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Author(s): Kenneth E. Laintz, L. Dale Sivils,
and W. Dale Spall

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SOLUBILITY IN SUPERCRITICAL FLUID CLEANING

KENNETH E. LAINTZ, L. DALE SIVILS, and W. DALE SPALL

Los Alamos National Laboratory
Chemical Science and Technology Division
CST-12, MS E537
Los Alamos, New Mexico 87545



1.0 ABSTRACT

With the ban of chlorofluorocarbons imminent, replacement solvents for many industrial processes must be implemented. The use of supercritical carbon dioxide as a cleaning solvent offers many advantages for the cleaning of selected materials. For supercritical CO₂ to be **effective** as a replacement solvent for cleaning, the contaminants normally removed using organic solvents must also exhibit solubility in supercritical CO₂. For this reason, solubility as it relates to cleaning will be discussed. A basic model for contaminant removal from a surface is presented. The implications of this model as it relates to cleaning and contaminant solubility are also discussed.

2.0 INTRODUCTION

When considering cleaning of an item, the type of soil that is to be removed must also be considered. In general, the type of soil and the degree of final cleanliness determine the cleaning method. Cleaning processes remove contaminants by overcoming the forces that bind the contaminant on the surface. These forces are varied and can range from electrostatic to molecular attraction forces. Commonly employed cleaning methods utilize mechanical abrasives, detergents, chemical reactants, and solvents. Cleaning with supercritical fluids (SCFs) generally falls into the category of cleaning with solvents. Solvent cleaners work by dissolving contaminants found on the substrate being cleaned. This dissolution process is simply illustrated in Figure 1. In the figure, the contaminant is illustrated by the globular shapes sitting on the surface to be cleaned. The dissolution of the contaminants occur as the solvent surrounds the contaminants and "lifts" them from the surface, thus leaving it clean. Of course, this is a very simplistic representation, and many factors are involved in the dissolution of a contaminant. In order for a solvent to effectively dissolve a contaminant in this manner, the contaminant must be soluble in the solvent.

In basic terms, solubility is the maximum amount of a substance, or solute, that can be dissolved in a given quantity of solvent. In general, for the dissolution of solutes or contaminants, the concept of "like-dissolves-like" is often used. This basically means that an inorganic or polar substance such as salt generally dissolves in a polar solvent such as water. On the other hand, a nonpolar compound such as an aliphatic hydrocarbon dissolves in a nonpolar solvent such as hexane. Besides aqueous based cleaning techniques, most common solvent cleaning methods use nonpolar solvents such as 1,1,2-trichlorotrifluoroethane, or Freon-113, for the removal of hydrocarbon based soils such as oils and greases. Since chlorofluorocarbon solvents like Freon-113 have been banned by the Montreal Protocol, alternative solvents with similar dissolution

capabilities are needed. One replacement solvent for solvent based cleaning methods is supercritical carbon dioxide.

In general, knowledge of the solubility of a particular compound in an SCF is important when considering SCF processing of that particular compound. For this reason, many theoretical calculations and experimental measurements have been made to determine the solubilities of a wide variety of compounds in various supercritical fluids as a function of temperature and pressure. Most of these measurements have been made on pure compounds, and in an industrial setting, the desired compound or contaminant often exists as a mixture of several compounds. In such cases, pure component solubilities can only suggest at extractability or cleanability. This knowledge does, however, provide a basis for designing an SCF processing or cleaning scheme. Many articles have appeared in the literature that list solubilities of a wide variety of pure components under a variety of temperature and pressure conditions. A recent review article by Bartle, et al. compiles solubility data on a wide variety of solids and liquids in supercritical CO₂ and is an excellent source for initial compound solubility data.¹ When using supercritical CO₂ as a replacement solvent for cleaning methods, the solvent strength of the SCF must be considered. The solvent strength of supercritical CO₂ is dependent upon temperature and pressure, but generally, it is considered a nonpolar solvent. Therefore, using a "like-dissolves-like" scenario, supercritical CO₂ is best suited for the removal of nonpolar hydrocarbon based soils like various machining and lubricating fluids. These compounds are all mixtures of many single components, and accurate solubility determinations of such mixtures have yet to be made. For this reason, the intent of this chapter is to present a basic model for contaminant removal from a surface. The implications of this model relating to cleaning and contaminant solubility will also be discussed.

3.0 CONTAMINANT SOLUBILITY

Solubilities are defined either as the mole fraction of solute in solution, x , or by the amount of solute per unit volume, or concentration, C , at saturation. The concentration in moles per unit volume is given by:

$$C = \frac{x}{V} \quad (3.1)$$

where V is the molar volume of the pure fluid. Contaminant volatility and SCF solvating power are two major factors that determine the solubility of a contaminant in an SCF. Supercritical fluid solvating power is primarily a function of density. In general, higher densities result in higher solvating power. These higher densities are most readily achieved through increasing pressure. However, temperature is an important variable in contaminant solubility since the volatility of a compound is directly related to temperature. Depending on equipment setup, increasing the temperature in a cleaning system can reduce solvent density, but the increase in contaminant volatility generally overcomes the decrease in density and enhances contaminant removal. The solubility of a solid or semi-solid in a liquid is related to the heat of fusion of the solid and the temperature of the solution by:

$$\ln x = \frac{\Delta H_f}{R} \left(\frac{1}{T_f} - \frac{1}{T} \right) \quad (3.2)$$

where x is the mole fraction of the dissolved solute, ΔH_f is the heat of fusion, T_f is the melting point of the solute and T is the temperature of the solution. Equation 3.2 is valid if the change in the heat capacity and volumes at different T 's is ignored. Ideal solution theory also requires that there is only dispersion force interaction between the solute and solvent. It can be seen from Equation 3.2 that an increase in solution temperature will increase the mole fraction of the dissolved solute. In an SCF system at constant pressure, the solubility of a solute will fall initially with increasing temperature

because the SCF density decreases, and hence its solvating power decreases, with increasing temperature. However, as the temperature rises, the volatility also rises, and eventually this effect exceeds the effect of the falling solvation and the solubility rises.

Section A-B in **Figure 2** shows that the solubility falls as the contaminant is diluted by the fluid. The rapid rise in solubility in section B-C occurs at pressures fairly higher than the critical pressure because of the rapid rise in density, and therefore solvating power, of the SCF at around this pressure. This region has been defined by King as the “threshold pressure” which is the pressure at which the solute begins to dissolve in the SCF². Obviously, this pressure is technique dependent and varies with the analytical method sensitivity used to measure the solute concentration in the SCF. A decrease in solubility, as shown in region C-D, may occur at higher pressures due to repulsive forces that may squeeze the solute out of solution. For moderately volatile solutes, a rise in solubility, as shown in section D-E, can occur if there is a critical line in the mixture phase diagram at higher pressures.

Solubility can also be enhanced by the presence of other compounds. This phenomenon is caused by one or more compounds acting as solubility enhancers for other compounds present on a surface. This phenomenon is sometimes called the *local cosolvent effect*. A typical method of enhancing contaminant solubility is through the addition of a small amount of secondary solvent to the SCF cleaning system. Alcohols are commonly used in this manner to increase solubilities of more polar contaminants. However, more subtle local cosolvent effects have been observed. Perhaps a classic example was first reported by Kurnik and Reid.³ In their study, they observed that the solubilities of both naphthalene and benzoic acid in supercritical CO₂ were enhanced by 107 and 280 %, respectively, when both species were present. It has also been shown that there needs to be enough of a secondary component present in solution about the local contaminant environment to enhance the solubility of another compound.⁴ This example demonstrated that an excess of phenanthrene promoted the solubility of anthracene in **supercritical** CO₂, but since anthracene was only present in

very small quantities, it did not help to enhance the overall solubility of phenanthrene. A similar result was seen in a cleaning study on the removal of TRIM[®] SOL, which is a water miscible cutting fluid, from stainless steel, copper, aluminum, and brass coupons.⁵ In this example, the metal substrates were cleaned using a SUPERSCRUB[™] CO₂ cleaning system, manufactured by EnviroPro Technologies[™], equipped with a 60 L cleaning vessel. TRIM[®] SOL was shown to have an average removal rate of 44.5 % from the metal surfaces when it was applied at a contamination level of 10 μg/cm². In contrast, the removal efficiency increased 167 % to a removal rate of 74.5 % when the contamination level was increased to 50 μg/cm². This phenomenon is caused by one or more components acting as solubility enhancers for other components. With more contaminant present at 50 μg/cm², it is possible that the overall solubilities of the contaminants were increased to yield the higher extraction efficiency. More detailed theoretical discussions of solubility and solute-solvent interactions and these interactions as applied to SCFs can be found elsewhere^{6,7}.

4.0 MODELS FOR CLEANING

In order to present a cleaning model, there are several factors that must be considered. The first factor under consideration is the partition coefficient. This coefficient is a ratio of the concentration of a contaminant on the surface to its concentration in the solvent and can be represented as:

$$P = \frac{[C_S]}{[C_F]} \quad (4.1)$$

where P is the partition coefficient, [C_S] is the concentration of the contaminant on a surface, and [C_F] is the concentration of the contaminant in the SCF solvent. In the case of cleaning, if [C_S] is plotted as a function of [C_F] as shown in **Figure 3**, the

distribution behavior of a contaminant between the surface and the SCF solvent can be illustrated. The curves shown in the figure relate the amount of contaminant on the surface to the amount in solution in the cleaning solvent. Initially, $[C_S]$ is high, and as the cleaning cycle progress, $[C_S]$ decreases as $[C_F]$ increases. In a cleaning process, line C of **Figure 3** represents a case where the partition coefficient is constant over a wide range of contaminant concentrations. Typically, however, a relationship similar to lines A or B is usually observed. Curve B is indicative of a contaminant with limited solubility in the cleaning solvent or where surface interactions limit contaminant dissolution. Curve A can be thought of as an adsorption isotherm. In this case, the concentration of contaminant in solution is related to the amount adsorbed onto a surface. As the curve approaches some asymptotic value, contaminant adsorption on the surface becomes the controlling factor in the dissolution of contaminant from the surface regardless of solubility. In general, such a curve results for a contaminant that is highly soluble in an SCF thus indicating the importance of the adsorption isotherm to SCF processing.

Overall, there are three different partitioning phenomena that must be considered when cleaning a contaminant from a surface. These three different partition coefficients, represented as P , are illustrated in **Figure 4**. The contaminant can partition between the surface and the solvent directly which is represented as P_{SF} , where the subscript S corresponds to the surface, L to the liquid contaminant, and F corresponds to the SCF. The term P_{SF} corresponds to the adsorption isotherm which was previously discussed. The term P_{SL} is the partitioning of the contaminant between the surface and the bulk contaminant phase, liquid, in this case, which can be thought of as an oil, for example. It should be noted that the term P_{SL} is equally applicable to a solid contaminant. Finally, the contaminant partitions between the bulk liquid and the cleaning solvent, represented as P_{LF} . The partitioning processes are usually expressed in terms of equilibrium concentrations. This is because contaminant partitioning occurs back and forth between two phases. For example, in the case of P_{LF} , the contaminant can partition into the cleaning fluid and back into the liquid adsorbed on the substrate

surface. If the contaminant is not very soluble in the cleaning fluid or if there is strong surface adsorption, the partitioning into the cleaning solvent is going to be small. However, this particular partition coefficient, P_{LF} , is directly related to solubility. Since solubility is related to contaminant vapor pressure and temperature, increasing the temperature of the cleaning cycle increases partitioning into the cleaning fluid, thus promoting overall cleaning of the surface. One can ideally visualize the partitioning process during a cleaning cycle as the contaminant partitioning initially into the solvent with subsequent partitioning from the surface into the liquid. Finally, when the contaminant concentration on the surface reaches a point where essentially no liquid is left, the contaminant partitions directly into the solvent.

The partition coefficients are not the only parameters that must be considered in the cleaning process. The diffusion coefficient, D , encompasses molecular motion and the tendency for a molecule to move from a concentrated region, the contamination site, to more dilute regions, the bulk solvent. Again, the subscript S corresponds to the surface, L to the liquid (or solid) contaminant, and F to the SCF. In order for contaminant removal and subsequent cleaning to occur, the contaminant must enter into the bulk flow of the supercritical solvent. Several processes need to occur for this to happen. There is partitioning from the substrate surface into the bulk liquid of the contaminant. The contaminant then diffuses to the surface in contact with the cleaning solvent, represented as D_L in **Figure 4**, where it can partition into the fluid phase of the boundary layer. This boundary layer can simply be thought of as a viscous solvent layer where there is essentially only static, nonflowing solvent in contact with the surface of the item being cleaned and the contaminant itself. Finally, the contaminant must diffuse from the surface through the boundary layer and into the bulk flow, D_F , in order to be removed from the surface. Since SCFs have gas-like diffusivities which are orders of magnitudes higher than liquids, it is often claimed that SCF extraction processes do not experience the mass transfer limitations of a liquid extraction process, thus yielding more efficient extraction or cleaning. This would be the case if the rate-limiting step of an extraction process is the actual transfer of a contaminant from the surface of a

substrate to the extraction medium, denoted by the adsorption isotherm or P_{SF} . In reality, resistance to diffusion in the liquid phase, D_L , is more likely the rate-determining step since extraction from the liquid phase into the SCF phase is probably more typical in an industrial cleaning situation. In this case, the gas-like diffusion characteristics of the SCF solvent will not have an enhancing effect on the overall mass transfer rate.

Now, as it turns out, the thickness of the boundary layer is quite important in terms of contaminant removal. If the boundary layer is thick, the diffusion of the contaminant into the bulk solvent layer is slow which would contribute to a very slow dissolution process. An example of such a scenario might be a static dissolution or extraction of a contaminant where no flow is occurring within the cleaning or extraction chamber. In this case, the boundary layer is essentially the bulk solvent, and once this solvent becomes saturated with the contaminant, dissolution or cleaning ceases. On the other hand, if the boundary layer is quite thin, as in a dynamic or flowing process, contaminant diffusion across the boundary layer into the bulk fluid phase occurs rapidly thus facilitating cleaning. This then suggests that for maximum cleaning potential, the flow of the solvent across the surface being cleaned needs to be maximized.

Overall, the thickness of the boundary layer and contaminant solubility effect the time it takes for contaminant removal or extraction. This is illustrated in **Figure 5**. Curve A of the figure represents several cleaning or extraction processes. Such a rapid removal rate is generally observed for a very soluble contaminant and for a soluble contaminant in a cleaning process that incorporates an efficient mixing system in order to generate a thin boundary layer. The extraction profile represented by curve A approaches an asymptotic value of an adsorption isotherm where surface interactions become dissolution limiting. Line C of **Figure 5** represents a case where the partition coefficient is constant over a wide range of contaminant concentrations. This can be due to a thick boundary layer as in a static process or due to a solubility limited contaminant. Curve B of the figure can be thought of as process intermediate to those of curves A and C where the boundary layer diffusion is effected by contaminant

solubility or surface interactions. Of course, all contaminant dissolution processes depend on contaminant solubility in the cleaning solvent. If the contaminant is insoluble in the cleaning solvent, an increased flow would, at best, simply move the contaminant along the surface by shear velocity forces and not dissolve it.

In addition to contaminant partitioning across the boundary layer, there is also partitioning directly from the surface into the fluid phase. The partition coefficient associated with P_{LF} in **Figure 4** is dependent on solubility which in turn is dependent on temperature. The partition coefficients associated with P_{SL} and P_{SF} are functions of surface interactions. These interactions consist primarily of sorption phenomena such as chemisorption or physisorption. In the case of chemisorption, the contaminant is chemically sorbed onto the surface through hydrogen bonding or other attractive chemical forces. In the case of physisorption, the contaminant can be thought of as physically trapped on the surface. For example, one would expect physisorption to be small on a highly polished surface. On the other hand, a highly porous surface would be expected to provide physical barriers to contaminant removal from sites within the substrate matrix. In any case, both chemisorption and physisorption are related to the adsorption isotherm. If there is minimal surface interaction, P_{SL} and P_{SF} are large, thus indicating the partition into the SCF phase is unidirectional. Conversely, if these coefficients are small, meaning a high degree of surface interaction, it will be difficult to dissolve the surface layers of the contaminant. The SCF also partitions into the liquid or solid contaminant, and depending on the rate of this diffusion, can either increase or decrease the kinetic rate of removal into the bulk solvent layer.

Figure 6 shows three possibilities that can result when cleaning a contaminant from a smooth substrate surface. The top model shows the desired result of cleaning which occurs when the solubility of a contaminant is high enough to overcome any chemical or physical sorption mechanisms which bind it to the surface. Possibility I can occur when the contaminant is not sufficiently soluble in the SCF and has a high intermolecular attraction which results in a high surface tension. In other words, the

contaminant likes itself better than the SCF or the substrate surface and subsequently forms beads on the surface. Possibility II can happen when $P_{SL} > P_{LF}$. The contaminant is partially solvated by the SCF but sorption to the substrate surface prevents complete contaminant removal.

Removing contaminants from rough surfaces can be a challenging proposition. Physical sorption plays a much larger role than chemical sorption when trying to dislodge contaminants. Supercritical fluids enjoy a distinct advantage over conventional liquid solvents when cleaning surfaces that have contaminants trapped in crevices or other physical barriers. This is because, supercritical fluids have much lower viscosities and surface tensions than conventional liquid solvents. This enables SCFs to have much more penetration into micro-crevices or cracks to dissolve trapped contaminants. Figure 7 shows what can happen when cleaning contaminants from rough surfaces. Obviously, the desired result is the complete removal of the contaminant from the crevice. This will occur if the contaminant is sufficiently soluble and it partitions to the bulk SCF flow. Less soluble contaminants can be removed if enough turbulence is applied to the system and the partially soluble contaminants are physically flushed from the physical barriers. Partial contaminant removal can occur if the contaminant's solubility is low and the bulk flow turbulence is insufficient to flush out the trapped contaminants. Nevertheless, if a trapped contaminant has a low solubility and a high affinity to the substrate surface it will be very difficult to remove regardless of the solvent system used.

A final place in the overall cleaning process where contaminant solubility is an issue is in the separation process where the contaminant is removed for the solvent. In the separator, the spent cleaning solvent is passed from the cleaning chamber into a vessel where it expanded into a gas. The extracted compounds are collected in the separator, and the gaseous CO_2 is passed back into the flow stream to be used again in the cleaning process. If the contaminant is miscible with the fluid and has a high vapor pressure, the possibility of contaminant carry-over into the solvent reservoir is

possible because such types of compounds are difficult to completely remove from the CO₂. While feasible from a solubility standpoint, the removal of volatile contaminants in CO₂ is difficult from an operational standpoint. Current studies indicate that the concentration of low vapor pressure compounds must be kept below 1 part per million to achieve cleanliness levels at or below 1 µg/cm².⁸ Efficient separator designs are engineering issues, but these are indeed commercially available.

5.0 CONCLUSION

In general, the higher the solubility of the contaminant, the better the cleaning or removal efficiency. Solubilities can be increased by increasing the SCF density. This is achieved through increasing pressure. However, an SCF cleaning method should be optimized to run at the lowest pressure possible to reduce overall equipment costs. Solubility can also be increased through increasing temperature. For this reason, The cleaning method needs to optimized to run at as high a temperature as reasonably possible. In most cases, temperature and pressure must be optimized simultaneously in order to give the most efficient contaminant solubility. Contaminant solubility can also be increased by minimizing the solvent boundary layer by operating in a turbulently flowing system. Finally, contaminant solubility can be increased through the addition of a secondary compound such as a cosolvent. In summation, all variables must be optimized together to achieve the highest contaminant solubility and most efficient cleaning process regardless of the solvent choice.

6.0 REFERENCES

1. Bartle, K.D., Clifford, A.A., Jafar, S.A., and Shilstone, G.F., Solubilities of Solids and Liquids of Low Volatility in Supercritical Carbon Dioxide, *J. Phys. Chem. Ref. Data* 20(4):713-756 (1991)
2. King, J.W., Fundamentals and Applications of Supercritical Fluid Extraction in Chromatographic Science, *J. Chromatogr. Sci.*, (27):355-364 (1989)
3. Kurnik, R.T., and Reid, R.C., Solubility of Solid Mixtures in Supercritical Fluids, *Fluid Phase Equilib.* 8:93-105 (1982)
4. Kwiatkowski, J., Lisicki, Z., and Majewski, W., An Experimental Method for Measuring Solubilities of Solids in Supercritical Fluids, *Ber. Bunsenges. Phys. Chem.* 88:865-869 (1984)
5. Williams, S.B., Laintz, K.E., Barton, J.C., and Spall, W.D., Elimination of Solvents and Waste by Supercritical Carbon Dioxide in Precision Cleaning, *Los Alamos National Laboratory Report* 1994, LAUR-94-3313.
6. Reid, R.C., Prausnitz, J.M., and Poling, B.E., *The Properties of Gases & Liquids*, 4th Ed., McGraw Hill, Inc., New York (1987)
7. McHugh, M. and Krukonis, V., *Supercritical Fluid Extraction*, 2nd Ed., Butterworth-Heinemann, Boston (1994)
8. Spall, W.D., Supercritical Carbon Dioxide Precision Cleaning for Solvent and Waste Reduction, *Intnl. J. Environ. Conscious Design & Manuf.*, 1(2-4):1-10 (1992)

7.0 FIGURE CAPTIONS

Figure 1. Simplified schematic of a contaminant dissolving off a surface.

Figure 2. Schematic representation of compound solubility in a supercritical fluid as a function of pressure.

Figure 3. Plot of contaminant partition coefficient as a function of surface, $[C_S]$ and fluid, $[C_F]$, concentrations.

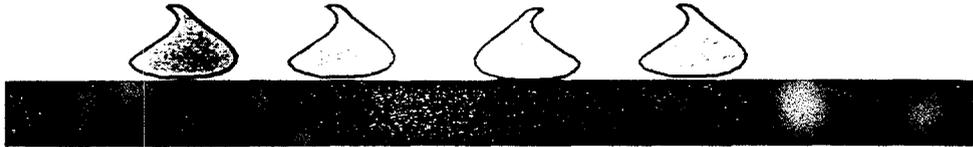
Figure 4. Simplified model of contaminant removal in a supercritical fluid. This model is applicable to both solid and liquid contaminants.

Figure 5. Plots of total contaminant extracted as a function of time.

Figure 6. Simplified model of contaminant removal from a smooth surface.

Figure 7. Simplified model of contaminant removal from a rough surface.

Contaminant on Surface



Contaminant Dissolved Off of Surface

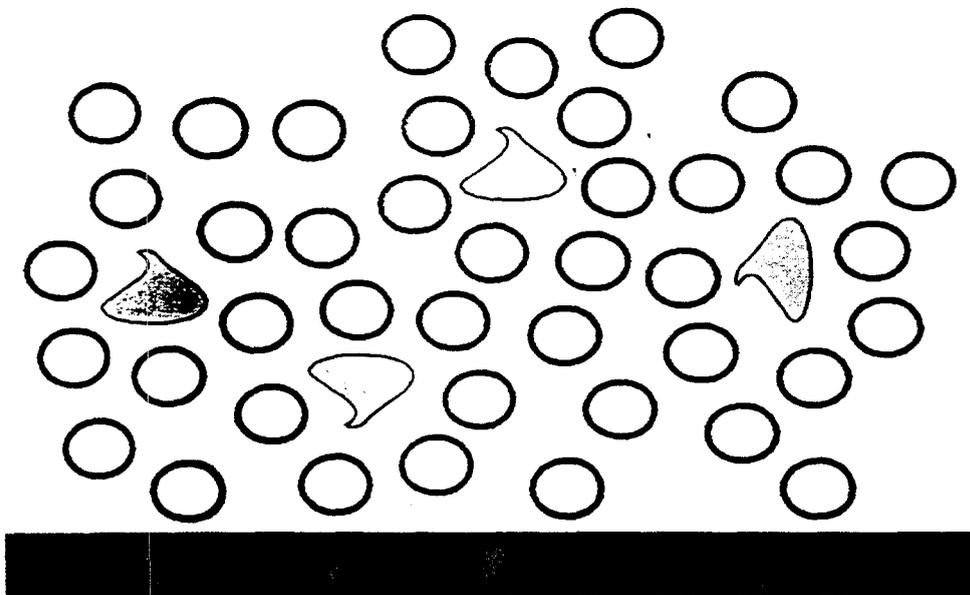


Figure 1.

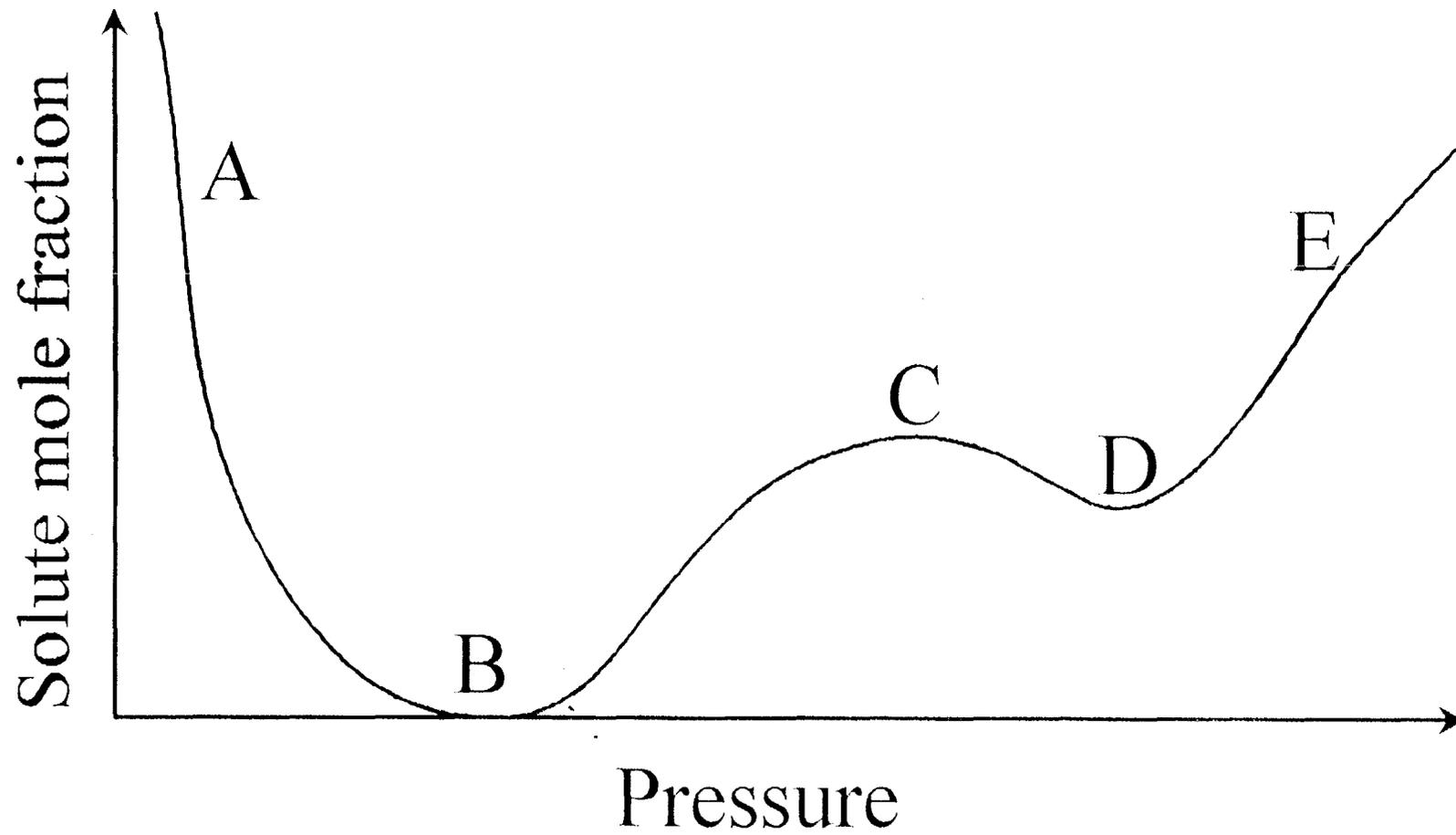


Figure 2.

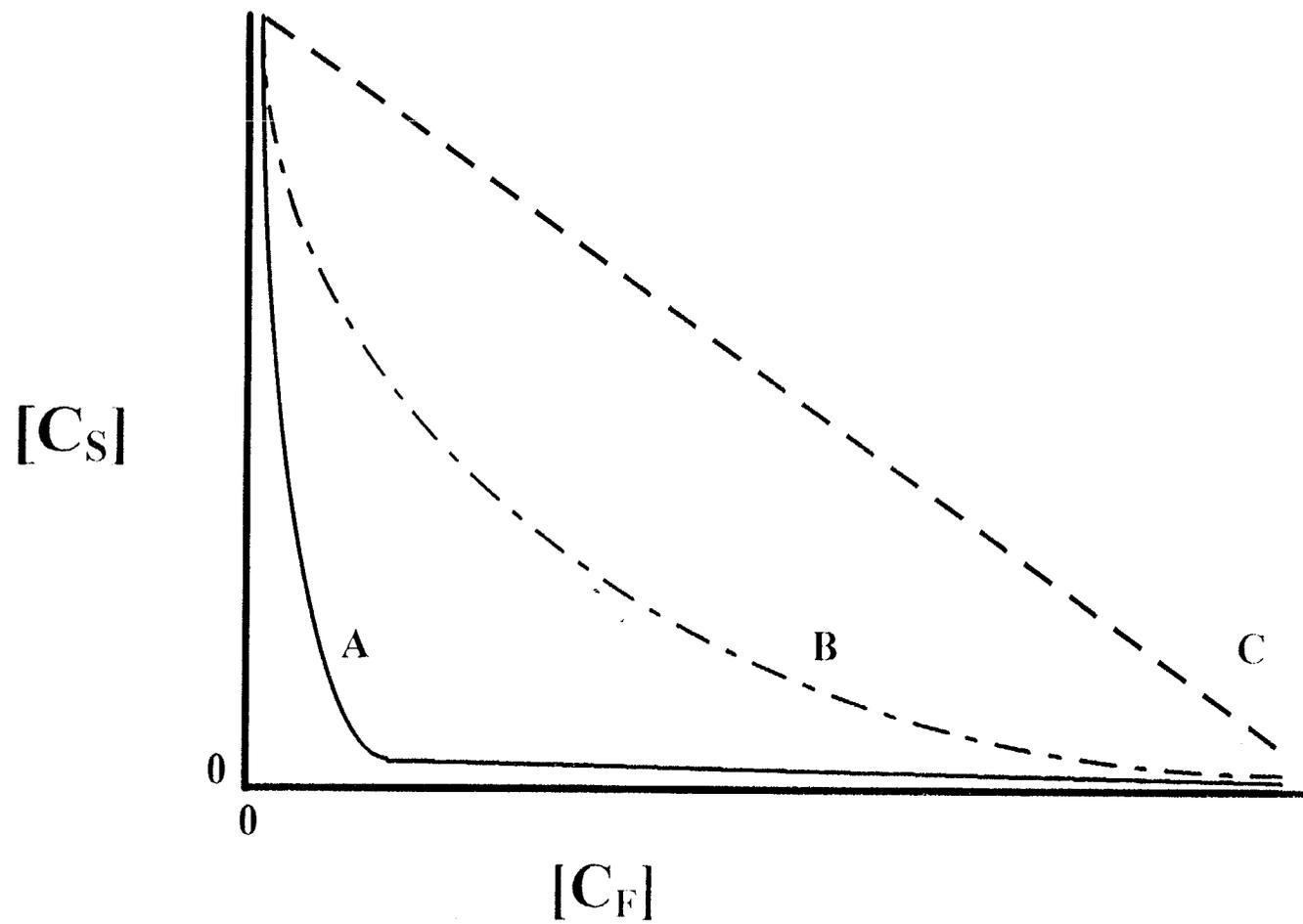


Figure 3.

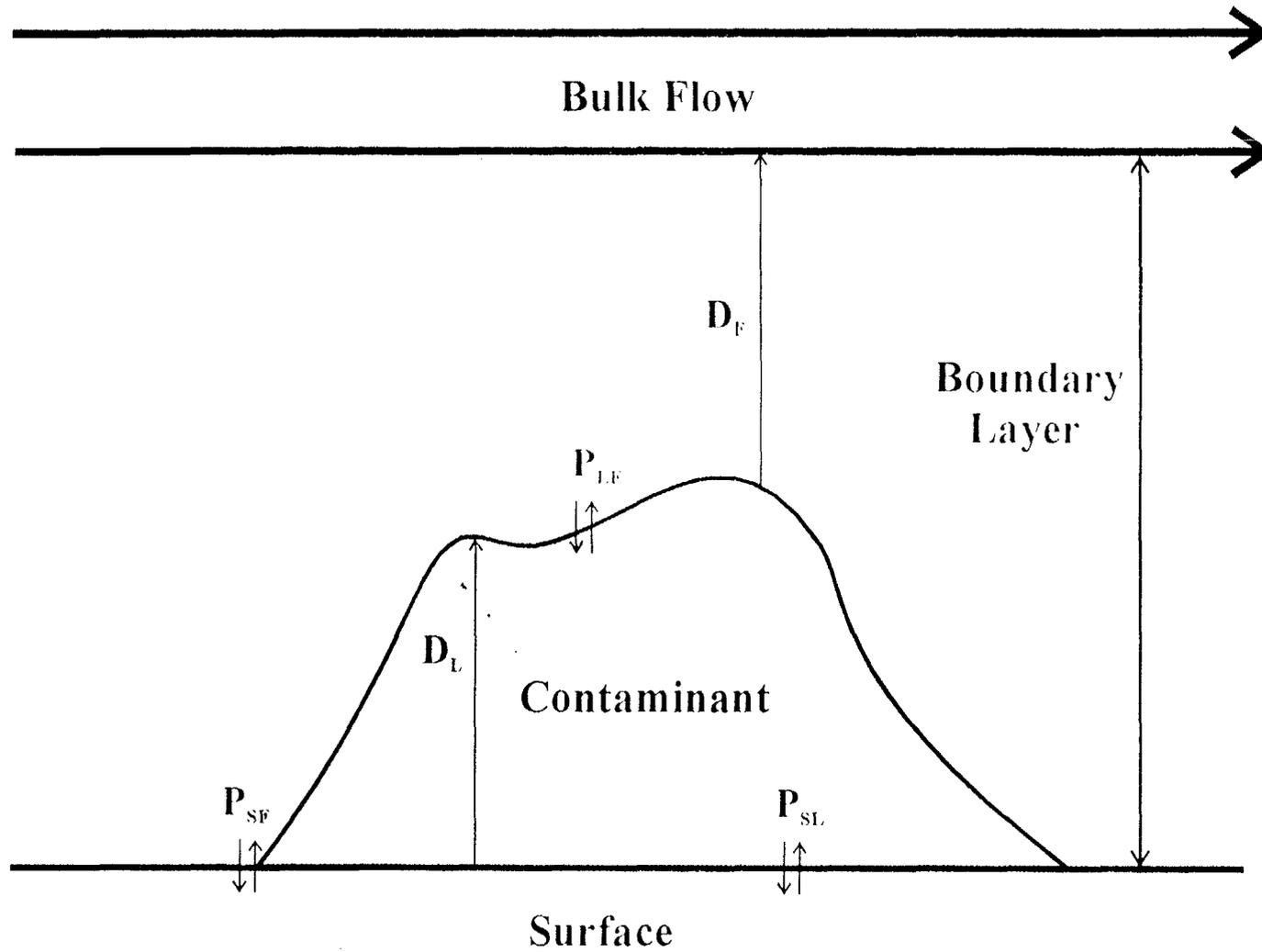


Figure 4.

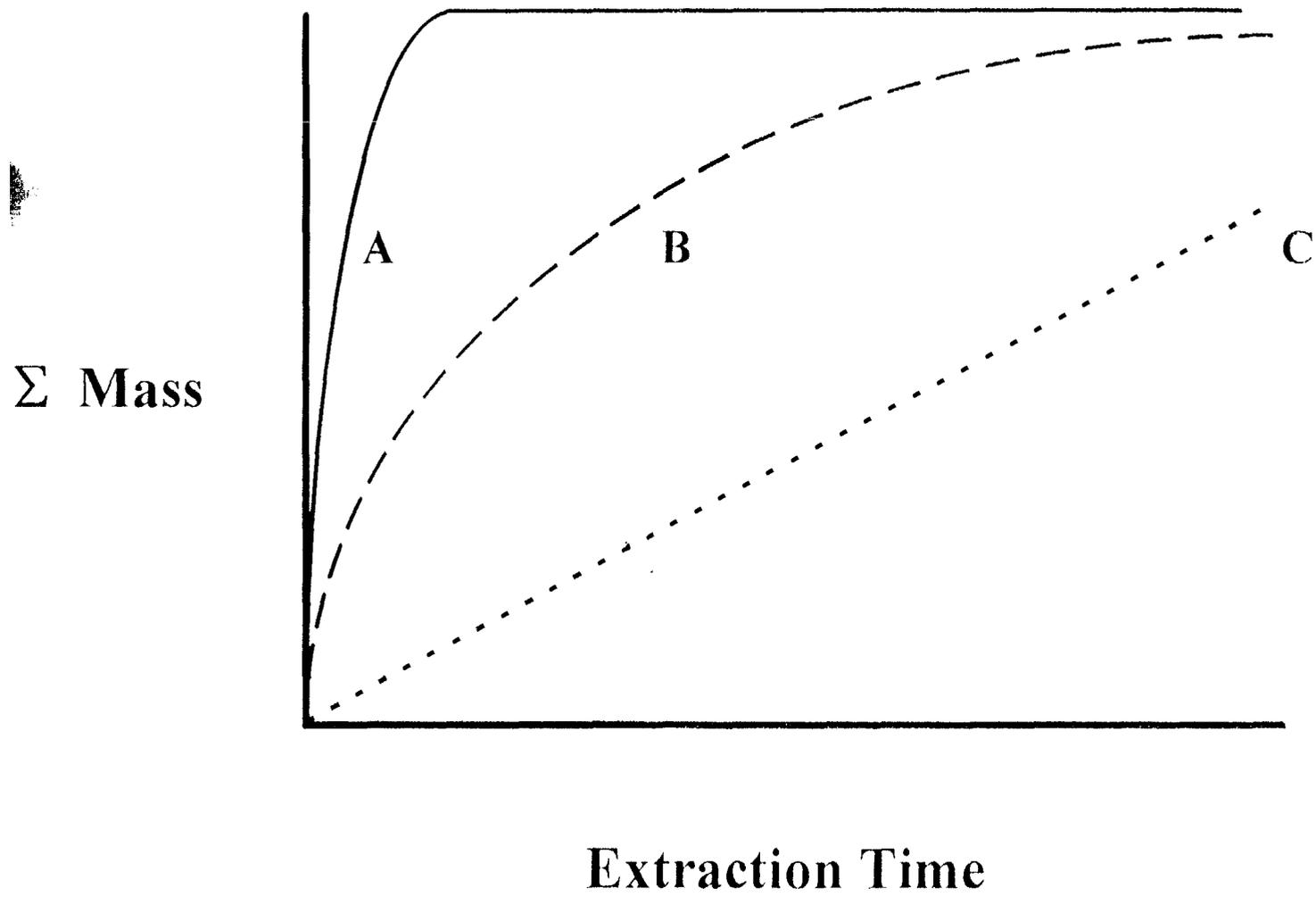


Figure 5.

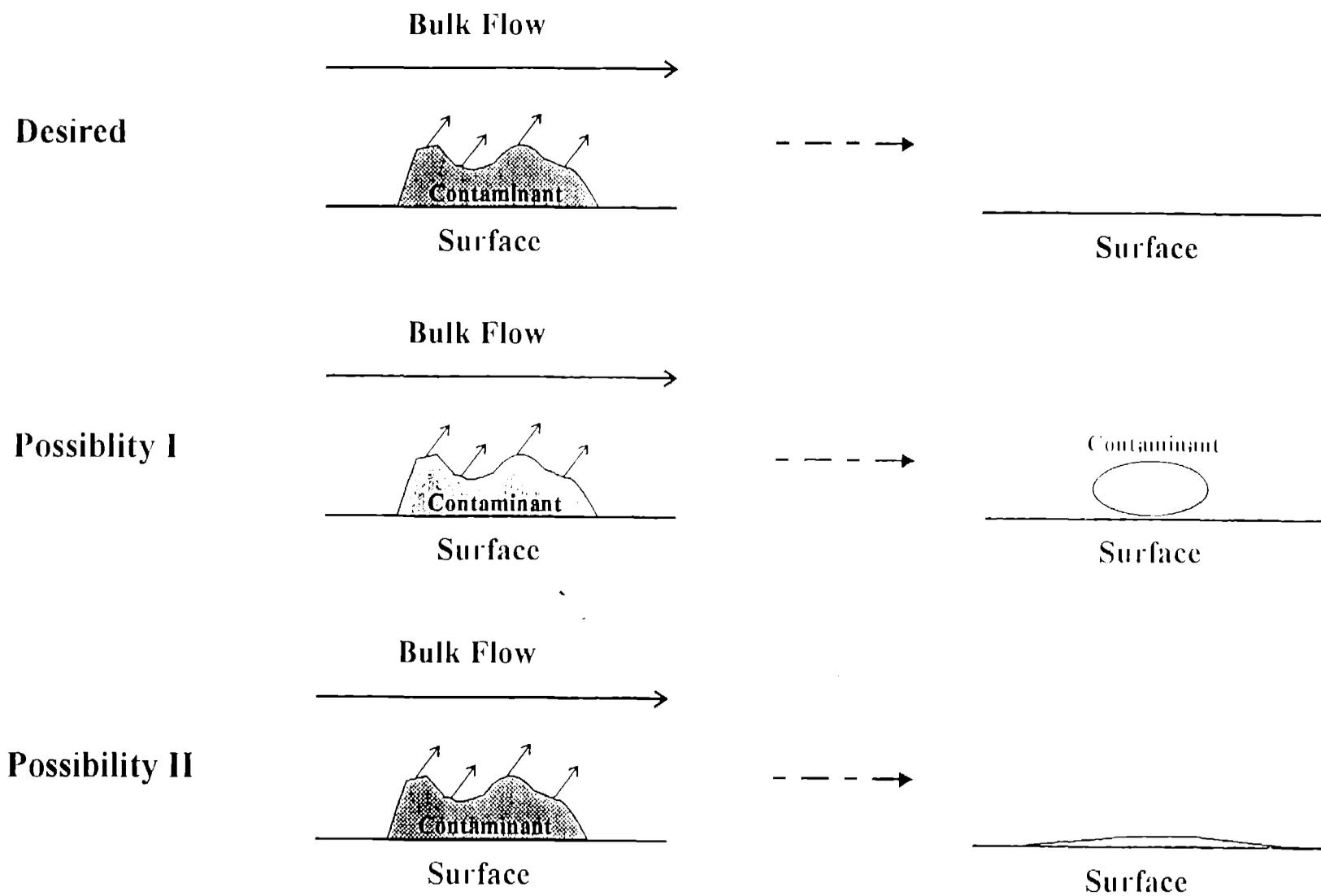


Figure 6.

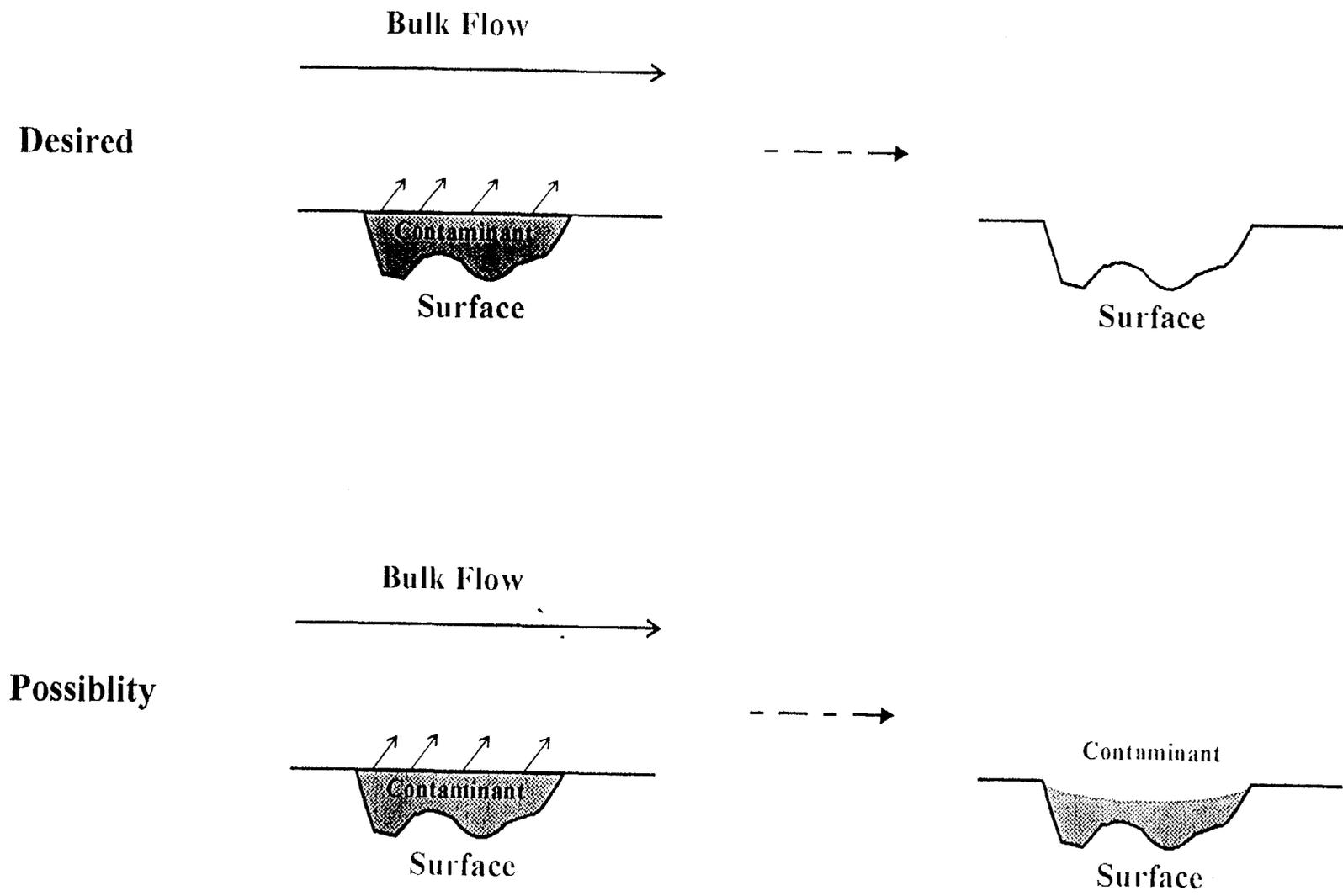


Figure 7.