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Recent Developments in Formulating Model Descriptors for Subsurface Transformation and Sorption of Trinitrotoluene^a

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TNT is a military explosive sometimes found in groundwaters at World War II vintage munitions production and handling facilities.^{1,2} The potential for off-site migration of TNT groundwater plumes after source remediation is a concern at many of these sites. Processes affecting groundwater transport of TNT include, but are not limited to, convection, hydrodynamic dispersion, biodegradation, abiotic transformations, sorption, and diffusion.³ Not all processes affect TNT subsurface transport equally, making it important to identify key processes involved and develop accurate descriptors for these processes.

This paper analyzes recent published data from batch and column studies conducted to improve the state of knowledge regarding subsurface transport of TNT and assembles available coefficients for modeling subsurface transport of TNT. A review of the early literature was provided by McGrath.³ Studies conducted since preparation of the McGrath report³ are the main focus of this paper.

TNT TRANSPORT PHENOMENA

TNT Transformation

Although TNT reductive transformation has been known for some time^{4,5} it is only recently that TNT reductive transformation products have been measured in laboratory soil columns.^{6–11}

TNT transformation in saturated soils involves sequential nitro group to amino

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group reductions (FIG. 1). Major reductive transformation products include 2-amino-4,6-dinitrotoluene (2A-DNT), 4-amino-2,6-dinitrotoluene (4A-DNT), 2,4-diamino-6-nitrotoluene (2,4-DANT), 2,6-diamino-4-nitrotoluene (2,6-DANT) and triaminotoluene (TAT). Ainsworth *et al.*¹² indicated the probable formation of 4A-DNT in TNT soil column experiments. Then, Comfort *et al.*,⁸ Selim, Xue, and Iskandar,⁹ and Townsend, Myers, and Adrian⁶ showed the formation of 2A-DNT and 4A-DNT in soil column experiments. Comfort *et al.*⁸ and Selim *et al.*⁹ did not analyze for diaminonitrotoluenes. Townsend *et al.*⁶ analyzed for but did not detect diaminonitrotoluenes. There is, however, evidence of diaminonitrotoluene formation in recent soil column studies.¹¹

Reductive transformation of TNT is significantly enhanced under anaerobic conditions, as would be expected since the predominant transformations in saturated soils are reduction reactions. Depending on the redox potential, one, two, or three of the nitro groups can be reduced to amino groups.^{4,13-15} Price *et al.*⁷ showed that

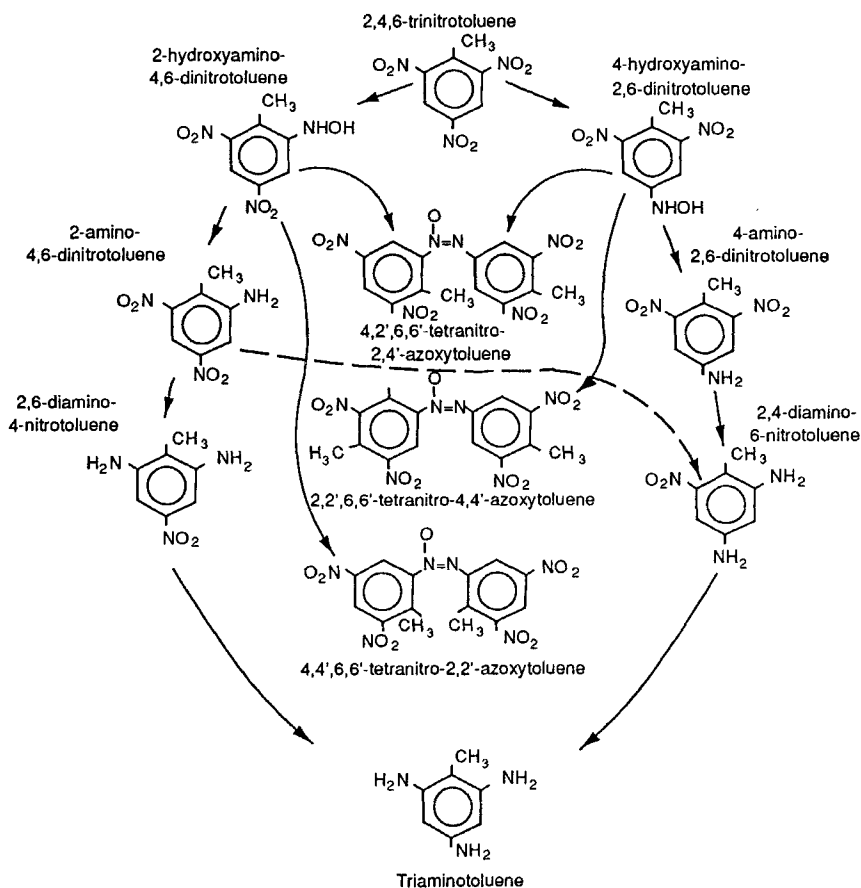


FIGURE 1. TNT transformation pathway diagram (from McGrath³).

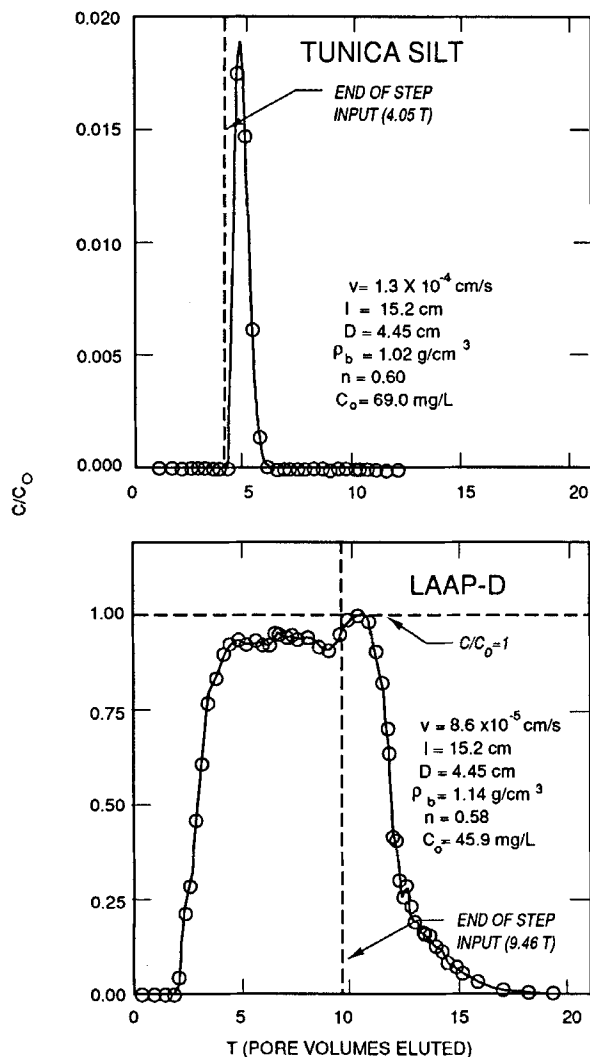


FIGURE 2. TNT breakthrough curves for a soil and LAAP-D (v = average pore water velocity, L = column length, D = column diameter, ρ_b = bulk density (from Myers *et al.*¹¹ and Myers and Townsend¹⁶).

TNT was not stable at any Eh tested (+500, +250, 0, -150 mV) for a clay soil, and that TNT was the most unstable at Eh = -150 mV.

FIGURE 2 shows normalized TNT breakthrough curves for two soils of different grain sizes.^{11,16} The Tunica silt is a loam (4% sand, 82% silt, 14% clay) from Vicksburg, MS, and the LAAP-D soil (22% sand, 36% silt, 42% clay) is from the Louisiana Army Ammunition Plant (LAAP), Shreveport, LA. The difference in breakthrough

curves is dramatic. Practically all of the TNT mass introduced to the LAAP-D soil eluted from the column as TNT (95.4 per cent), whereas very little of the TNT mass input to the Tunica silt eluted from the column as TNT (< 1 per cent) (FIG. 3). FIGURE 4 shows 2A-DNT, 4A-DNT, 2,4-DANT, and 2,6-DANT elution curves associated with the TNT breakthrough curve for Tunica silt. The majority of the

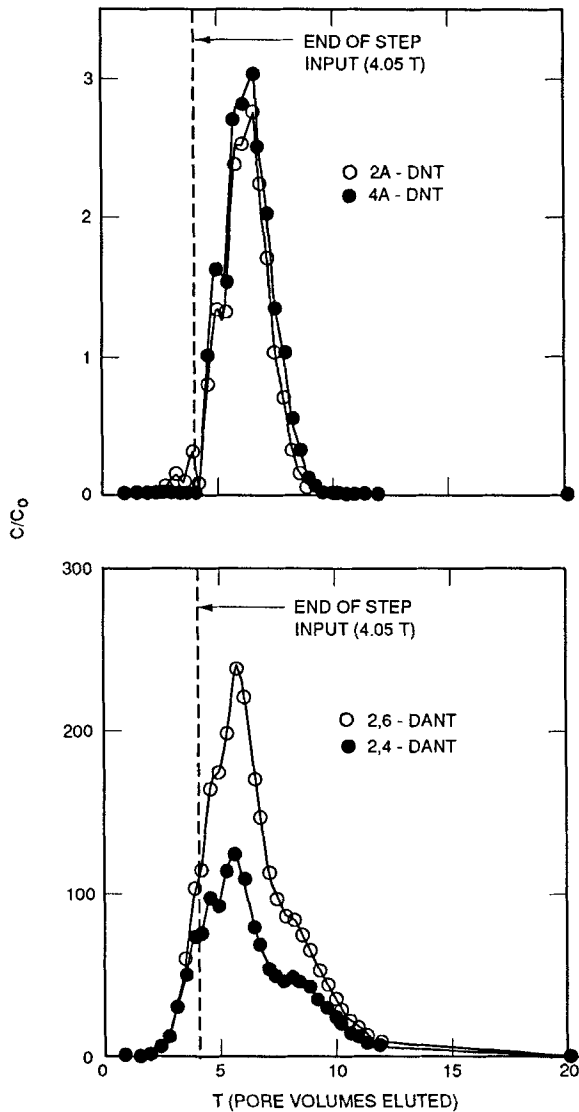
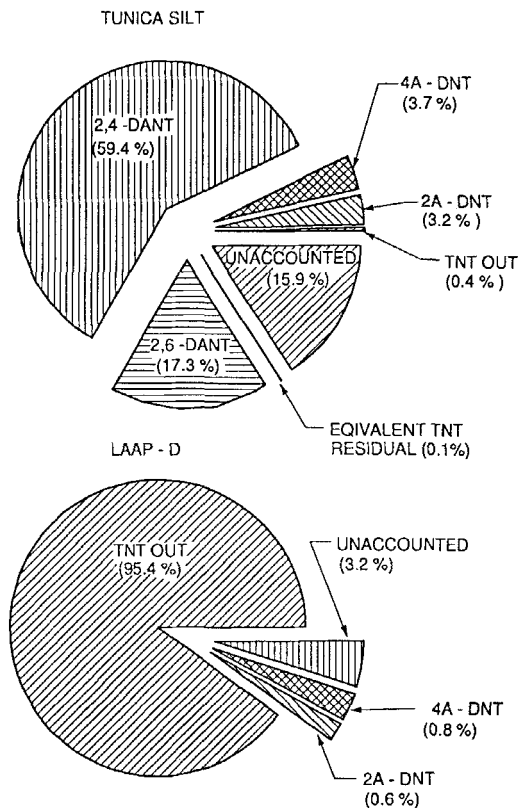


FIGURE 3. Tunica silt TNT transformation product breakthrough curves (from Myers *et al.*¹¹).

FIGURE 4. TNT column mole balances for Tunica silt and LAAP-D (from Myers *et al.*¹¹ and Myers and Townsend¹⁶).



TNT input to the Tunica silt eluted as measurable transformation products, whereas TNT transformation in the LAAP-D soil was negligible.

The transformation data for Tunica silt in FIGURES 3 and 4 indicate that caution should be used when interpreting soil column data solely on the basis of TNT or TNT, 2A-DNT and 4A-DNT analyses. For example, on the basis of TNT alone, the Tunica silt TNT data could be misinterpreted to mean that most of the TNT input was irreversibly sorbed. Even if 2A-DNT and 4A-DNT analyses are included, the data could still be misinterpreted to mean that most of the TNT input was irreversibly sorbed. The difference between irreversibly sorbed (does not elute) and eluted as reductive transformation products is important since amino substituted toluenes tend to be more toxic than nitro substituted toluenes.

As indicated in FIGURE 4, about 20% of the TNT input to the Tunica silt was unaccounted for. Several possibilities exist for the unaccounted for fraction. These are as follows:

- Formation/transformation of TAT. Reduction of DANTs to TAT in cell suspensions was reported by Preuss and Rieger.¹⁴ TAT is highly unstable¹⁴ and therefore likely to react before it can be collected and analyzed. In addition, TAT requires $E_h \leq -250$ mV for formation.¹⁵ Neither TAT nor E_h were measured in Tunica

soil column eluates. However, the significant formation of DANTs is indicative of low Eh. Overall, TAT formation and transformation is consistent with the available data and therefore likely.

- Azoxy compound polymerization. Accumulation of azoxytoluene compounds in Tunica clay soil column eluates was minimal compared to accumulations of aminonitrotoluenes. However, if azoxy compound formation is intermediate to further polymerization and further polymerization is a fast reaction, no accumulation of azoxytoluenes would be expected, and the fraction unaccounted for could be due to irreversible disappearance via azoxytoluene polymerization.
- Irreversible soil binding. Azoxytoluene polymerization is a form of irreversible soil binding. Other irreversible soil binding mechanisms include TNT incorporation into soil organic matter and chemisorption to soil inorganic surfaces. Irreversible soil binding has been suggested as the mechanism accounting for TNT disappearance in soil column studies.^{8,9} It should be noted that TNT and TNT transformation products in acetonitrile extracts from the Tunica silt at the termination of the column study were insignificant contributors to the overall mole equivalent balance (Fig. 4).
- TNT mineralization. TNT mineralization to CO₂ and H₂O has not been significant in laboratory soil studies.^{7,17} TNT mineralization therefore probably does not explain the fraction unaccounted for.

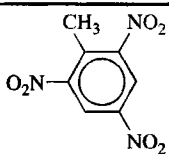
There is evidence that TNT transformations are biologically mediated. Townsend *et al.*⁶ pumped over 150 pore volumes of TNT-contaminated feed solution into Tunica silt and found that TNT transformations were still occurring at the end of the loading step. These data suggest a non-exhaustible transformation process, which is consistent with biological transformation. Price and Brannon⁷ tested several specific soil components for their abilities to transform TNT. When montmorillonite, kaolinite, or Fe²⁺ alone were tested, no transformations were observed. However, when montmorillonite or kaolinite was combined with Fe²⁺ significant amounts of transformation were observed, suggesting that Fe²⁺ plays an important role in TNT reductions. Since Fe²⁺ alone could not transform TNT, microorganisms and/or surfaces are also needed. Price and Brannon⁷ suggested that under anaerobic conditions, Fe³⁺ is biologically reduced to Fe²⁺. In turn, Fe²⁺ provides electrons for nitro group reductions to amines. The Fe³⁺ is then again biologically reduced, thus forming a cycle. Similar ideas have also been postulated by Ainsworth *et al.*¹² and Preuss and Rieger.¹⁴ In experiments where both sterilized and unsterilized soils were used^{11,18} transformations were observed under both conditions, suggesting the presence of a purely abiotic transformation component. However, transformations were far more extensive in unsterilized soils than in sterilized soils.

Pseudo-first-order TNT disappearance rate constants have been measured ranging from 0.17×10^{-2} to $14.0 \times 10^{-2} \text{ hr}^{-1}$ (TABLE 1). These constants are lumped parameters that reflect reductive transformations, polymerizations, and irreversible binding. They should not be viewed solely as irreversible sorption rate constants or transformation rate constants.

TNT Sorption

Several investigators^{8,10,12,18,19} have reported batch-determined equilibrium sorption coefficients. The isotherm plots in all these studies are well behaved and in all respects appear to be reliable data. Recent batch experiments of Price, Brannon, and Hayes⁷ and Myers *et al.*,¹¹ however, show that TNT in batch tests for some soils

TABLE 1. 2,4,6-trinitrotoluene (TNT) Solubility and Transport Properties

CAS Reg. No.: 118-96-7			
Formula: C ₆ H ₂ CH ₃ (NO ₂) ₃ or C ₇ H ₅ N ₃ O ₆			
Molecular Mass: 227.13 g · mol ⁻¹			
Aqueous Solubility			
0 °C	100 mg · L ⁻¹		Urbanski (1964) ²⁴
10 °C	110 mg · L ⁻¹		Urbanski (1964) ²⁴
15 °C	200 mg · L ⁻¹		Verschueren (1983) ²⁵
20 °C	120 mg · L ⁻¹		Urbanski (1964) ²⁴
25 °C	130 mg · L ⁻¹		Urbanski (1964) ²⁴
	~100 mg · L ⁻¹ (~0.01%)		Merck (1983) ²¹
	150 mg · L ⁻¹		Urbanski (1964) ²⁴
Transport Properties			
	K _d = 0.5 – 5.5		Ainsworth <i>et al.</i> (1993) ¹²
	1.5 – 10.0		Townsend <i>et al.</i> (1995) ⁶
Partitioning	0.0 – 1.8		Myers <i>et al.</i> (1997) ¹¹
Coefficients from soil	1.67, 4.80		Comfort <i>et al.</i> (1995) ⁸
Column breakthrough	Freundlich		
Curves	K _c = 3.6 cm ³ g ⁻¹ , b = 0.8		
	K _c = 9.6 cm ³ g ⁻¹ , b = 0.5		Selim <i>et al.</i> (1995) ⁴
	Water: 6.71 E-06 cm ² · s ⁻¹ (25° C; est.)		Rosenblatt <i>et al.</i> (1989) ²⁶
Diffusion	Air: 0.064 cm ² · s ⁻¹ (25° C; est.)		
First order	1.7 E-03 – 8.7 E-02 h ⁻¹		Ainsworth <i>et al.</i> (1993) ¹²
Disappearance rate	8.0 E-03 – 2.5 E-02 h ⁻¹		Townsend <i>et al.</i> (1995) ⁶
Constants from soil	3.2 E-03 – 1.4 E-01 h ⁻¹		Myers <i>et al.</i> (1997) ¹¹
Column breakthrough	1.9 E-02 – 1.05 E-01 h ⁻¹		Comfort <i>et al.</i> (1995) ⁸
Curves	8.4 E-02 – 1.6 E-01 h ⁻¹		Selim <i>et al.</i> (1995) ⁹

does not reach nonzero steady concentrations in either soil or dissolved phases due to transformation reactions.

Thus, a portion of the batch literature on batch TNT sorption highlights measurement of constants for equilibrium partitioning of TNT between soil and water phases. Another portion of the batch literature emphasizes TNT transformation and the absence of equilibrium concentrations in soil and water phases. Causes for these radically different perspectives include confusion over sorbed TNT concentrations and poorly defined redox conditions during batch testing.

Ainsworth *et al.*,¹² Price *et al.*⁷ and Myers *et al.*¹¹ measured both dissolved and soil phase TNT concentrations. In the batch studies of Leggett,¹⁹ Pennington and Patrick,¹⁸ Xue *et al.*,¹⁰ and Comfort *et al.*,⁸ only TNT dissolved phase concentrations were measured. In the absence of measured soil phase TNT concentrations, sorbed concentrations are calculated by difference, that is, the TNT that disappears from the water phase is assumed to have been sorbed by the soil phase. Thus, calculated sorbed concentrations reflect both TNT disappearance from solution by sorption and transformation (unmeasured). The direct measurements of soil phase TNT concentrations by Myers *et al.*¹¹ and Price *et al.*⁷ showed that equilibrium in the sorbed phase for some soils is not reached because TNT continues to transform, especially under anaerobic conditions.

With the exception of the Price *et al.*⁷ study, redox conditions have not been measured during batch testing. Price *et al.*⁷ showed that redox is a major environmental factor affecting TNT transformation. Redox conditions in an uncontrolled batch test are highly variable and depend on the head space gas, initial concentration of oxygen in the water, soil organic matter, iron, manganese, sulfur, and numerous other substances. TNT transformation is more rapid when nitrogen is the head space gas and de-aired water is used than when air is the head space gas and air-equilibrated water is used.¹¹ TNT transformation may have occurred in the batch studies of Leggett,¹⁹ Pennington and Patrick,¹⁸ Ainsworth *et al.*,¹² Xue *et al.*,¹⁰ and Comfort *et al.*,⁸ but the significance of transformation on these sorption data appear to be minimal.

Soil column studies have shown that some type of sorption term, in addition to an irreversible disappearance term, is needed to obtain good model fits for TNT breakthrough.^{6,8,9,11,12} Equilibrium-controlled sorption (linear and nonlinear) has been the preferred model formulation for TNT sorption in column studies. The equilibrium approach has worked well for a wide range of average pore water velocities (10^{-5} to 10^{-2} cm/s).^{6,9,11,12}

Conceptual Process Model

FIGURE 5 shows a conceptual process model that is consistent with the available experimental data and the models that have been used to simulate TNT soil column breakthrough curves. The basic processes are instantaneous and reversible sorption followed by irreversible and rate limited disappearance in the soil phase. The conceptual model identifies two irreversible disappearance mechanisms. One is redox dependent and involves the reductive pathways shown in FIGURE 2. This process may be principally biotic or at least biologically mediated, that is, microbes provide the necessary redox conditions for essentially abiotic reductive transformation of TNT.

Since the reductive transformation products desorb, reversible sorption of reductive transformation products is included in the model. These transformation products compete with TNT for sorption sites. The significance of competitive sorption has not been investigated.

Since elution of reductive transformation products may not always account for total TNT disappearance, other irreversible disappearance processes are possible.

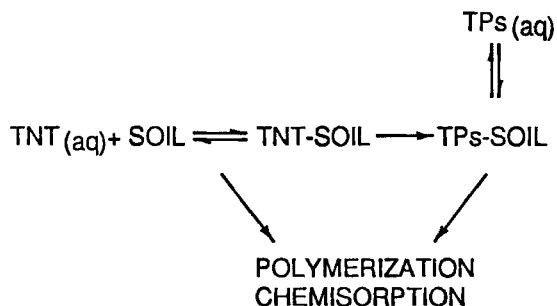


FIGURE 5. Conceptual model of TNT-soil process phenomena.

In the proposed model, these include polymerization of azoxytoluenes and chemisorption. Chemisorption includes incorporation into soil organic matter and irreversible binding to soil mineral surfaces.

The conceptual model shown in FIGURE 5 has only one reversible sorption site. In reality, there may be many different reversible sorption sites due to natural soil chemical heterogeneities. The above model simply implies a composite reversible sorption result, regardless of the number of sites actually involved. Multisite sorption models can provide better process descriptions, but require information on the sorptive properties of various sites. Since in most studies sorption sites are not experimentally segregated, a multisite sorption model for TNT provides little practical advantage over a single composite-site model.

The apparent disparity between the soil column data (TNT sorption is equilibrium controlled) and some batch data (equilibrium between soil and water phases is not always possible for TNT) can now be explained as rapid TNT sorption followed by redox dependent TNT transformation in the soil phase. When reductive transformation rates are low due to unfavorable redox conditions, well-behaved sorption isotherms can be obtained. However, when transformation rates are sufficiently high, steady-state concentrations cannot be obtained. In both cases, sorption is rapid and reversible.

SUMMARY

Recent published data show that transformation and sorption are key processes involved in the subsurface transport of TNT. The state-of-the-art understanding of TNT soil transformation and sorption phenomena is summarized below:

- There is unequivocal evidence of reductive transformation of TNT in soils. However, soil properties affecting TNT transformation are only partially understood. Edaphic factors such as redox are probably important since highest reductive transformation rates occur under anaerobic conditions.
- TNT transformation products include 2A-DNT, 4A-DNT, 2,4-DANT, and 2,6-DANT. Azoxytoluenes have also been reported. Triaminotoluene may be an important TNT transformation product, but this product has not been routinely measured.
- TNT soil sorption is rapid and can be modeled as equilibrium controlled.
- Poor mass balances are difficult to interpret owing to lack of information on transformation products. Various irreversible disappearance mechanisms other than transformation to elutable transformation products are possible.

RECOMMENDATIONS

Laboratory transport experiments and field groundwater monitoring for TNT should include analysis of reductive transformation products. It should not be assumed that transformations are inoperative. Additional work on chemical analytical procedures for analysis of reductive TNT transformation products, such as TAT, is needed before the relative significance of irreversible soil binding and transformation can be fully evaluated.

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