



## *Project Summary*

# Removal of Water Soluble Hazardous Materials Spills from Waterways by Activated Carbon

George R. Schneider

A model for removing water soluble organic materials from water by carbon-filled, buoyant packets and panels is described. Based on this model, equations are derived for removing dissolved organic compounds from waterways by buoyant packets that are either (a) cycled through a water column, or (b) suspended in the waterway by natural turbulence and by panels mechanically suspended in waterways. Computed results are given for phenol spills. The report considers the effects of turbulence on the suspension of buoyant packets; it also examines how turbulent mixing and longitudinal dispersion of spills in waterways affect the removal of water soluble hazardous materials.

Buoyant packets are found to be ineffective for removing spills from waterways. The rapid dilution of spills also renders panels ineffective unless the spill is massive and the response is rapid.

*This Project Summary was developed by EPA's Municipal Environmental Research Laboratory, Cincinnati, OH, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).*

### Introduction

Activated carbon in one form or another (packaged or loose, floating or

sinking in water, powdered, granular, or fibrous) has been proposed for adsorbing spilled, water soluble hazardous organics from waterways. Limited laboratory experiments and small field tests have been conducted with carbon to determine its spill cleanup potential. The results of these programs have been mixed, and it is not clear whether the use of carbon-filled packets and panels to clean up spills in large nonimpoundable waterways is technically or economically feasible.

A technical feasibility study has been conducted of the various *in-situ* approaches to the removal of water soluble hazardous organics from nonimpoundable waterways by means of adsorption on carbon. The objective of this study was to determine the removal rate of dissolved pollutant and the percent of dissolved pollutant likely to be removed by using activated carbon in packets and panels under the best possible conditions. Related steps such as the retrieval of the carbon-filled packets and carbon regeneration were not considered.

### Analysis

#### *Adsorption Model Basics*

Packets or panels of carbon granules immersed in a polluted waterway will be considered to behave as fixed-bed adsorbers with a small depth; the carbon will adsorb dissolved organic material only from fluid that is inside the

packet (either stagnant or flowing through). Packets of carbon that are merely immersed in fluid with no flow through them will adsorb organic material only from the stagnant liquid in the void space of the packet. Movement of fluid through the porous packets is induced by pressure differences across the packets resulting from buoyancy forces, turbulence, and velocity differences between the packets and the surrounding fluid.

When the flowrate through the carbon-filled packets or panels was calculated, the flow resistance offered by the fabric used to encase the adsorbent was neglected, and the packets were always assumed to be oriented broadside to the external fluid flow.

The overall resistance to mass transfer from the bulk liquid to the solid includes the resistive contribution of (a) the layer of solution around the particles, (b) diffusion of solute through the pores within the particles, and (c) physical adsorption at active sites on the solid.

The mass transfer coefficients from the bulk liquid to the exterior surface area of the carbon particles (step a above) were computed using general correlations obtained in packed beds at low *Re* numbers.

For steady-state mass transfer from the water phase to the carbon, and for piston flow through the packed bed (or packet),

$$-\bar{U}_a dC = k_c a (C - C_i) dx. \quad (1)$$

The resistance offered by the pore diffusion and physical adsorption steps is assumed to be very small relative to the resistance to mass transfer from the bulk liquid to the exterior surface of the carbon. Therefore,  $C_i$  can be closely approximated as the concentration of the solute in equilibrium with the solid. That is, the solute concentration  $C_i$  is assumed to be given by an experimentally determined adsorption equilibrium isotherm. The latter could be used to relate  $C_i$  to the bulk fluid concentration,  $C$ , by means of a material balance if the initial moles of solute and the mass of carbon were known. Since the carbon packets considered in this study are fairly thin, and since the packets moving through the liquid may have fluid passing through them in either direction (depending on which of the two broad sides are facing the flow),  $C_i$  will be assumed to be constant for all carbon granules and hence independent

of distance,  $x$ , through the packet.  $C_i$  will vary with time as the concentration of organic material on the carbon increases. The change in concentration across a packet is given by integrating Equation 1 from 0 to  $L$  and  $C_{in}$  to  $C_{out}$  to yield after rearrangement

$$\frac{C_{out} - C_{in}}{C_{in}} = \left( 1 - \frac{C_i}{C_{in}} \right) \left[ 1 - \exp \left( - \frac{k_c a L}{\bar{U}_a} \right) \right] \quad (2)$$

For fresh activated carbon,  $C_i$  is negligible for many organics, and the fraction of pollutant removed from water passing through a fresh carbon packet is then given as

$$\frac{C_{in} - C_{out}}{C_{in}} = 1 - \exp \left( - \frac{k_c a L}{\bar{U}_a} \right) \quad (3)$$

### Pollutant Removal by Buoyant Packets

#### Buoyant Packet Cycling

Some proponents have suggested that waterways or lakes polluted by spills of water soluble hazardous organic compounds could be cleaned up faster or more efficiently if buoyant packets of activated carbon adsorbent were used. These packets would be fabricated in sizes small enough to be mixed with water and injected at the bottom of a polluted volume of water by a solids-handling pump; they would be buoyant enough to rise through the pollutant water at some known terminal velocity. The movement of the packet upward through the water would enhance mass transfer of the pollutant to the carbon. Upon arrival at the water surface, the packets would be automatically gathered and pumped down to the bottom of the water column again to start another cycle.

A packet size of 10.2 by 10.2 cm (4 by 4 in.) with a thickness of either 1.27 cm (0.5 in.) or 0.64 cm (0.25 in.) was chosen. Buoyancy was assumed to be provided by adding foamed plastic particles with a specific gravity of 0.2 to the carbon granules used to fill the packets. The foamed plastic would be equal in size to the carbon granules used. Calculations were performed for carbon granules with a diameter of 0.12 and 0.06 cm (14 and 28 mesh).

For the purpose of this study, the cycling of buoyant packets was assumed

to be used for the clean up of 3,786 m<sup>3</sup> (10<sup>6</sup> gal) of water contaminated with 100 ppm of phenol. A carbon-to-phenol ratio of 10 was assumed. The packets were assumed to rise with the large rectangular face normal to the flow direction. The  $\Delta P$  required to produce a given terminal rise velocity,  $v_t$ , for the packet was calculated. This computed  $\Delta P$  was in turn used to calculate the flowrate through the packet,  $\bar{U}_a$ .

A packet rising through the water column of depth  $D$  at velocity  $v_t$  will treat  $\bar{U}_a A_p D / v_t$  units of water. The fraction of phenol removed from the water passing through a packet is given by Equation 3. Thus the amount of phenol removed from the water by  $N$  packets of fresh carbon after one pass through a depth  $D$  at  $v_t$  is given by the equation

$$V \Delta C = \frac{D}{v_t} \bar{U}_a A_p N C \left[ 1 - \exp \left( - \frac{k_c a L}{\bar{U}_a} \right) \right] \quad (4)$$

As the packets float on the water surface before they are gathered and returned to the river bottom, the carbon will adsorb phenol from the fluid remaining in the void space of the packets. To account for this adsorption, it has been assumed that for each cycle, in addition to the pollutant adsorbed while rising through the water, the carbon in a packet will remove enough phenol to attain equilibrium with a volume of phenol-water mixture sufficient to occupy the packet void space—that is,  $(C - C_i) N V_p \theta$ . Thus the total amount of phenol removed per cycle is given by adding this quantity to Equation 4.

The total number of cycles,  $n$ , required by fresh carbon packets to remove a given fraction of the phenol (or any pollutant) can be found from Equation 5,

$$1 - \frac{C}{C_o} = - \frac{N n}{V} \left\{ \frac{D}{v_t} \bar{U}_a A_p \left[ 1 - \exp \left( - \frac{k_c a L}{\bar{U}_a} \right) \right] + V_p \theta \right\} \quad (5)$$

The total time required to reduce the phenol concentration from  $C_o$  to  $C$  is primarily a function of the packet

retrieval time, the solids-handling pump capacity, and the number of cycles,  $n$ . According to Equation 5, if  $N$  should be increased, the number of packet cycles will be unaffected ( $N/V$  is determined by the carbon to phenol ratio and the amount of flotation matter required). This effect applies to fresh carbon packets only (the restrictions under which Equation 5 was derived). Thus to complete the desired cleanup job, the same number of packets would have to be retrieved and pumped to the bottom of the water column. The volume of fluid-solids handled by the recycling pump (using a 15% maximum solids loading as typical) is  $NnV_p/0.15$ .

Numerical solutions of the mass transfer equations for a carbon-phenol ratio of 10 (using values of  $C$ , determined from an adsorption isotherm for phenol and Nuchar C-190 obtained for 80% removal of phenol from a mixture with an initial concentration of 100 ppm phenol) are plotted in Figure 1.

### Buoyant Packets Suspended in Turbulent Rivers

If buoyant packets were injected into a turbulent river, the random buffeting of the packets by the eddies would increase the immersion time. To remain suspended in a river, a packet must encounter a net downward force of sufficient strength to counter the steady, buoyant force. Suspension is assumed to occur when the average slip velocity is equal to the terminal rise velocity of the packet. As before, it is assumed that the packet will be oriented broadside to the flow. Fluid entering each packet is assumed to be well mixed and hence representative of the river in the surrounding vicinity. Fluid exiting from a packet is assumed to mix very rapidly with the surrounding fluid. Figure 2 presents a simple schematic to illustrate the adsorption model.

The differential equation for this case is

$$-V \frac{dC}{dt} = \bar{U}_a A_p N C$$

$$\left[ 1 - \exp \left( - \frac{k_c a L}{\bar{U}_a} \right) \right] \quad (6)$$

or, separating variables and integrating,

$$\ln \frac{C}{C_0} = - \frac{\bar{U}_a A_p N t}{V}$$

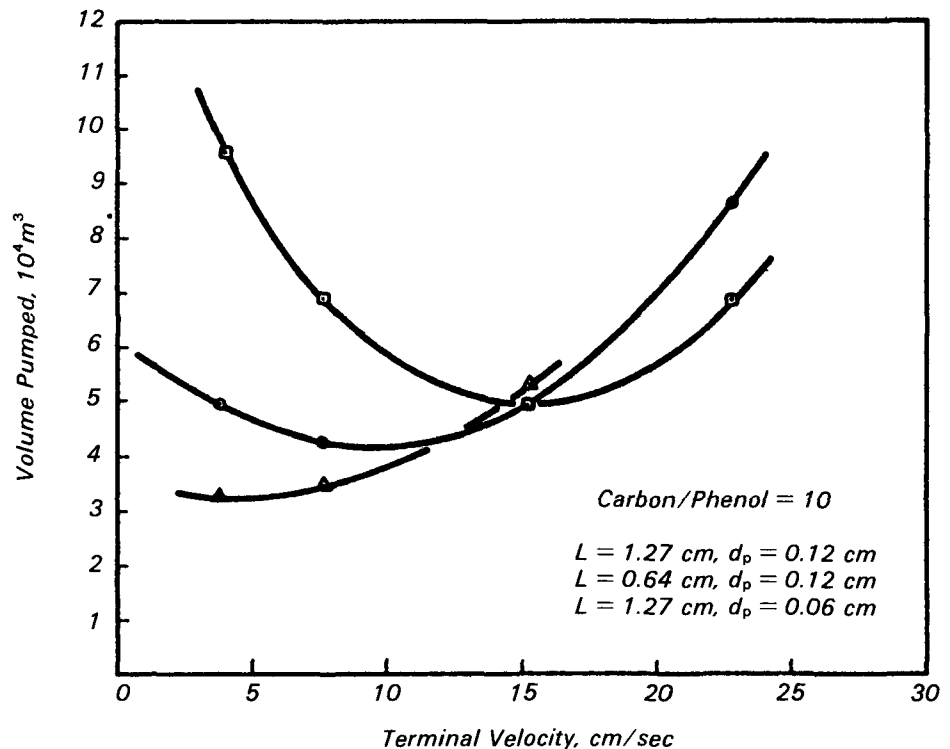


Figure 1. Fluid pumping required to remove 80% phenol from  $3,785 \text{ m}^3$  ( $10^6 \text{ gal}$ ) with buoyant carbon packets ( $10.2 \text{ cm} \times 10.2 \text{ cm} \times L$ ).

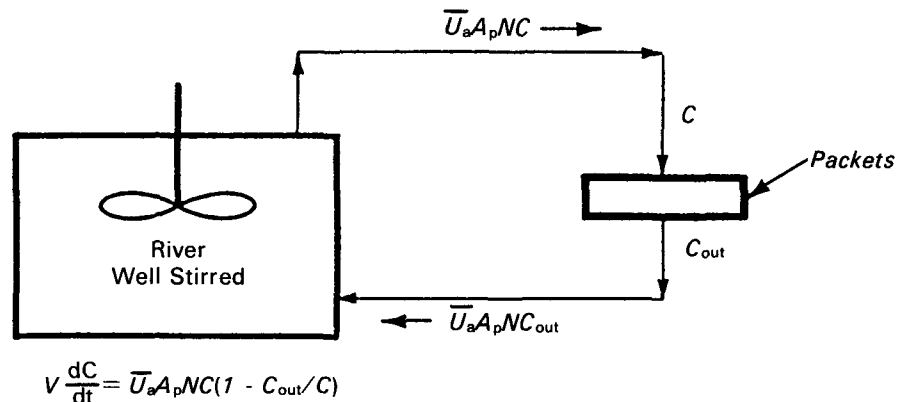


Figure 2. Model buoyant packets suspended in turbulent rivers.

$$\left[ 1 - \exp \left( - \frac{k_c a L}{\bar{U}_a} \right) \right] \quad (7)$$

The  $V$  in the denominator of Equation 7 refers to the volume of water to be treated, and  $t$  is the time the packets remain in suspension.

Equation 6 was solved numerically for a carbon-phenol ratio of 10 to obtain values of  $C/C_0$  as a function of  $t$ . The results of the numerical solutions for the rate of phenol removal by packets

suspended in a turbulent river are plotted in Figure 3. These results are independent of spill size or of the amount of water to be treated as long as the water initially contains 100 ppm phenol and the carbon-to-phenol ratio is 10. If, for example, the initial concentration of phenol were 250 ppm, Equation 7 indicates that the carbon packet concentration,  $N/V$ , would be 2.5 times greater than it would be for a 100-ppm phenol-water mixture to maintain a carbon-to-phenol ratio of 10. The

information given in Figure 3 can be easily converted to 250-ppm phenol-water mixtures by merely dividing the time axis by 2.5.

### Pollutant Removal by Carbon-Filled Panels Hanging in Rivers

Spills of water soluble pollutants can be removed from water courses by panels packed with activated carbon hanging in the water flow in some homogeneous pattern downstream of the spill and turned broadside to the flow. The impact of the flowing water on the panels will provide the  $\Delta P$  for flow through the porous panels and over the activated carbon granules.

The system can be treated as a very loosely packed bed of adsorbers consisting of carbon-filled panels. Because the panels would be located at various distances downstream from a spill, the amount of pollutant adsorbed in a panel will depend on the location of the panel along the watercourse. As in a packed bed, the pollutant concentration will be assumed to be constant over any cross-section normal to the flow.

Assuming fresh carbon (i.e.,  $C_i$  is negligible), the equation for the system can be shown to be

$$\ln \frac{C}{C_o} = - \frac{\bar{U}_a A_c}{\bar{Q}}$$

$$\left[ 1 - \exp \left( - \frac{k_c a L}{\bar{U}_a} \right) \right] \quad (8)$$

where  $\bar{Q}$  is the volumetric discharge rate relative to the carbon panels and  $A_c$  is the total cross-sectional area of the panels in the watercourse.

Calculated results obtained by using Equation 8 are plotted in Figure 4 as the percent of phenol removed per pass over the carbon panels versus  $\bar{Q}$ . The spill size in pounds of phenol appears as a parameter, and the carbon-to-phenol ratio is 10. The solid curves in Figure 4 are for a slip velocity of 30.5 cm/sec (1 ft/sec). For a spill of 454 kg (1000 lb) of phenol, dashed curves are given for slip velocities of 61.0 cm/sec and 91.4 cm/sec (2 and 3 ft/sec). Note that increasing  $v_s$  from 30.5 to 61.0 cm/sec (1 to 2 ft/sec) (which also doubles  $\bar{Q}$ ) for a 454-kg (1000-lb) spill, for example, will result in a smaller percent of phenol removal. For 1.27-cm-thick panels filled with 0.12-cm carbon granules, the percent of removal is maximized at a  $v_s$

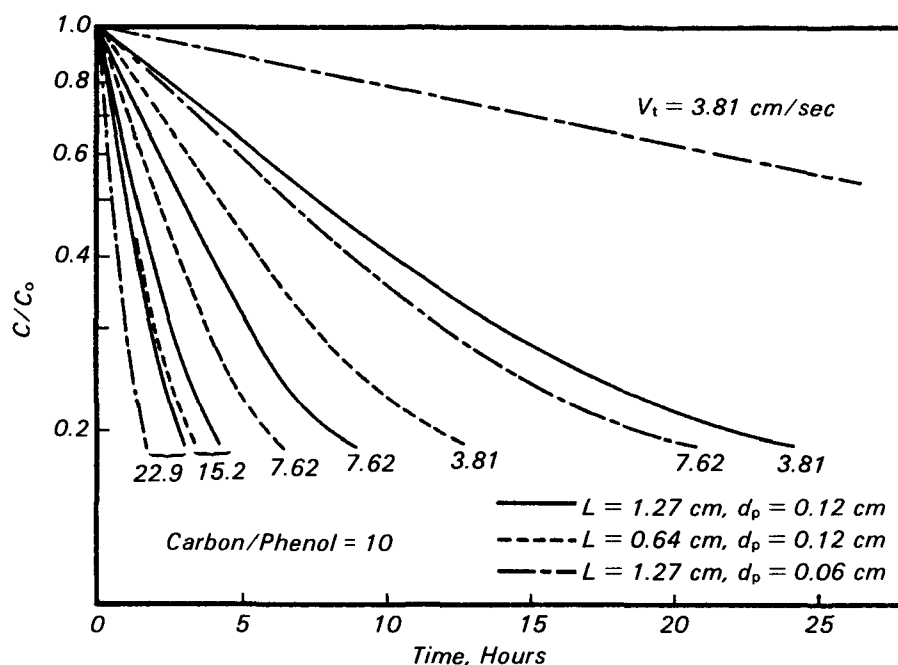


Figure 3. Removal of phenol by suspended buoyant packets of activated carbon ( $10.2 \times 10.2 \text{ cm} \times L$ ,  $C_o = 100 \text{ ppm}$ ).

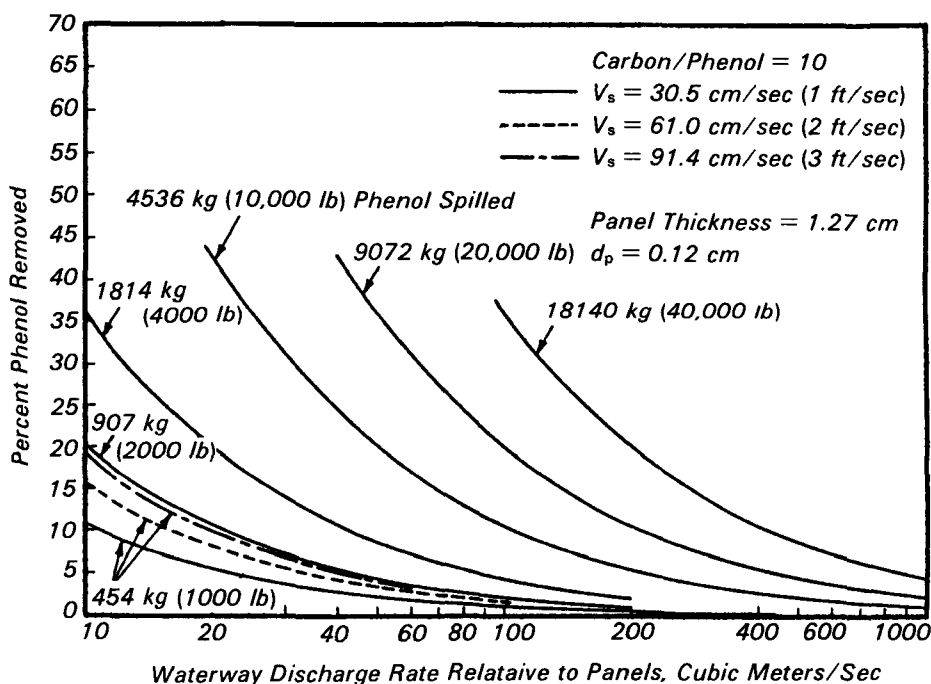


Figure 4. Removal of spills from waterways by carbon-filled panels.

of about 15.2 cm/sec (0.5 ft/sec). If the river velocity were 61.0 cm/sec (2 ft/sec), for example, and if the panels could be allowed to drift down the river at 45.7 cm/sec (1.5 ft/sec), the calcula-

tions indicate that the panels would remove more phenol. But the polluted stretch of water would take four times longer to move past the panels, and during this additional time, longitudinal

dispersion will further dilute the pollutant. The calculations ignore this complicating factor.

Calculations in Figure 4, which are based on Equation 8, are good for the first portions of the spill-polluted water to pass through the panel-festooned region of the river. As more of the contaminated water passes through the panel region, the mass transfer equation (a precursor of Equation 8) would have to be numerically integrated (taking into account a variation of adsorbed material on the panel) with the axial distance of the panel from the head of the panel region. This is especially true for the large spills and low values of  $\bar{Q}$ . We believe that the percent removal results appearing in Figure 4 are higher than can be attained in practice.

### Turbulent Diffusion and Dispersion in Waterways

Spills of water soluble materials into waterways are rapidly diluted by eddy diffusion and dispersion, making cleanup attempts very difficult. Eddy diffusion coefficients, though quite large compared to molecular diffusion coefficients, do not describe the primary dilution action in watercourses, which is longitudinal dispersion. Longitudinal dispersion involves the spreading out of a water soluble substance along the length of a waterway as a result of variations in flow velocity across the channel. Values of longitudinal dispersion coefficients measured for real waterways are given in Table 1.

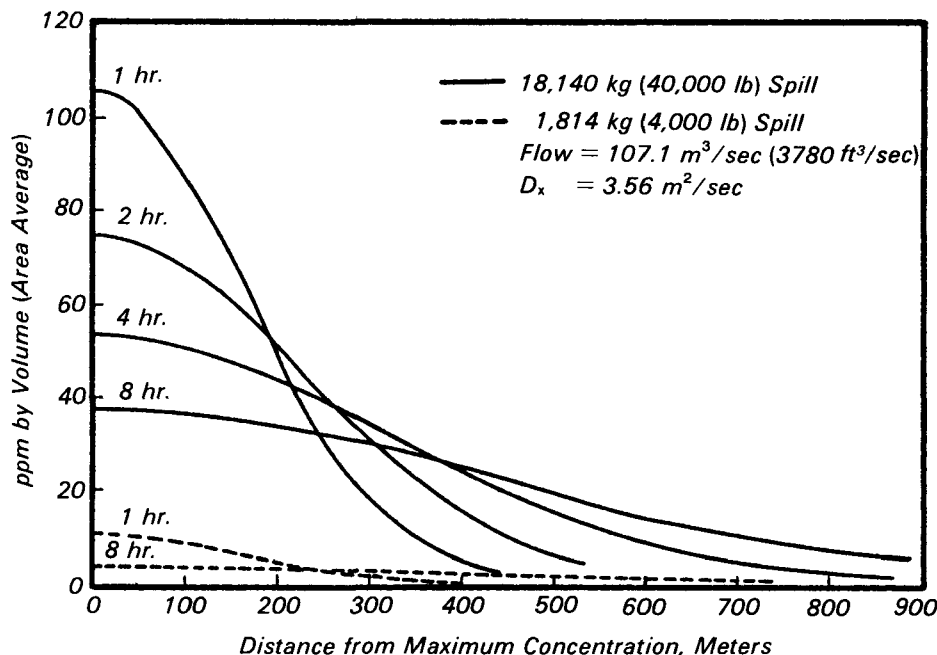
Profiles of mean concentration versus distance for phenol spills of 18,140 kg (40,000 lb) and 1,814 kg (4,000 lb) were calculated for the Chicago Sanitary and Ship Canal (CSSC) using data given in Table 1. This waterway has the lowest longitudinal dispersion (Table 1), and the profiles plotted in Figure 5 are thought to provide conservative values of spill dilution that would occur in rivers of comparable flowrate.

### Discussion

The equations derived for the adsorption rate of pollutant from waterways by buoyant carbon-filled packets (Equations 5 and 7) contain the total volume of fluid to be treated,  $V$ , in the denominator. As a result, an increase in  $V$  with time resulting from turbulent mixing and dispersion in waterways will increase either the number of cycles or the suspension time required to remove a specified fraction of the pollutant,

**Table 1.** Typical Measured Dispersion Coefficients

Watercourse and Test Location	$\bar{Q}$ $m^3/sec$	$\bar{v}$ $cm/sec$	$D_x$ $m^2/sec$
Chicago Sanitary and Ship Canal (Calumet Sag)	107.1	27.1	3.56
Missouri River (near Omaha, Nebraska)	957.1	171.0	1490
Clinch River (near Clinchport, Virginia)	6.80	18.1	19.7
Copper Creek (near Gate City, Virginia)	9.15	18.7	9.1
Powell River (Sneedville, Tennessee)	3.96	16.4	26.8
Coachella Canal (Holtville, California)	37.29	68.3	17.7



**Figure 5.** Longitudinal dispersion of water soluble spills in the Chicago Sanitary and Ship Canal.

unless the number of carbon packets is also increased with time so as to maintain  $N/V$  constant.

### Packet Cycling

Assume that response is required within 1 to 8 hr to an 1,814-kg (4,000-lb) phenol spill into the CSSC. With 18,140 kg (40,000 lb) of activated granular carbon and 8,645 kg (19,060 lb) of flotation material in 897,000 buoyant packets, phenol would be removed from a mixture in which the maximum concentration would be between about 4 and 10.5 ppm by volume dissolved in roughly  $3 \times 10^5$  to  $6.8 \times 10^5 m^3$  ( $80 \times 10^6$  to  $180 \times 10^6$  gal) of water spanning 800 to 1,800 m (2600 to 5900 ft) along the channel. (Portions of the canal are ignored where the calculated phenol concentration is less than 0.5 ppm.) For a response 1 hr after the spill, calcula-

tions in Equation 5 indicate that a 10% reduction in phenol concentration would require 155 cycles of the packets; after 8 hr, 368 cycles would be needed to effect a 10% reduction in concentration. With a factor of 15% solids by volume (which can be handled by the pumps),  $6.07 \times 10^4 m^3$  (16.05 pumped (391.8  $m^3/cycle$ , or 103,500 gal/cycle). If it were possible to reduce the packet cycle time to 10 min, the time required for 155 cycles (starting cleanup operations 1 hr after the spill) would be 61.3 hr. The solids-handling pumps would have to circulate  $39.4 m^3/min$  (10,400 gal/min). Of course, the phenol will continue to spread longitudinally along the channel during the cleanup process.

### Buoyant Packets

If it were possible to keep the buoyant packets suspended in the CSSC by

turbulence (which appears to be highly unlikely), a response to the 1,814-kg (4,000 lb) spill in 1 to 8 hr would produce a situation requiring 25 to 60 hr to remove 10% of the spilled phenol (according to Equation 7), even if the dispersion process were to cease. A continuing dispersion process will prevent the success of a carbon-filled-panel approach to cleanup.

### Carbon-Filled Panels

Unlike the equations derived for the buoyant packets, Equation 8 (which is derived for adsorption by panels hanging in a waterway) does not contain the volume of water to be treated. The fraction of pollutant removed is directly proportional to the panel area facing the flow and inversely proportional to the volumetric discharge rate relative to the panels.

Carbon panels fixed in a watercourse the size of the CSSC will remove about 4% of a 1,814-kg (4,000-lb) phenol spill as the polluted fluid passes by the panels, according to the model used to compute Figure 5. Since the percent of spill adsorbed is directly proportional to the total panel area facing the flow, as much as 33% of the phenol could be removed if the carbon-to-phenol ratio were 100 (i.e., if 181,400 kg (400,000 lb) of carbon were used to clean up an 1,814-kg (4,000-lb) spill).

This work assumes that equilibrium is rapidly established at the activated carbon surface. That is, the concentration at the fluid/external particle interface is that value dictated by the adsorption isotherm. With fluids containing 100 ppm of dissolved pollutant, the neglect of small deviations from equilibrium at the fluid/particle interface (perhaps 1 or 2 ppm) will cause errors of a few percentage points in the computations. But when the fluid contains an average of less than 5 ppm of pollutant, as it does after 8 hr of dispersion of an 1,814-kg (4,000-lb) spill into the CSSC, the neglect of similar deviations from equilibrium can result in substantial errors in the computations.

Unless the spill is massive compared with the total flow of the waterway, or unless the spill response team begins cleanup operations very shortly after the spill, carbon-filled panels mechanically suspended in the waterway will be able to remove only a small percentage of the pollutant.

### Nomenclature

$A_c$	Total cross-sectional area of panels normal to the flow direction in the watercourse
$A_p$	Cross-sectional area of a packet (10.2 x 10.2 cm for this study)
$a$	Total exterior particle surface area for mass transfer per unit volume of packed space
$a_x$	Cross-sectional area of panels in length $dx$
$C$	Concentration of solute, moles/volume, in the bulk fluid
$C_i$	Concentration of solute at the exterior of the adsorbent particle
$C_{in}$	Concentration of solute in fluid entering a packet or panel
$C_o$	Initial concentration of solute (at time = 0)
$C_{out}$	Concentration of solute in fluid exiting a panel or packet
$D$	Depth of fluid
$D_x$	Dispersion coefficient in $x$ direction, longitudinal dispersion ( $m^2/sec$ )
$d_p$	Diameter of particles in packets or panels
$k_c$	Mass transfer coefficient ( $cm/sec$ )
$L$	Thickness of carbon-filled packet or panel
$N$	Number of packets

$n$	Number of cycles
$Q$	Volumetric discharge rate relative to carbon panels
$Re$	Reynolds number for a packed bed, $d_p \bar{U}_a \rho / (\mu \theta)$
$t$	Time
$\bar{U}_a$	Superficial flow velocity, the average linear velocity through a bed computed on the basis of the empty cross-sectional area
$V$	Volume
$V_p$	Volume of a packet
$\bar{V}$	Velocity, cross-sectional area mean
$v_s$	Slip velocity, the velocity difference between an object and the fluid in which it is suspended
$v_t$	Terminal velocity
$x$	Distance, as defined where used
$\theta$	Packed bed void fraction or void space
$\mu$	Viscosity of fluid
$\rho$	Density of fluid

The full report was submitted in partial fulfillment of Contract No. 68-03-2648 (Task 8) by Rockwell International, Environmental Monitoring & Services Center, under sponsorship of the U.S. Environmental Protection Agency.

*George R. Schneider is with Rockwell International, Environmental Monitoring & Services Center, Newbury Park, CA 91320.*

*John E. Brugger is the EPA Project Officer (see below).*

*The complete report, entitled "Removal of Water Soluble Hazardous Materials Spills from Waterways by Activated Carbon," (Order No. PB 82-103 813; Cost: \$8.00, subject to change) will be available only from:*

*National Technical Information Service  
5285 Port Royal Road  
Springfield, VA 22161  
Telephone: 703-487-4650*

*The EPA Project Officer can be contacted at:*

*Oil and Hazardous Materials Spills Branch  
Municipal Environmental Research Laboratory—Cincinnati  
U.S. Environmental Protection Agency  
Edison, NJ 08837*

United States  
Environmental Protection  
Agency

Center for Environmental Research  
Information  
Cincinnati OH 45268

Postage and  
Fees Paid  
Environmental  
Protection  
Agency  
EPA 335



Official Business  
Penalty for Private Use \$300

RETURN POSTAGE GUARANTEED

PS 0000329  
U S ENVIR PROTECTION AGENCY  
REGION 5 LIBRARY  
230 S DEARBORN STREET  
CHICAGO IL 60604