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TECHNICAL COMPLETION REPORT

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TITLE: MONOLAYER FORMATION AND ITS ROLE IN THE TRANSPORT OF
ORGANIC CONTAMINANTS WITHIN GROUNDWATER SYSTEMS

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KEY WORDS: Contaminant Transport, Ground Water Quality, Organic
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PROBLEM AND RESEARCH OBJECTIVES:

Groundwater contamination by organic solvents, gasoline and other petroleum products, and similar nonaqueous phase liquids (NAPLs) is a widespread phenomenon resulting from leaking storage tanks, spills, and improper disposal techniques (Duffy et al., 1980; Harris et al., 1982; Mackay et al., 1985). Due to the potential health problems associated with the occurrence of these carcinogenic or mutagenic organic compounds within groundwater systems, considerable interest in the dynamics of NAPLs within the vadose and phreatic zones exists.

Current efforts at understanding NAPL dynamics within subsurface environments are principally directed toward successful description of transport processes through the use of numerical solutions to flow equations (Kuppasamy et al., 1987; Faust, 1985). Immiscible phase flow, dispersive, diffusive, and convective transport of dissolved components, volatilization, sorption, and degradation are all recognized as important processes contributing to net organic contaminant transport (Baehr, 1987).

Evidence for yet another potentially important transport process can be traced to observations of Benjamin Franklin on "... the sudden, wide, and forcible spreading of a drop of oil on the face of the water..." (Jaycock and Parfitt, 1986). In particular,

it was the surprising swiftness and extent of spreading with which very small quantities of oil covered water surfaces that intrigued Franklin (Jaycock and Parfitt, 1986). It is now well-established that the spreading phenomenon noted by Franklin is related to surface free energies, and thus rooted in chemical thermodynamics (Adam, 1941; Harkins, 1952).

Not all organic liquids will spread when in contact with a second immiscible liquid. The surface tensions of the two liquids and the interfacial tension between them governs whether the liquid will spread (Adam, 1941). Harkins (1952) defined a spreading coefficient for a liquid b on a, $S_{b/a}$, as the difference between the work of adhesion, W_A , and the work of cohesion, W_C ,

$$S_{b/a} = W_A - W_C \quad (1)$$

For the case where W_A is greater than W_C , a net attractive force exists between liquid b and the substrate liquid a, and thus b will spread upon a and attain a minimum free energy.

The work of adhesion is defined by the Dupre' equation:

$$W_A = \gamma_a + \gamma_b - \gamma_{a/b} \quad (2)$$

where γ_a and γ_b are the surface tensions of liquids a and b, respectively, and $\gamma_{a/b}$ is the interfacial tension. The work of cohesion is given by:

$$W_C = 2\gamma_b \quad (3)$$

which then allows eq 1 to be rewritten as:

$$S_{b/a} = \gamma_a - (\gamma_b + \gamma_{a/b}) \quad (4)$$

That is, spreading of an NAPL on water results when attractive forces between the NAPL and water (adhesion) exceed attractive forces between molecules within the NAPL (cohesion). Conversely, when cohesive forces exceed adhesive forces, the NAPL will remain as a small disk on the water surface, distorted from a spherical shape only due to gravity.

Thus, the propensity for spreading can be readily determined from available compilations of surface tensions and interfacial tensions (e.g., Jasper, 1972) or from estimation procedures (Grain, 1982a; 1982b). Spreading coefficients and other chemical properties for a number of the most frequently detected industrial site soil and groundwater contaminants are provided in Table 1 (Hunt et al., 1988; Harkins, 1952). One notices that most of the typical groundwater contaminants possess positive spreading coefficients (Table 1), and thus could be expected to generate thin (monolayer) films over water surfaces, irrespective of their density relative to water.

Inquiries into the surface spreading phenomenon have measured spreading velocities on the order of 20 cm s^{-1} (Adam, 1941), with the translational motion of water molecules at the air-water interface are envisioned to provide the actual transport of the organic molecules and establish the monolayer (Langmuir, 1921).

Environmental applications of this phenomenon, i.e., the tendency of certain organic compounds to spread and establish a monomolecular layer on aqueous surfaces, includes suppression of evaporation from reservoirs within arid climates (LaMer, 1962) and hurricane abatement (Mallinger and Mickelson, 1973). The presence of an organic monolayer serves to increase resistance to mass transport across the air-water interface (LaMer, 1962) and also tends to damp both capillary and gravity waves on water surfaces due to an alteration in viscosity (Mallinger and Mickelson, 1973).

Given the tendency for certain organic compounds to form thermodynamically-favored and extensive monomolecular layers on aqueous surfaces and the apparent swiftness with which such monolayers establish, it is suggested that an additional transport process for certain so-called spreading liquids may exist within unconfined aquifer systems. The objective of this project was to evaluate the role of surface chemical spreading on the migration and distribution of NAPLs on free water surfaces and in unconfined aquifers through the use of aquifer microcosms.

surface tension values from about 32 mN/m to 65 mN/m, corresponding to increasing (less negative) spreading coefficients (-30 to -1 mN/m).

Spreading or lens formation proceeded nearly instantaneously, generally reaching their equilibrium diameters in less than 4 s. Spreading of toluene on water proceeded at a rate of approximately 5 cm/s. Previous data regarding the kinetics of spreading are relatively limited. Adam (1941) reported that the velocity of spreading has often been observed to be on the order of 20 cm s⁻¹. Cary and Rideal (1925) found that the rate of spreading of oleic acid was related to drop size, with the larger circumference favoring slightly faster spreading (approx. 10 cm s⁻¹) than a smaller drop (approx. 6 cm s⁻¹), and also that the rate of spreading appeared to maintain a constant velocity. Harkins (1952) noted that the rate of spreading tends to increase with the magnitude of the spreading coefficient and with a decrease in the viscosity of the layer which spreads.

Toluene lens diameter was also found to increase with increasing NAPL added to a constant surface tension solution (5 x 10⁻⁵ M SDS solution, which yielded a surface tension of 64.8 mN/m and a spreading coefficient of -1.2 mN/m) (Figure 2).

Spreading in Sand Microcosms

As previously noted, a water-soluble dye was added to the wetting solutions to aid in identifying the water table surface in the sand aquifer microcosms. Dye additions had only slight influence on surface tension of the water, tending to lower it somewhat, and had no discernible influence on the surface tension of the surfactant solutions. Based upon results for the free water surface studies, the sand was wet with water ($S_{b/a} = + 5$ mN/m) and a dilute SDS solution which yielded a surface tension of about 56 mN/m ($S_{b/a} = -10$ mN/m).

As noted for the free water surface, surface tension was also found to have a substantial influence on toluene distribution in the sand aquifer microcosms (Figure 3). Toluene infiltrating into

the unsaturated water-wet sand from the line source formed an elliptical plume which, upon impinging the water table surface (at approximately 45 s), then spread laterally (Figure 3a). The intensity of the plume image is qualitatively related to the NAPL saturation; after 30 min most of the toluene is floating on the water table surface as an LNAPL with relatively little retained as residual saturation in the unsaturated zone (at least near the line source). An increase in the width of the plume in the unsaturated zone with increasing time was also observed, indicating spreading in the unsaturated zone. Under non-spreading conditions, the plume was slightly more dispersed in the horizontal direction at 15 s, and exhibited significant fingering with no discernible spreading on the water table surface nor horizontal dispersion in the unsaturated zone with increasing time (Figure 3b). Preliminary studies with *o*-xylene yielded very similar results which are not presented here.

The extent of toluene contamination (area-basis, in the x-y plane) with time for duplicated experiments was quantified using image analysis (Figure 4). Under spreading conditions, the toluene plume increased in areal extent over the 30 min in which the plume was photographically recorded, whereas under non-spreading conditions, no change in the areal extent of contamination was observed after approximately the initial infiltration (Figure 4). The observed are of toluene contamination in the x-y plane was larger under spreading than non-spreading conditions (Figure 4). Had the x-z plane been monitored, even more substantial differences (like those noted for the free water surfaces above) would have been observed.

As the net flux of organic contaminant to the aqueous phase via dissolution is related to the area of NAPL-water contact via (Fried et al., 1979):

$$M = ESt \quad (5)$$

where M = mass of dissolved product, E = mass transfer coefficient, S = area of contact, and t = time of contact, the significance of spreading and monolayer formation lies then in the potential for such a process to hasten organic contaminant transport and contamination of the aquifer relative to simple convective-dispersive and diffusive processes. Contrasting the simple case considered above where 0.33 mL of toluene on a free water surface covered a surface 20 cm in diameter or about 314 cm² (recognizing that spreading would have continued if not being constrained by the container walls) with that in which toluene formed a lens only 3.1 cm in diameter, or 2 cm², under non-spreading conditions, 157x more toluene mass would be dissolved at equal times under spreading than non-spreading conditions (eq 5).

It should be noted that, since both water and organic compounds have some slight to moderate mutual solubilities (e.g., Table 1), with the dissolution of even minimal quantities of hydrophobic compounds in water significantly lowering its surface tension (Jaycock and Parfitt, 1986), the surface spreading phenomenon is often observed to proceed until the water and thin monolayer phases saturate and then reverse and undergo film compression (i.e., the work of cohesion is then greater than the work of adhesion, eq 1). As diffusion and volatilization reduce the organic compound concentration at the interface, however, the surface tension of the water phase increases, again favoring the spreading condition (eq 4). Thus the surface free energy will in all instances be minimized, though the rate of the spreading and gaseous and liquid phase diffusion processes within the aquifer system will serve to control attainment of the thermodynamically-favored spread monolayer condition.

Assuming a similar relationship governs volatilization from an NAPL (Drivas, 1982), correspondingly similar increased rate of contamination of the gas phase in the unsaturated zone can also be anticipated for spreading NAPLs relative to non-spreading situations.

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PUBLICATIONS: A manuscript is currently being drafted based upon the results of this study. If published, reprints will be provided to the Water Resources Center.

Table 1. Spreading coefficients^a and other chemical properties of common groundwater contaminants (Hunt et al., 1988; Harkins, 1952).

Compound	$S_{b/a}$ (mN/m)	Solubility (mg/L)	Density (g/cm ³)	Viscosity (cP)
Trichloroethylene	5.1	1100	1.46	0.83
Tetrachloroethylene	-6.4	140	1.63	0.89
Trichloromethane	13.0	7900	1.49	0.56
Toluene	6.8	540	0.87	0.59
<u>o</u> -Xylene	6.8	185	0.88	0.85
Gasoline	0.2	100-300	0.73	0.45

^aon water with a surface tension of 72.8 mN/m

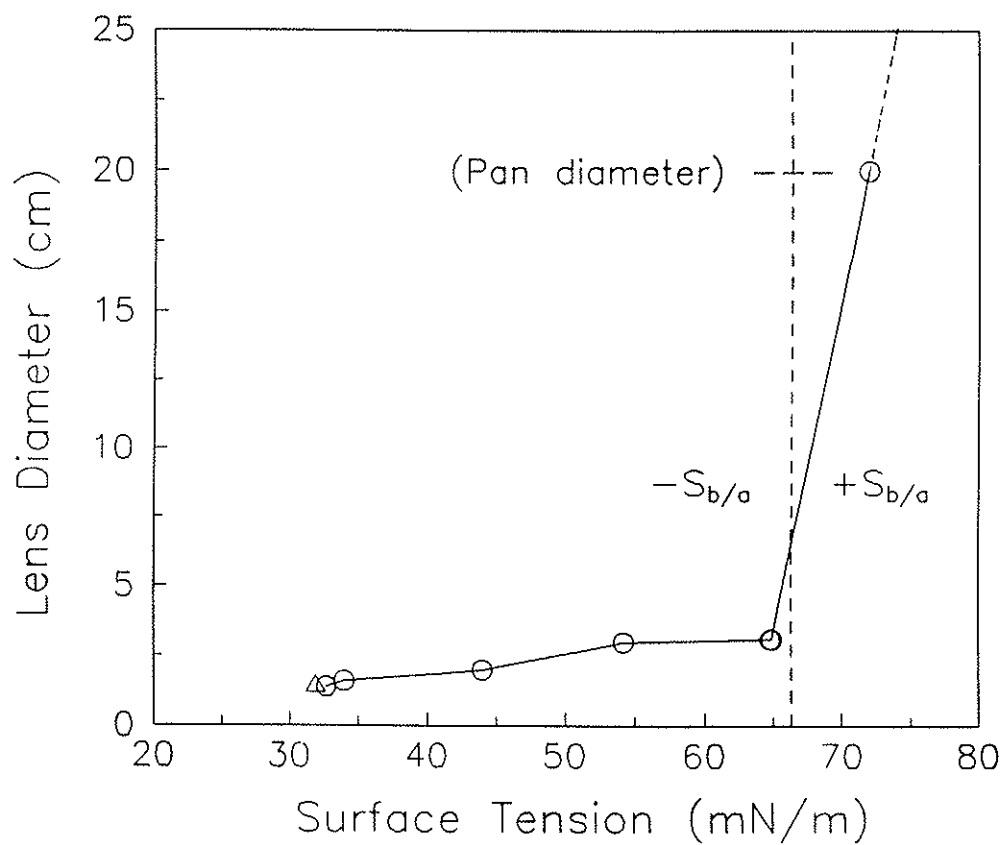


Figure 1. Toluene spreading on free water surface as a function of solution surface tension and spreading coefficient.

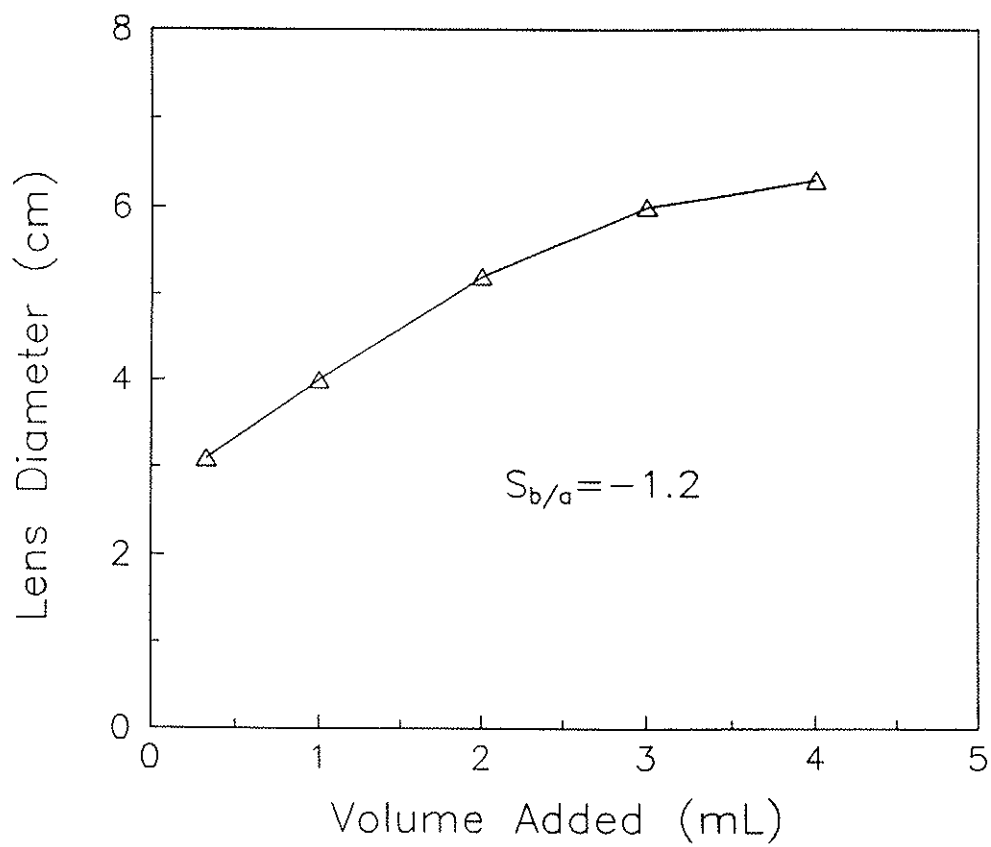


Figure 2. Lens diameter formed on 5×10^{-5} M SDS ($S_{b/a} = -1.2$ mN/m) as a function of toluene volume added.

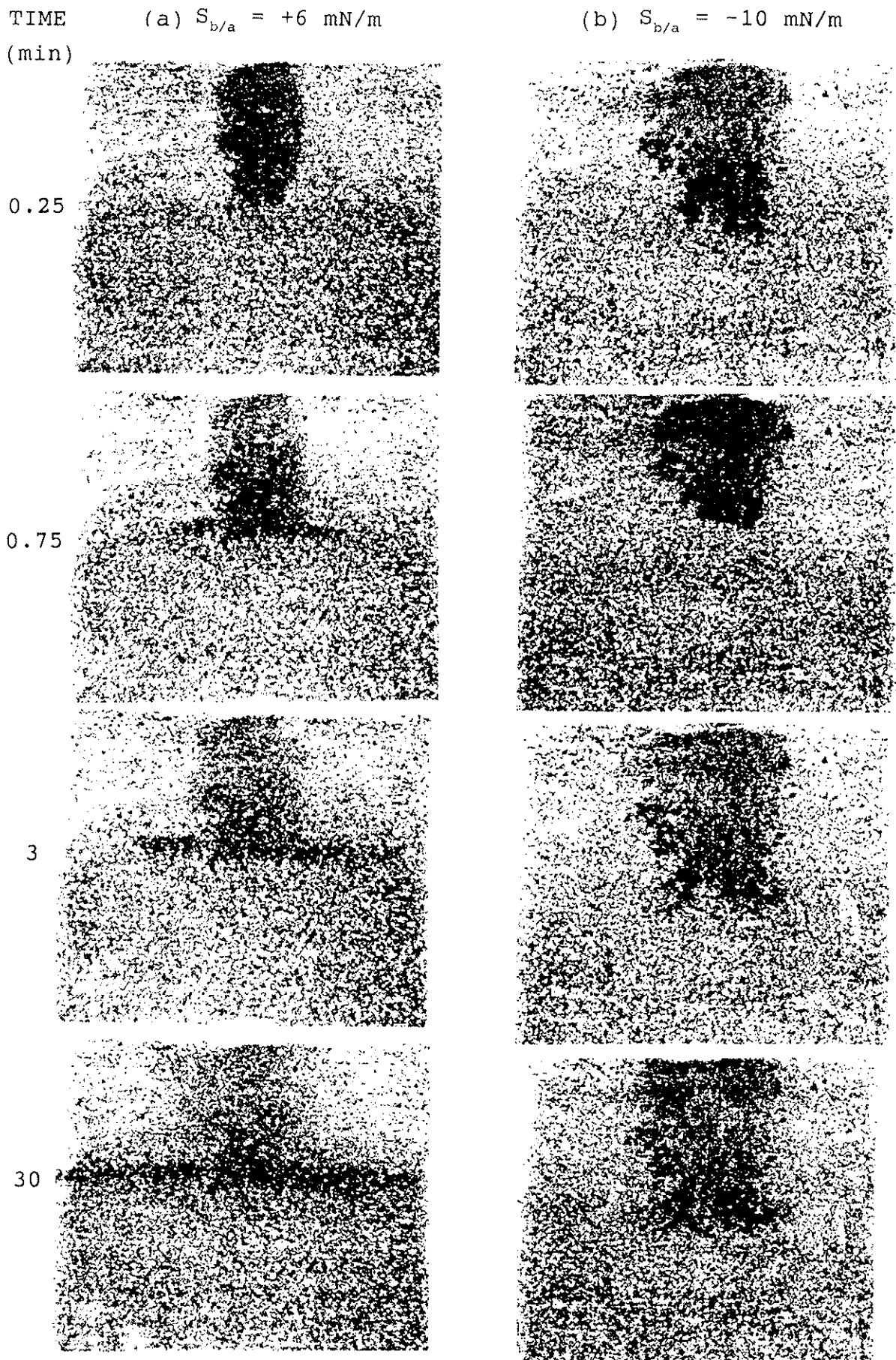


Figure 3. Toluene migration in model sand aquifers wet with (a) water ($S_{b/a} = +6 \text{ mN/m}$) and (b) $2 \times 10^{-5} \text{ M}$ SDS ($S_{b/a} = -10 \text{ mN/m}$).

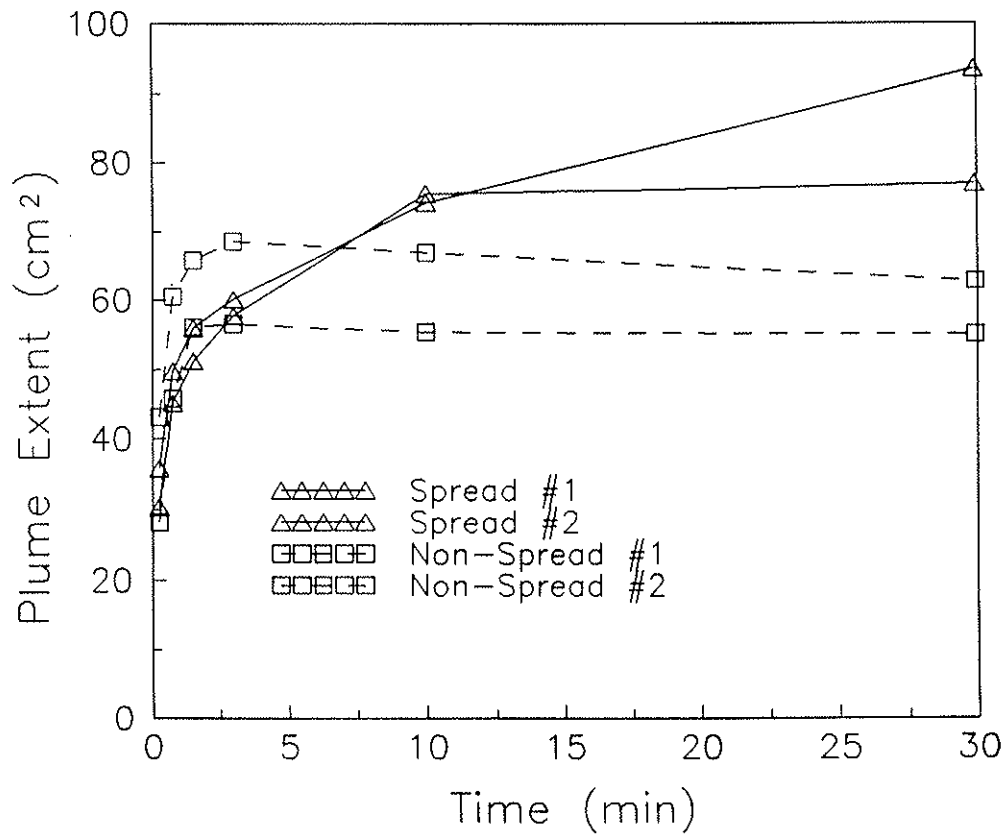


Figure 4. Area of toluene contamination (x-y plane) in model sand aquifers under spreading and non-spreading conditions (Figure 3).