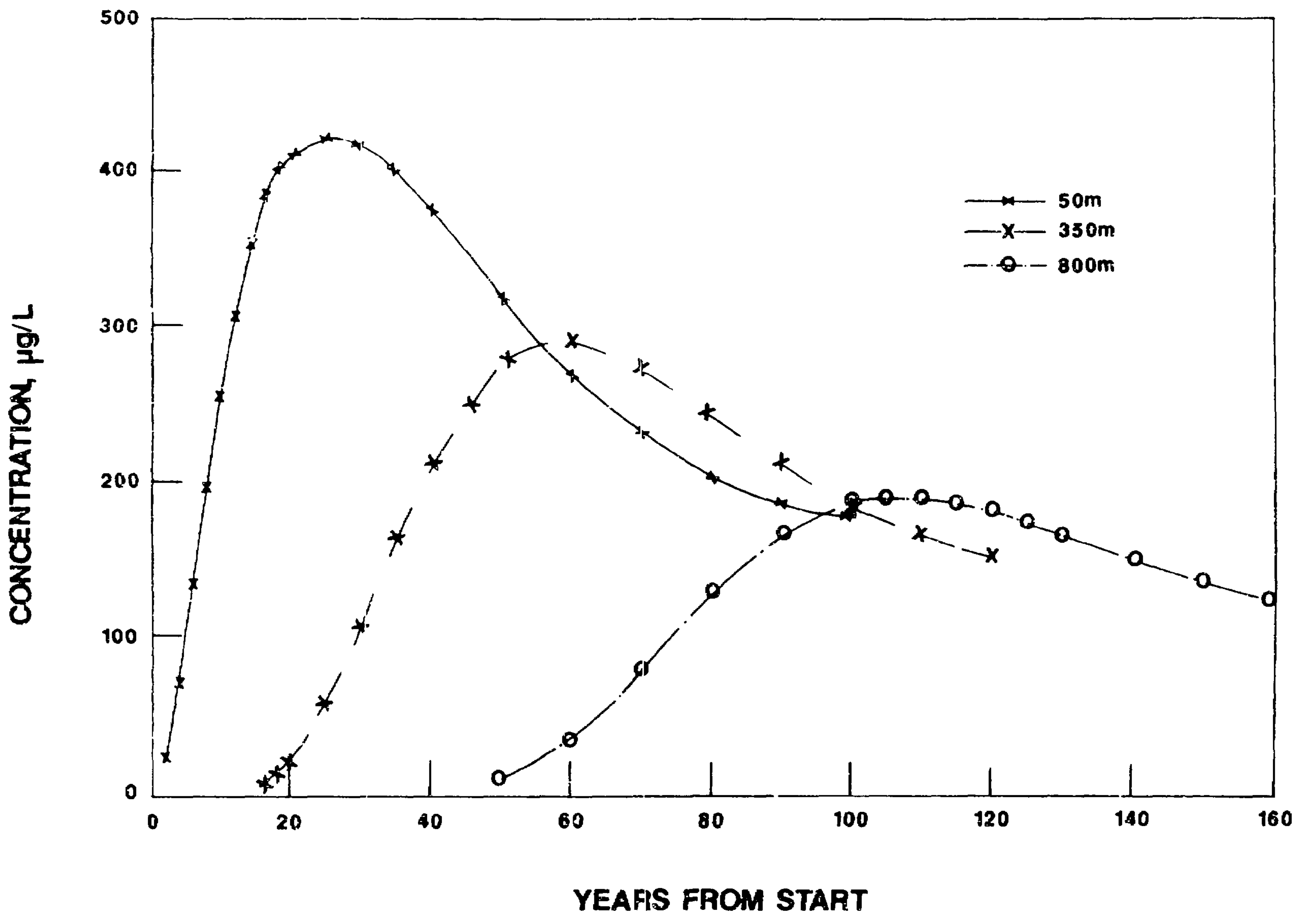

Figure C-5 Concentration-Time Profiles of TNT Migration at Three Downgradient Locations the effect of longitudinal dispersion within the bounds of the Area P. Rather, the model forces contamination to be confined to the 200 m width of the model area; realistically, the plume would have been more widely-spread. The effect of this simplification cannot be quantified; qualitatively, it leads to lower DCSLs than would be obtained from a more realistic portrayal.

While the model includes infiltration as a means of transferring contaminants from the UPUSC, the volume of infiltration water does not add to the aquifer. For example, in one year, the volume of water corresponding to 2 cm/year infiltration over the area of the pits is 880 m^3; the volume of water passing into the aquifer below the pits is 3000 m^3. The additional infiltration water would serve to dilute contamination levels in the Alluvial aquifer, and if accounted for, would have lead to about 28% (8/30) higher DCSLs than are here computed.

The pollutants are not expected to appreciably sorb physically to Alluvial aquifer soil. Such sorption would result in a retardation of movement of pollutants relative to that of the groundwater. This factor, called Rd, is defined as:

$$Rd = 1 + (\text{soil density}/\text{porosity}) * Kd$$

While Kd values have been estimated for the explosives in LAAP soil, these values may not apply in the Alluvial aquifer (probably, Kd in the aquifer is lower than in the unsaturated soil column). The shape and progression downgradient of some contaminant plumes shown in the remedial investigation[3] suggest retardation. However, the trend is not consistent for all explosives contaminants, nor is sufficient information available from past LAP operations from which to calibrate the model to account for Rd. Moreover, the plumes are interpolated from only three to five well position assays, so the concentration contours presented are subject to some uncertainty. In the absence of more convincing evidence to model otherwise, all substances were assumed to have an Rd=1.

The groundwater velocity in the Alluvial aquifer is a variable that influences the DCSL determination. While it could be included in a sensitivity analysis (see next section), a range of applicable values is difficult to define. In other sections of LAAP, groundwater flows at a somewhat lower velocity, but flow is also in a different direction. Moreover, the velocity may have been higher when the pits were in active use than when the remedial investigation occurred, and with removal of the pits as recharge features, it could decrease in the future.

SENSITIVITY ANALYSIS

This procedure is useful when input variables are not accurately known. Alternative values of such variables are introduced and alternative solutions generated. In some cases, a variable can have a wide range of reasonable values with little effect on results. In other cases, results can vary dramatically within the range of variables, indicating that efforts to improve the accuracy of the input are warranted. Here, the analysis was performed for the TNT LAC estimation at a 350 m downgradient point. The baseline LAC was 242 µg/L TNT per mg/kg TNT initially in soil (hereafter, the units will be dropped). The corresponding DCSL was 0.58 mg/kg.

Kd is input tothe leaching model. LACs computed for other compounds can be used directly to gauge the sensitivity. The estimated Kd for DNT (0.504) is about one-half that estimated for TNT (1.069), while the Kd estimated for HMX (2.42) is somewhat more than twice the Kd of TNT. These Kd values offered a reasonable range in which the "true" Kd of TNT would be found. The LAC for DNT at 350 m is 355; for HMX, 161. The corresponding DCSL range would be 0.39 to 0.87 mg/kg. Thus a five-fold difference in Kd caused slightly more than two-fold difference in DCSL.

The infiltration rate controls the amount of pollutant recharge from the UPUSC to the LPUSC. A reasonable range of values for this was considered to be from 0.1 cm/year, which would approximate a nearly water-tight cap, to 7 cm/year, a value typical of regions in the Southeastern United States[25]. The LAC for the 0.1 cm/year case is 160, that for the 7 cm/year case, 438; corresponding DCSLs are 0.88 and 0.32 mg/kg. This analysis suggests that extraordinary efforts to reduce the infiltration rate as a remedial action may not be cost-effective.

Water table variations (rise and fall) define the allocation of the unsaturated soil column to a UPUSC and a LPUSC, and the mass of contaminated soil available for the leaching and infiltration processes. Two alternative values were selected for analysis, 0.5 and 1.5 m. The LAC for the 0.5 m case was 178, that for the 1.5 m case, 306; corresponding DCSLs are 0.79 and 0.46 mg/kg. If the actual water table variation is within the range of these values, the difference in DCSL from that reported would not be great.

The dispersivities ax and ay are addressed together since they depend on soil properties and are probably related. They function in two ways: first as a dilution factor since the term $(ax*ay)^{0.5}$ appears in the denominator of the puff equation, and to determine the eccentricity of the plume (the plume may be considered as an ellipse). The range selected consisted of the two pairs ax=100 m, ay =10 m and ax= 10 m, ay= 3 m. The first set are high-sided values expected for sandy soils[31]; the other set are low-sided values for silty soils. With these sets, LAC was found to be 189 and 323, corresponding to DCSLs of 0.74 and 0.43 mg/kg.

Two reasons explain why rather wide ranges in alternative values lead to relatively small changes in LAC. First, the volume of water per compartment (VWCMIX = 5×10^5 L) is small compared with the corresponding soil mass (MSCMIX = 2.8×10^6 kg). This limits the rate of washout. Second, LAC are determined on a 70-year averaged basis.

APPENDIX D. DOCUMENTATION OF INPUT INFORMATION AND CALCULATIONS FOR CONSTRUCTION WORKER SAFETY-RELATED CONTAMINATED SOIL LIMITS

The time-frame for Area P clean-up is estimated at 15 months[32], which seems a reasonable model time for other construction projects requiring extensive excavation. Table 1, main text, presents reference doses (RDs), which are based on lifetime exposure. With respect to toxic substances (all except the DNTs), accepted procedures for devising RDs for a 1.25 year time-frame have not been established. However, in drinking water advisories, acceptable doses for less-than-one-year term exposures are either as high or higher than for lifetime exposure. Thus, use of RDs should be conservative for this case. With respect to the potentially carcinogenic DNTs, LAAP should be the only place at which workers would be exposed to them. Hence, their doses should be adjusted for actual time of exposure vs. lifetime exposure without altering the ARL. Based on an 10^{-6} ARL, the RD for 2,4-DNT is 3.1x10^{-6} mg/kg/day. Based on 1.25 years exposure, a dose of (70/1.25)*RD could be allowed, or 1.8x10^{-4} mg/kg/day. The applicable doses for this scenario are shown in Table D-1.

INTAKE OF DISSEMINATED PARTICULATES

Particulate levels in air resulting from industrial operations are expected to be much higher than those seen under ambient conditions, which are of the order of 0.1 mg/m^3. Measurements have been made of dust levels in the vicinity of tracked vehicles, and are of the order of 10-100 mg/m^3 [33]. Although similar vehicles may be employed during excavation of a site, it is doubtful whether such dust levels could be continually maintained without detriment to operations. If they were, operators would be obliged to wear protective equipment which would reduce intakes to acceptable levels; for example, the occupational standard for nuisance dust is 15 mg/m^3 [34]. For model purposes, a 10 mg/m^3 dust concentration is chosen.

In an eight-hour workday, an individual engaged in moderate effort can inhale about 20 m^3 of air. Thus, on days when dust is raised, a worker could inhale 200 mg/day of particulates. For simplicity, it is assumed that this superficial intake is delivered to the lungs; realistically, some particulates will be intercepted in the nasal passages and progress no further, while others will wind up in the digestive tract.

Workers may inadvertently ingest soil during smoking or eating. The quantitative data relating to this is sketchy; Hawley[35] provides some, and based on the specific assumption involved, estimated soil ingestion levels can range from 20 to 480 mg/day. In his intake scenario analysis, a 110 mg/day value was chosen, which was based on pesticide dust deposition on cigarettes of mosquito control workers. This value is also used here. Hawley also discusses the potential for intake via dermal adsorption.

Based on his analysis, the intake would be about an order of magnitude lower than that for either inhalation or ingestion, and is not included here.

Based on the above discussion, worker could inhale and ingest about 310 mg/work day of contaminated particulates. Adjustment should be made for time, since RDs are based on a daily intake. Work days would probably entail at most two-thirds of calendar days, assuming a 5-day work week and provision for off time. Thus, a 0.667 factor is included; the time-averaged intake would be 207 mg/day.

A particulate soil limit (PSL) is calculated on the basis of the above intake. The allowable daily intake (ADI) of a substance for a 70 kg person is the product 70*applicable dose. If this is supplied only by contaminated particulates,

$$PSL = 10^6 * ADI / 207$$

where 10^6 converts mg/day of particulates to kg/day. In terms of an applicable dose, the PSL is 338000*applicable dose. The PSLs are presented in Table D-1.

SOIL LIMITS BASED ON VAPORS GENERATED FROM SOIL

Three factors need to be defined for the vapor pathway: a mechanism by which vapors emanate from soil-associated explosives; diffusion of the vapors through soil pores to the surface; and dispersion of diffused vapors into ambient air which a worker can inhale.

The Vapor Generation Mechanism

The term "soil-associated explosive" is restricted to material sorbed on soil. In the model used here, equilibrium is presumed to exist between sorbed explosive in soil and water held in soil pores (called the soil solution). Moreover, equilibrium is presumed to exist between soil solution and air in soil pores (soil air). Experiments with pesticide-contaminated soil[36] have established the validity of such a model, and that a 3% moisture content in soil was sufficient to maintain saturation vapor pressure in soil-air provided sufficient pesticide was in soil (more on this later). The first equilibrium is represented by Kd, the second by the Henry's Law Constant, Kh.

The Diffusion Model

Models for several vapor diffusion from contaminated soil situations were developed by Farmer and Letey[37] and modified by Hwang[38]. Here, the diffusion model used involves an infinite-depth soil mass that initially is uniformly contaminated. At an initial time, the air concentration of contaminant at the soil

Table D-1. Applicable Doses and PSLs

Chemical	Applicable Human Dose, mg/kg/day	PSL, mg chemical/kg soil
RDX	$3.0\text{x}10^{-3}$	1020
HMX	$1.0\text{x}10^{-2}$	3380
TNT	$4.0\text{x}10^{-3}$	1350
TNB	$2.5\text{x}10^{-3}$	850
DNB	$1.0\text{x}10^{-3}$	340
NB	$5.0\text{x}10^{-3}$	1690
2,4-DNT	$1.8\text{x}10^{-4}$[a]	61
2,6-DNT	$3.0\text{x}10^{-5}$[a]	10
Tetryl	$1.5\text{x}10^{-3}$	510

---

a. Limits based on 15-months exposure in a lifetime at an 10^{-6} ARL.

surface suddenly drops to zero and is maintained there. This initial condition would correspond to a situation where rapid removal of contaminant occurred at the surface. This model is conservative (a more real-world surface condition would lead to lower vapor flux generation) and provides a simple closed-form expression for surface flux as a function of time. If the ground concentration were 1 mg/kg initially, at a specified time T, the surface flux would be:

$$N(T) = 10^3 * Da * ea^{(4/3)} * (Kh/Kd)/([\pi * Da * ea^{(4/3)} * T]/[ea+\rho s * Kd/Kh])^{0.5}$$

where:
N(T) = Flux at time T, mg/m^2-day per mg/kg soil
Da= the molecular diffusivity of a pollutant in air, m^2/day
ea= the fraction of soil volume occupied by air
Kh= Henry's Law constant, dimensionless.
Kd= Soil-water partition coefficient, L water/kg soil
T= time elapsed since start of process, days
ρs= bulk density of soil, kg/L.

The 10^3 is included to convert m^3 to liters. The time-averaged surface flux for this soil situation is defined as:

$$Nav(T) = 1/T * \int_0^T N(t)dt$$

Nav(T) is related to N(T): Nav(T) = 2*N(T). Nav(T) is used to represent the average vapor generation that can enter the ambient air at a worksite during a work-day.

Vapor Concentration in the Breathing Zone

Following diffusion through and from the soil surface, vapors are diluted by mixing in the bulk air. The extent of this dilution is approximated by a box model suggested by Hwang[38]. Conceptually, the mass (normalized to a mg/kg soil content) emanating from a contaminated surface of area AS m^2 during the time interval from "zero" to T is the product Nav(T)*AS*T. This mass is mixed into a volume of air given by VA = MH*VW*T*LA, where

VA= Volume of air available for dilution, m^3
MH= the mixing height at the site, m
VW= average wind velocity in m/day (86400*m/sec)
LA= Crosswind length dimension of site, m.

In this model, the pollutant concentration in air is uniform from ground level to the MH. However, no horizontal mixing occurs to extend the "box" to a width greater than LA.

As an adverse-case situation, an on-site worker is located in the center of a contaminated area. If this area is square, the worker could be exposed to a normalized concentration of at most

$$0.71*Nav(T)*LS / (MH*VW)$$

where LS is the side of the square*. The corresponding normalized time-averaged intake is

$$Iav = 0.71*IR*SM*Nav(T)*LS / (MH*VW)$$

where IR is the workday air volume inhaled by a worker and SM is the time adjustment for work days and calendar days. The soil limit set by model vapor inhalation of a specific compound (VSL) equals ADI/Iav.

Estimation of Input Variables

The physical properties and Kd for the substances of concern appear in Table D-2. Each Kh is the dimensionless ratio of saturation vapor pressure to water solubility (mg/m^3 in air divided by mg/m^3 in water). The vapor pressures given are for the liquid state of the contaminants at 25 °C. Since most of the compounds are solids at 25°C, With the exception of NB (a liquid at 25 °C), the liquid state vapor pressures are based on extrapolations, and are subject to considerable error, ranging from at least a factor of two for pressures of the order of 0.1 mm Hg to at least an order of magnitude for pressures of

---

* In this case, if the worker were in the center of this square, the area contributing to his exposure would be $LS^2/2$, while at worst, LA =1.414*LS. While the shape of future construction sites is not known, a square shape seems a reasonable model.

Table D-2. Physical Properties of LAAP Soil Contaminants

Compound	Kd	MolWt	Vapor pressure mm Hg, 20 °C	Water sol. mg/L,20 °C	Kh	Da
RDX	1.588	222	$9.0x10^{-9}$ [a]	44 [b]	$2.5x10^{-9}$	0.55
HMX	2.42	296	$3.1x10^{-10}$ [c]	6 [d]	$8.4x10^{-10}$	0.48
TNT	1.069	227	$2.8x10^{-4}$ [b]	124 [b]	$2.8x10^{-5}$	0.55
TNB	0.605	213	$2.2x10^{-4}$ [b]	340 [b]	$7.6x10^{-6}$	0.56
DNB	0.225	168	$3.9x10^{-3}$ [b]	360 [b]	$9.9x10^{-5}$	0.63
NB	0.53	123	0.19 [e]	1900 [f]	$6.7x10^{-4}$	0.74
2,4-DNT	0.504	182	$5.1x10^{-3}$ [b]	273 [b]	$1.8x10^{-4}$	0.61
2,6-DNT	0.504	182	0.018 [b]	273 [g]	$6.6x10^{-4}$	0.61
Tetryl	0.637	278	$1.3x10^{-9}$ [h]	75 [i]	$2.7x10^{-10}$	0.49

---

a. Urbanski[40] cites a relation for the vapor pressure (VP) of solid RDX from 110-138.5 °C, log VP (mm Hg)= 10.87 - 5850/TK, where K is the Kelvin temperature. This expression is used to estimate the vapor pressure at 205 °C, the melting point of RDX[41], as 0.043 mm Hg. This is assumed equal to the vapor pressure of liquid RDX at that temperature (usually the melting point and triple point of a substance occur at nearly the same temperature). The Watson correlation, equation 14-25 of Lyman, et al.[26], is used to extrapolate to 20 °C.

b. Spanggord,et al.[42]

c. Kitchens, et al.[43] present a temperature-pressure curve for the vapor pressure of solid HMX. The curve was extrapolated to the reported HMX melting point at 286 °C, where an 0.54 mm Hg saturation vapor pressure was estimated. The procedure described above for RDX was used to back-extrapolate to 20 °C.

d. Kitchens,et al.[43]

e. Computed by author from temperature-vapor pressure data of liquid in Perry and Chilton[44].

f. Reference 44.

g. Assumed to have the same aqueous solubility as 2,4-DNT.

h. The author estimated the boiling point of tetryl at 574.4 °C by Miller's Method[26]. Next, Watson's Method[26] (equation 14-20 therein) was used to predict the liquid saturation pressure at 20°C.

i. Reference 41.

the order of 10^{-9} mm Hg*.

The Da for each substance was based on a reported value of 0.0645 cm^2/sec for m-chlorotoluene[26] at 25°. This is converted to m^2/day units (0.75), and adjusted to 0.73 m^2/day at 20° assuming a $TK^{1.75}$ proportionality. For other substances, further adjustment was made for molecular weight (126.6 for chlorotoluene), such that:

$$Da(substance) = 0.73 * (126.6 / Molecular\ weight)^{0.5}$$

The parameters ea and ρs were assumed to be 0.25 and 1.35 kg/L respectively in lieu of field data. The time chosen for analysis was 8 hours. This would be in keeping with an excavation activity where at the start of each day, a fresh surface of soil would be exposed to the open air. IR is 20 m^3/day, as discussed in evaluation of the PSL. SM is then 0.667. LS was assumed to be 45 m, corresponding to a square of area 2025 m^2, the average area of an Area P pit.

The terms VW and MH are often associated with air dispersion model input data; however, such models are performed for situations where target individuals are at least 100 m away from a source. Here, target individuals are on the source, so to speak. Valuations of 2 m/sec and 2 m respectively have been suggested by the Environmental Protection Agency for a closely-related situation[39], but the values are admittedly conservative. For the construction situation, where there is considerable moving of equipment to stir the air, and activities occur in the daytime, when vertical mixing is enhanced, a mixing height of 20m should be reasonable.

Results and Interpretation

The resulting VSLs are listed in Table D-3. They must be first be reconciled to model equilibrium assumptions and the physical constraints of saturated aqueous solution and vapor pressure. These two conditions would be expected to occur at a soil concentration of a pollutant equal to the product, water solubility*Kd. The soil solution could not become more saturated if the soil concentration were increased, and corresponding to this, soil air would not be more saturated with vapor. A constant Kd is probably only an approximation to real behavior. More likely, as the soil solution approaches saturation, the relation between soil and soil solution concentration becomes non-linear (an asymptotic soil solution concentration limit is approached).

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* Usually, the term $\rho s*Kd/Kh >> ea$, so that for a given Kd, N(T) nearly proportional to $Kh^{0.5}$. Thus, a two-order of magnitude uncertainty in Kh usually leads to an one-order magnitude uncertainty in VSL. However, for most compounds at this level of Kh, one order of magnitude difference in VSL makes little difference in the CCSL ultimately computed.

For purposes of computing soil concentration limits, a constant Kd is probably a conservative approach; it should lead to a soil limit lower than that which would be computed if equilibrium relations were better-known. Thus, there is a limiting flux that can be generated from soil, which limits the ambient air concentration.

The solubility*Kd product is also shown in Table D-3. If the VSL is less than this value, the VSL and PSL can be used to develop the CCSL:

$$CCSL = 1/\ (1/PSL + 1/VSL)$$

If the VSL exceeds the product water solubility*Kd, a different approach is taken, whereby the intake that could be provided from soil with pollutant concentration (solubility*Kd) is accounted for prior to performing the PSL calculation. This intake is ADI*(solubility*Kd)/VSL. Then the CCSL is:

$$CCSL = (10^6\ /\ 207)*ADI*(\ 1-[solubility*Kd]/VSL)$$

Table D-4 provides the calculations involved in computing VSL and CCSL for TNT (where the second equation is used) and for 2,4-DNT (where the first equation is used).

Table D-3. VSL and CCSLs for LAAP Soil Contaminants

Compound	VSL, mg/kg	Solubility*Kd, mg/kg	CCSL,mg/kg
RDX	$6.4\text{x}10^4$	70	1010
HMX	$4.8\text{x}10^5$	14	3380
TNT	660	132	1080
TNB	590	206	550
DNB	38	81	34
NB	100	1010	97
2,4-DNT[a]	4.0	137	3.7
2,6-DNT[a]	0.67	137	0.63
Tetryl	$6.6\text{x}10^4$	48	510

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[a] This calculation is based on an ARL of 10^{-6}. For a higher ARL, the VSL may exceed the product Kd*solubility. In that case, the other CCSL procedure should be applied.

Table D-4. Sample Calculation of VSL and CCSL for TNT and 2,4-DNT

Calculation or value[a]	Result for TNT	Result for 2,4-DNT
1. Time, days	0.333	0.333
2. $Da*ea^{4/3}$	$8.66x10^{-2}$	$9.61x10^{-2}$
3. Kh/Kd	$2.62x10^{-5}$	$1.33x10^{-3}$
4. N(T) numerator	$2.27x10^{-3}$	$1.27x10^{-1}$
5. Term $\pi*Da*ea^{4/3}*T$	$9.07x10^{-2}$	0.101
6. Term $ea+\rho s*Kd/Kh$	$5.15x10^{4}$	$1.02x10^{3}$
7. Term 5/ Term 6	$1.76x10^{-6}$	$9.90x10^{-5}$
8. N(T) denominator[b]	$1.33x10^{-3}$	$9.95x10^{-3}$
9. N(T)[c]	1.71	12.8
10. Nav(T)	3.42	25.7
11. 0.71*IR*SM*LS/(MH*VW)	$1.23x10^{-4}$	$1.23x10^{-4}$
12. Iav (Term 10 * Term 11)	$4.22x10^{-4}$	$3.17x10^{-3}$
13. ADI, mg/day	0.28	$1.26x10^{-2}$
14. VSL, mg/kg	664	4.0
15. Solubility*Kd, mg/kg	132	137
16. Maximum intake by from diffused compound,mg/day	$5.56x10^{-2}$	$1.26x10^{-2}$
17. Reduced ADI[d]	0.0224	Not applicable
18. $10^6/207$ * Reduced ADI= CCSL	1084	Not applicable
19. PSL (Table D-1)	1350	61
20. 1/ (1/VSL + 1/PSL)	Not applicable	3.7

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[a] See text or Table D-2 for input values.
[b] Square root of Term 7.
[c] Units of $(mg/m^2\text{-day})/(mg/kg)$
[d] ADI-Term 16

GLOSSARY OF SYMBOLS AND ACRONYMS

ACSL	Aquatic life safety-related contaminated soil limit, mg/kg
ADI	Acceptable daily intake for construction model, mg/day
ARL	Acceptable risk level
AS	Contaminated surface area in construction model, m^2
ASWL	Aquatic life safety-related water limit, mg/L
ax	Longitudinal dispersivity, m
ay	Transverse dispersivity, m
az	Vertical dispersivity, m
C(X)	Receptor concentration, mg/m^3.
C(X,i)	Concentration at receptor attributable to puff release occurring i years after "time zero"
CCSL	Construction worker health-related contaminated soil limit, mg/kg
CSMIXIN	LPUSC pollutant concentration in a compartment prior to mixing with incoming groundwater
CWIN(j)	Pollutant concentration in groundwater entering jth compartment
Da	Molecular diffusivity of pollutant in air, m^2/day
DCSL	Drinking water-related contaminated soil limit, mg/kg
DNB	1,3-Dinitrobenzene
2,4-DNT	2,4-Dinitrotoluene
2,6-DNT	2,6-Dinitrotoluene
DWL	Drinking water limit, µg/L
ea	Fraction of soil volume occupied by air
EPA	Environmental Protection Agency
fw	Fraction of watershed occupied by Area P
HMX	Cyclotetramethylene tetranitramine, a major explosive
Iav	Time-averaged intake of vapors in construction model, mg/day per mg/kg in soil
IR	Daily air intake by construction worker, m^3
Kd	Soil-water partition coefficient, L water/kg soil.
Kh	Henry's Law constant, unitless
Koc	Organic carbon fraction of soil-water partition coefficient, L water/kg soil organic carbon.
Kow	Octanol-water partition coefficient
LA	Crosswind length of model contaminated area, m
LAAP	Louisiana Army Ammunition Plant
LAC	Lifetime-averaged normalized concentration in water, µg/L per mg/kg in soil
LAP	Load, assembly and pack
LPUSC	Lower portion of the unsaturated soil column
LS	Length of a square area, m

M0...Mj	Release at 0 to j^{th} year from linear source, mg/m
MASSMIX	Pollutant in the LPUSC part of a soil compartment, mass units
MH	Mixing height in construction model, m
MP	Melting point, °C
MSCMIX	Soil mass in the LPUSC portion of a soil compartment
Nav(T)	Time-averaged normalized flux, (mg/m^2-day)/(mg/kg)
NB	Nitrobenzene
NOEL	No-observable effect level dose, mg/kg
N(T)	Normalized flux from soil at time=T, (mg/m^2-day)/(mg/kg)
PSL	Soil limit based on particulate intake, mg/kg.
q^*	Estimated carcinogenic potency, (mg/kg/day)$^{-1}$
Qm	Maximum value of one-dimensional normal distribution.
Q(x,y,t)	Normalized concentration at a receptor from a linear source t years after a release of 1 unit mass/length (z -dimension).
Rd	Retardation factor of pollutant relative to groundwater flow.
RD	Reference dose, mg/kg/day
RDX	Cyclotrimethylene trinitramine, a major explosive.
SM	Calendar work days adjustment factor (2/3).
SOL	Aqueous solubility limit of pollutant, mole fraction.
t	Time, in years in groundwater plume equations
T	Specific time, in days for construction scenario.
TK	Temperature, °K
TLV	Threshold limit value, mg/m^3
TNB	1,3,5-Trinitrobenzene
TNT	2,4,6-Trinitrotoluene, a major explosive
UPUSC	Upper portion of the unsaturated soil column
USATHAMA	US Army Toxic and Hazardous Materials Agency
V	Groundwater velocity, m/year.
VA	Air volume for diluting diffusing vapors, m^3.
VFIN	Volume of water infiltrating to LPUSC in a compartment.
VWCMIX	Groundwater in aquifer in a soil compartment.
VP	Saturation vapor pressure, mm Hg
VSL	Soil limit based on diffusing vapor intake, mg/kg.
VW	Average windspeed, m/day.
x	Downgradient distance from source to receptor,m
XCW	Pollutant in groundwater in soil compartment after mixing and equilibrium.
y	Cross-gradient distance from source to receptor,m

z	Vertical dimension distance
Zd	Specific vertical position
ϵ	Effective porosity of soil in aquifer and LPUSC.
ρs	Bulk density of soil, kg/L
$\sigma(z,1)$	Normal distribution z-directed dispersion parameter one year after puff release, m.

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