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ENVIRONMENTAL RISK ASSESSMENT FOR FOUR MUNITIONS-RELATED CONTAMINANTS AT SAVANNA ARMY DEPOT ACTIVITY

DAVID H. ROSENBLATT, Ph.D.

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

by

U S ARMY MEDICAL BIOENGINEERING RESEARCH & DEVELOPMENT LABORATORY
Fort Detrick
Frederick, Maryland 21701

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This report presents the results of calculations indicating that four munitions-related soil/sediment (or groundwater) pollutants identified at the Savanna Army Depot Activity present no serious health risk through the two exposure routes considered. The pollutants are TNT, DNT, 1,3,5-trinitrobenzene and RDX. The exposure routes are via ingestion of bottom-feeding fish or via Mississippi River water in downstream drinking water supplies.

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INTRODUCTION

Concern for environmental consequences has prompted examination of the risks associated with munitions-related soil and sediment pollutants at military installations.[1,2] Pollutants at such installations appear to raise sets of issues quite specific to each site. Thus, the two overriding questions relating to the Savanna Army Depot Activity were:

1. Would trinitrotoluene or dinitrotoluene from polluted sediments contaminate bottom-feeding fish in internal waterways to levels dangerous for human beings who might consume the fish?

2. Could TNT, dinitrotoluene, RDX, or 1,3,5-trinitrobenzene found in old dry munitions washout lagoons--or in the ground beneath them--significantly pollute nearby waterways or wells?

SITE BACKGROUND

The Savanna Army Depot Activity (SADA) lies north of Savanna, IL, stretching 21 km along the Mississippi River, and is at most 5 km in width. Its area is approximately 5,330 ha (hectares), of which 1740 ha, along the river, is in the flood plain, and includes 223 ha of waterways. More than half the installation consists of bluffs and low hills above the flood plain.[3,4] The rainfall, R, is 86 cm (8.6 dm) per year.[4]

Several munitions-related activities were conducted there since SADA was activated as the Savanna Proving Ground in December 1918. Of these activities, the most significant, as regards the present study, are: (1) disposal of munitions, through burning,[3,4] which appears to have contaminated sediments over a 10 ha area of internal waterways (but so far, only one sediment sample has shown any contamination, 0.289 mg/kg of TNT[3]), and (2) washing out of munitions during TNT reclamation operations.[3,4] The latter activity is linked to the presence of four abandoned contaminated lagoons in the flood plain and two above the flood plain (Table 1). The normally dry lagoons do not drain catchment areas beyond their own borders, since they are protected by berms. In addition to the measurements shown in Table 1, 0.420 mg/L trinitrotoluene and 0.314 mg/L trinitrobenzene were found in water taken from porous limestone bedrock below the upland dry lagoons.[3] The direction of flow of groundwater into which the pollutants in the lagoons are leached appears to be entirely towards the Mississippi River.[3] Thus pollution of wells on farms to the east is not considered further.

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TABLE I. AREAS AND CONTAMINATION OF THE SEDIMENT OF DRY LAGOONS[3]

Location	Area (ha)[a]	Contamination (mg/kg)[b]		
		TNT[c]	DNT[d]	RDX[e]
Flood plain	0.113	Up to 290,000	Up to 94,000	-
Flood plain	0.048	Up to 3,000	-	-
Flood plain	0.048	Up to 3,000	-	-
Flood plain	0.048	Up to 3,000	-	-
Upland	0.132	12,000-181,000	-	3,000-4,000
Upland	0.132	12,000-181,000	-	3,000-4,000

a. One hectare (ha) = 10^6 dm^2. The total area of the six lagoons is 5.21×10^5 dm^2.
b. The fourth compound, 1,3,5-trinitrobenzene was not found in the lagoons, only in groundwater. If it is present in the lagoons, the analytical methods used may have failed to identify it.
c. 2,4,6-Trinitrotoluene.
d. 2,4-Dinitrotoluene (with lesser amounts of isomers, especially 2,6-*dinitrotoluene*).
e. Hexahydro-1,3,5-trinitro-1,3,5-triazine.

BACKGROUND ON FISH CONSUMPTION[5]

Commercial fishing in SADA's internal waterways is subject to license. The catch is sold in Chicago, primarily for nonfood uses. During the first half of 1981, this had amounted to about 15,000 lb of buffalo carp and 500 lb of catfish. Recreational fishing is currently licensed to 230 employees and retirees of SADA. Of these, not more than 20 to 30 are steady fishermen. Since such people have adequate incomes, it may be presumed that none depends on this source for his main food supply. It was estimated that a fisherman might take about 6 kg of fish per year, of which bottom feeders (carp and catfish) might amount to perhaps 3 kg; 5 kg of bottom feeders would represent an exceptionally large annual recreational catch. Fish consist of about 50 percent refuse or more;[6] therefore, a fisherman would have at most perhaps 2.5 kg per year of the flesh of bottom feeders, most frequently divided among several members of a family. As a safesided estimate, one might assume a maximum daily consumption of $W_f = 10$ g of bottom-feeder flesh per person per day (3.65 kg/year) for the small population most at risk.

RELATING THE CONCENTRATION OF A CONTAMINANT IN SEDIMENT TO THAT IN FISH

The problem addressed in this section is to define the relationship between the concentration of a contaminant in the flesh of a bottom-feeding fish and the concentration of that compound in sediment covering a certain fraction, f, of the floor beneath the fish's habitat. The water is considered to be free of the compound,[3] so that sediment is the only source of flesh contamination. It is further assumed that the fish's daily diet amounts to no more than 6 percent of its body weight;[7] that all the contaminant is extracted from the diet and is initially assimilated; and that, as a worst case, the diet consists entirely of sediment contaminated at an assumed level, C_s', adjusted for the contaminated fraction, f, of waterway floor. This assumes that the fish roam freely over the entire internal waterway. Thus the intake rate is

$$r_i = C_s'(\text{mg/kg}) \times f \times 0.06 \text{ (kg sed/kg fish/day)}$$
$$= 0.06 \, f \, C_s' \text{ (mg/kg/day)} \tag{1}$$

The rate constant for loss of the contaminant from the fish into the surrounding water, k_2 (day^{-1}), was related by Spacie and Hamelink[8] to the octanol-water partition coefficient[9] through the equation

$$\log k_2 = 1.47 - 0.414 \log K_{ow} \tag{2}$$

The loss rate depends both on k_2 and on the concentration in the fish, C_f', i.e.,

$$r_1 = k_2 C_f' \tag{3}$$

The maximum <u>allowable</u> value for C_f', if one assumes that such fish are the only exposure source of the contaminant to human beings, is

$$C_f = 70 \, D_T / W_f \tag{4}$$

where D_T is the acceptable daily dose[1,10,11] of the contaminant. Hence, at the maximum allowable level,

$$r_1 = 70 \, k_2 D_T / W_f \tag{5}$$

At equilibrium, $r_i = r_1$, whence the maximum <u>allowable</u> value for contaminant concentration in the sediment is

$$C_s = \frac{70 \, k_2 D_T}{0.06 \, f \, W_f} = \frac{1{,}167 \, k_2 D_T}{f \, W_f} \tag{6}$$

Since f = 10/223 = 0.045 (i.e., 10 hectares contaminated out of a total of 223 hectares of waterway) and W_f = 0.01 kg/day, Equation (6) reduces to

$$C_s = 2.6 \times 10^6 \, k_2 D_T \tag{7}$$

DILUTION OF LEACHATE BY THE MISSISSIPPI RIVER

River flow is commonly expressed in cubic feet per second (cfs or more properly cf/s). This may be converted to liters per year by the following factor:

$$1 \text{ cf/s} \times 3.1536 \times 10^{7} \text{ s/yr} \times 28.3 \text{ L/cf} = 9.92 \times 10^{8} \text{ L/yr} \quad (8)$$

For the Mississippi's historic lowest-flow year (1964) since the river was dammed,[12] the average flow rate at Clinton, Iowa (about 50 km below SADA) was $F = 28{,}220$ cfs, or $F = 2.5 \times 10^{13}$ L/yr. The dilution factor for leachate is

$$f_d = V_w/F \quad (9)$$

where V_w is the volume of leachate. Where the total contaminated lagoon area is A,

$$V_w(\text{L}) = A\ (\text{dm}^2) \times R(\text{dm}) = 8.6A \quad (10)$$

Thus,

$$f_d = 8.6\ A/F = 3.4 \times 10^{-13}A \quad (11)$$

As a worst-case assumption, the concentration of pollutant in the leachate of a dry lagoon will be considered to be at the solubility limit, S, of the pollutant, although this is probably not true. (And if it were true, the lagoon would be rapidly cleansed.) Thus (where f_d' is the dilution factor for the lagoons known to be contaminated and f_d'' is the calculated dilution factor assuming all lagoons to be contaminated), the maximum possible Mississippi River concentration of any pollutant initially found in the lagoons would be

$$C_w' = S\ f_d' \quad (12a)$$

$$\text{or } C_w'' = S\ f_d'' \ (\text{with } f_d'' = 1.792 \times 10^{-7}) \quad (12b)$$

If C_w' or $C_w'' < C_w$ (where C_w is the permissible concentration level for the contaminant in drinking water, shown in Table 2), then the lagoons do not present a river contamination problem. (<u>Note</u>: Because of the relatively low bioconcentration of the compounds of interest, water acceptable for drinking could not be a significant source of fish contamination.)

TABLE 2. PHYSICOCHEMICAL CONSTANTS, ACCEPTABLE DAILY DOSES (D_T), AND PERMISSIBLE CONCENTRATION LEVELS IN DRINKING WATER FOR SADA CONTAMINANTS

Compound	Solubility(S) (mg/L)	Log K_{ow}	k_2[a] (day^{-1})	D_T (mg/kg)	C_w[b] (mg/L)
2,4,6-Trinitro-toluene (TNT)	124[c]	1.84[d]	5.11	1.4×10^{-3}[e] (or 1.4×10^{-5})	5.0×10^{-2} (5.0×10^{-4})
2,4-Dinitrotoluene (DNT)	273[c]	1.98[f]	4.47	3.2×10^{-5}[e]	1.1×10^{-3}
1,3,5-Trinitro-benzene (TNB)	32[c]	1.18[g]	9.58	5.8×10^{-3}[e] (or 5.8×10^{-5})	2.0×10^{-1} (2.0×10^{-3})
Hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX)	44[c]	0.87[h]	12.87	1.0×10^{-3}[i]	3.5×10^{-2}

a. See Equation (2) in text.
b. The value of C_w is, numerically, 35 D_T (c.f. References 10,11).
c. Reference 13.
d. Estimated by method of Reference 14 from log K_{ow} for TNB given in Reference 9, p. 195.
e. Reference 1. Numbers in parentheses are alternative values obtained through application of a factor of 10^{-2} to address the possibility of oncogenicity that was raised by the findings, for TNT and TNB, of mutagenic effects on microorganisms; this conservative approach, which is strictly judgmental, was suggested by Mr. Jesse J. Barkley of this Laboratory, and was first presented in reference 1. The value of D_T for DNT, cited from reference 1, was derived from a water quality criterion that was corrected to change it to a drinking water criterion. For DNT, the correction involved deletion of the contribution of fresh water and estuarine fish consumption, a very small numerical change. Thus, a drinking water criterion is expressed as:

Concentration = (Allowable daily intake) ÷ 2

For a water quality criterion

Concentration = (Allowable daily intake) ÷ (2 + (BCFxDC))

Here,

BCF = Bioconcentration factor in fish = 3,8 for DNT (reference 17)

DC = Daily fish consumption = 0.0065 kg (reference 17).

f. Reference 9 p. 215.
g. Reference 9, p. 195.
h. Reference 15.
i. Reference 16.

COMPOUND-SPECIFIC CALCULATIONS FOR SADA

PPLVs (preliminary pollutant limit values[10,11]) for the SADA inland waterway sediments and predicted maximum levels for these pollutants in the Mississippi River were calculated, respectively, from equations (7) and (12). They are shown in Table 3. These PPLVs represent the level of contaminants in the waterway sediments at or below which it is estimated that unacceptable fish contamination will not occur. Although 1,3,5-trinitrobenzene was identified in only one groundwater sample, it is a known photochemical degradation product of TNT, and was included in the PPLV calculations for this reason. The limit values for the four compounds in the waterway sediments are quite high (above 190 mg/kg in all cases, even when allowances are made for the possibility that TNT and TNB will later be shown to cause cancer). The one contaminated waterway sediment sample showed only TNT--and this nearly three orders of magnitude less than the PPLV (0.289 mg/kg, as stated above). Since the only detected contaminant (i.e., TNT) occurred at such a low level, bottom-feeding fish are unlikely to be a significant dietary source of the contaminants. Therefore, the current level of inland waterway sediment contamination does not represent a significant health hazard from the standpoint of consumption of fish caught in the waterway.

TABLE 3. SEDIMENT PPLVs AND PREDICTED MAXIMUM MISSISSIPPI RIVER CONCENTRATIONS OF SADA POLLUTANTS

Compound	Preliminary Pollutant Limit Values for the SADA Inland Waterway Sediments[a]	Predicted Maximum Concentrations in the Mississippi River Resulting from Leaching of Contaminated Dry Lagoons[b]	
	C_s (mg/kg)	C_w' (mg/L)	C_w'' (mg/L)
TNT	1.9×10^{4} (1.9×10^{2})	2.2×10^{-5}	2.2×10^{-5}
DNT	3.7×10^{2}	1.05×10^{-5}	5.8×10^{-5}
TNB	1.4×10^{5} (1.4×10^{3})	--	5.7×10^{-6}
RDX	3.3×10^{4}	3.9×10^{-6}	7.8×10^{-6}

a. Numbers in parentheses are based on D_T values that are safesided to allow for possible oncogenicity, in view of demonstrated mutagenicity, as explained in Reference 1 and in footnote e to Table 2. See Equation (7).

b. C_w' is calculated only for dry lagoons in which the contaminated was found. C_w'' assumes presence of the contaminant in all the lagoons. See Equation (12).

The maximum estimated pollutant concentrations in the Mississippi River resulting from the leaching of contaminated dry lagoons, certainly less than 6×10^{-5} mg/L, are an order of magnitude or more below the most stringent permissible concentrations for drinking water. It is probable that the lagoon sediments will be removed and disposed of. If so, the underlying unsaturated zone, presumably containing pollutant only as a solute in the water retained there, will be subject to the flushing action of the rain. In a finite time, depending on its depth, the unsaturated zone should be essentially cleansed.

CONCLUSIONS

Assessments, on the basis of assumed lifetime exposures, have been made for the potential of four SADA soil/sediment contaminants to present human health risks. It is posited that all probable sources of these contaminants have been accounted for, and that exposures would occur only through drinking contaminated Mississippi River water or eating contaminated bottom-feeding fish. If so, there are not significant risks to human beings.

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GLOSSARY OF SYMBOLS

A = Area of dry lagoon sediments assumed to be contaminated.

BCF = Bioconcentration factor in fish

C_f = Maximum allowable value of C_f'.

C_f' = Concentration of contaminant in fish flesh.

C_s = Maximum allowable value of C_s'.

C_s' = Concentration of contaminant in internal waterway sediments.

C_w = Permissible concentration level of contaminant in drinking water.

C_w' = Predicted concentration of contaminant in downstream Mississippi River water, assuming conditions of f_d'.

C_w'' = Predicted concentration of contaminant in downstream Mississippi River water, assuming conditions of f_d''.

cfs = cf/s = Cubic feet per second.

D_T = Acceptable daily dose of a contaminant for humans.

DC = Daily fish consumption

dm = Decimeter (i.e., 10 cm).

DNT = Dinitrotoluene. (In the present context, the data are for the principal isomer, 2,4-dinitrotoluene.)

F = Average historic low flow (of the Mississippi River at Clinton, Iowa).

f = Fraction of SADA's internal waterway floor sediments assumed to be contaminated by a given pollutant.

f_d = Dilution factor for the mixing of rainwater that has percolated through dry lagoon sediments with water of the Mississippi River.

f_d' = Value of f_d when only dry lagoon sediments known to be contaminated with the compound in question are considered.

f_d'' = Value of f_d when it is assumed that the sediments of all the dry lagoons are contaminated.

K_{ow} = Octanol-water partition coefficient.

k_2 = Rate constant for loss (depuration) of a specific contaminant from fish to the surrounding water.

PPLV = Preliminary pollutant limit value.

R = Rainfall (in decimeters) per year.

r_i = Rate of intake by a bottom-feeding fish of a specific contaminant present in sediment.

r_l = Rate of loss (depuration) of a specific contaminant present in its flesh.

RDX = Hexahydro-1,3,5-trinitro-1,3,5-triazine.

S = Solubility of a contaminant in water (ambient temperature).

SADA = Savanna Army Depot Activity.

TNB = 1,3,5-Trinitrobenzene.

TNT = 2,4,6-Trinitrotoluene.

V_w = Volume of dry lagoon leachate that mixes with Mississippi River water annually.

W_f = Weight of fish consumed daily by high-level consumers.

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