Selected Papers in the Hydrologic Sciences 1984

July 1984

A technique to measure oxygen in the root zone of saturated and unsaturated soils
By Virginia Carter, D. J. Shultz, M. K. Garrett, and W. E. Webb

A system for measuring surface runoff and collecting sediment samples from small areas
By J. R. Gray and M. P. deVries

Geochemical studies of organic carbon associated with volcanic ash from Mount St. Helens, Washington
By W. E. Pereira and C. E. Rostad

Organochlorine pesticide and polychlorinated biphenyl residues at four trophic levels in the Schuylkill River, Pennsylvania
By J. L. Barker

A solution-chemistry model of the interference of cadmiun-carbonate precipitation in the determination of cation-exchange separation factors
By R. L. Miller, D. B. Grove, and K. G. Stollenwerk

Confidence limits for determining concentrations of tracer particles in sediment samples
By C. F. Nordin, Jr., and P. W. Mielke, Jr.

Determination of aquatic humic substances in natural waters
By E. M. Thurman

Evolution of the use of channel cross-section properties for estimating streamflow characteristics
By K. L. Wahl

United States
Geological
Survey
Water-Supply
Paper 2262

U.S. DEPARTMENT OF THE INTERIOR
March 3, 1849

Selected Papers in the Hydrologic Sciences 1984

Edited by Eric L. Meyer

July 1984

A technique to measure oxygen in the root zone of saturated and unsaturated soils
By Virginia Carter, D. J. Shultz, M. K. Garrett, and W. E. Webb

A system for measuring surface runoff and collecting sediment samples from small areas
By J. R. Gray and M. P. deVries

Geochemical studies of organic carbon associated with volcanic ash from Mount St. Helens, Washington
By W. E. Pereira and C. E. Rostad

Organochlorine pesticide and polychlorinated biphenyl residues at four trophic levels in the Schuylkill River, Pennsylvania
By J. L. Barker

A solution-chemistry model of the interference of cadmiun-carbonate precipitation in the determination of cation-exchange separation factors
By R. L. Miller, D. B. Grove, and K. G. Stollenwerk

Confidence limits for determining concentrations of tracer particles in sediment samples
By C. F. Nordin, Jr., and P. W. Mielke, Jr.

Determination of aquatic humic substances in natural waters
By E. M. Thurman

Evolution of the use of channel cross-section properties for estimating streamflow characteristics
By K. L. Wahl

U. S. GEOLOGICAL SURVEY WATER-SUPPLY PAPER 2262

UNITED STATES DEPARTMENT OF THE INTERIOR
WILLIAM P. CLARK, Secretary

GEOLOGICAL SURVEY
Dallas L. Peck, Director

UNITED STATES GOVERNMENT PRINTING OFFICE, WASHINGTON: 1984

For sale by the Superintendent of Documents
U.S. Government Printing Office
Washington, DC 20402

Library of Congress Cataloging in Publication Data
Main entry under title:

Selected papers in the hydrologic sciences.

(United States Geological Survey water-supply paper; 2262)
Bibliography: p.
Supt. of Docs. no.: I19.13:2262
contents: A technique to measure oxygen in the root zone of saturated and unsaturated soils/by Virginia Carter...[et al.]—A system for measuring surface runoff and collecting sediment samples from small areas/by J.R. Gray and M.P. deVries—Geochemical studies of organic carbon associated with volcanic ash from Mount St. Helens, Washington/by W.E. Pereira and C.E. Rostad—[etc.]
C.E. Rostad—Addresses, essays, lectures.
I. Geological Survey (U.S.) II. Series: U.S. Geological Survey water supply paper ; 2262.
GB662.4.s45 1984 551.48 84-600177

FOREWORD

This Water-Supply Paper is the first in a periodic series that will present short papers in the hydrologic sciences. The emphasis will be on new methods, techniques, and ideas or innovative applications of known techniques to solve hydrologic problems. Reviews and syntheses of recent work, available only in scattered publications, also will be included. Publication will be twice a year or more frequently as the number of contributions warrants.

The series is intended to be a forum for new ideas in hydrology. Dialogue between readers and authors is encouraged, and a discussion section for readers' comments and authors' replies will be included in each issue after the first.

Address comments to Editor, Selected Papers in the Hydrologic Sciences, U.S. Geological Survey, 423 National Center, Reston, VA 22092.

Philip Cohen
Chief Hydrologist

SI UNITS AND U.S. CUSTOMARY EQUIVALENTS

SI, International System of Units, a modernized metric system of measurement. All values have been rounded to four significan digits. Use of hectare (ha) as an alternative name for square hectometer (hm^2) is restricted to measurement of land or water areas. Use of liter (L) as a special name for cubic decimeter (dm^3) is restricted to the measurement of liquids and gases.

SI unit			U.S. customary equivalent
		Length	
nanometer (nm)	=	0.000 000 39	inch (in)
micrometer (μm)	=	0.000 039 37	inch (in)
millimeter (mm)	=	0.039 37	inch (in)
centimeter (cm)	=	0.3937	inch (in)
meter (m)	=	3.281	feet (ft)
		1.094	yards (yd)
kilometer (km)	=	0.621 4	mile (mi)
		Area	
centimeter^2 (cm^2)	=	0.155 0	inch^2 (in^2)
meter^2 (m^2)	=	10.76	feet^2 (ft^2)
		1.196	yards^2 (yd^2)
		0.000 247 1	acre
hectometer^2 (hm^2)	=	2.471	acres
kilometer^2 (km^2)	=	0.386 1	mile^2 (mi^2)
		Volume	
centimeter^3 (cm^3) milliliter (mL)	=	0.061 02	inch^3 (in^3)
decimeter^3 (dm^3) liter (L)	=	61.02	inches^3 (in^3)
		1.057	quarts (qt)
		0.264 2	gallon (gal)
		0.035 31	foot^3 (ft^3)
meter^3 (m^3)	=	35.31	feet^3 (ft^3)
		1.308	yards^3 (yd^3)
		264.2	gallons (gal)
		0.000 810 7	acre-foot (acre-ft)
hectometer^3 (hm^3)	=	810.7	acre-feet (acre-ft)
kilometer^3 (km^3)	=	0.239 9	mile^3 (mi^3)

SI unit			U.S. customary equivalent
		Volume per unit time (includes flow)	
liter per second (L/s)	=	0.035 31	foot^3 per second (ft^3/s)
		15.85	gallons per minute (gal/min)
meter^3 per second (m^3/s)	=	35.31	feet^3 per second (ft^3/s)
		15 850	gallons per minute (gal/min)
		Mass	
microgram (μg)	=	0.000 00 1543	grain (gr)
gram (g)	=	0.035 27	ounce avoirdupois (oz avdp)
kilogram (kg)	=	2.205	pounds avoirdupois (lb avdp)
		Mass per unit volume	
microgram per kilogram (μg/kg)	=	1	part per billion (ppb) by weight
microgram per liter (μg/L)	=	0.000 05841	grain per gallon (gr/gal)
milligram per liter (mg/L)	=	0.05841	grain per gallon (gr/gal)
		Temperature	
kelvin (K)	=	[degree Fahrenheit (°F) (°) + 459.67]/1.8	
degree Celsium (°C)	=	[degree Fahrenheit (°F) (°) − 32]/1.8	
		Electric conductance	
microsiemens (μS)	=	1	micromho

CONTENTS

A TECHNIQUE TO MEASURE OXYGEN IN THE ROOT ZONE OF SATURATED AND UNSATURATED SOILS

By Virginia Carter, David Shultz,
Mary Keith Garrett[1], *and* Wayne E. Webb

Abstract

The rapid, accurate measurement of the oxygen content of soil gas in the unsaturated zone or dissolved oxygen in soil water in the saturated zone can be useful in wetland vegetation studies. A method has been devised and tested in the Great Dismal Swamp, a wetland with fine silt-clay and organic soils, that appears to provide good results. A 60-milliliter sample of soil gas or water is withdrawn from permanently installed chambers at various depths in the soil profile. The oxygen concentration of air samples is measured with a specially constructed analyzer cell fitted to the polarographic oxygen electrode of a portable oxygen meter. The dissolved oxygen concentration of water samples is measured directly with the oxygen electrode while stirring the sample in a 32-milliliter glass bottle with a portable magnetic stirrer. Field tests with duplicate chamber installations showed that consistent results are obtained for soil gas and water.

INTRODUCTION

The oxygen content of the soil gas or water in the root zone is a sensitive indicator of the amount of oxygen available to roots. Low oxygen concentrations in soil water are probably the primary limiting factor for wetland plants, although toxic accumulations of ions, organic acids, and gases resulting from anaerobic respiration by soil bacteria may exert secondary effects (Whitlow and Harris, 1979; Gill, 1970). Anaerobic soil conditions lead to a decrease or cessation of aerobic root respiration, decreased root growth and translocation, and accumulation of toxic metabolic products (Gill, 1970; Patrick and others, 1973). Although the optimum amount of gaseous oxygen for root development and plant growth varies greatly with species and age of plant, it appears that most plants require an oxygen content greater than 10 percent in the soil gas (Patrick and others, 1973).

In spite of the importance of oxygen in the root zone, the oxygen content of soil air or water has not been measured routinely in wetlands. There is no fast, reliable method of performing a large number of analyses in the field, and the fluctuation in wetland water levels necessitates making oxygen measurements in whichever of the two phases are at the root level. Methods have been developed for measuring soil gases with a diffusion chamber (for example, Robinson, 1957; Yamaguchi and others, 1962), but these involve large volumes of gas or transfer to a gas chromatograph in the laboratory. Fox and Rolfe (1982) developed a field method for collecting soil solutions from flooded soils to determine oxidation-reduction potentials. Patrick (1977) developed a field method for the rapid measurement of soil oxygen at various depths in the soil profile above the water table; the method was used to determine oxygen content of soil air and root development of cotton (Patrick and others, 1973) and sugar cane (Patrick and others, 1969) in Mississippi River alluvial soils.

More recently, Patrick (1977) developed a field method to measure oxygen concentrations in the saturated and unsaturated zones in wetland transition zones in Mississippi and Louisiana. A small plastic chamber connected to the surface by a copper tube is inserted into an augered hole, the hole is sealed above the chamber, and the air in the chamber is allowed to equilibrate with the water surrounding the chamber. After about 3 weeks, the oxygen content of the chamber air approximates that of the water in the root zone. Oxygen measurements are made using a standard Yellow Springs Instrument oxygen meter and polarographic electrode fitted with a specially constructed analyzer cell of small internal volume. This method is difficult to use in fine silt-clay soils high in organic material; chamber emplacement is difficult because auger holes tend to cave in and the chamber screens tend to clog when air is withdrawn.

This paper describes a method for making oxygen measurements in the saturated and unsaturated zone of such soils. The technique requires 60-mL samples of air or water and provides a rapid analysis of oxygen concentration. Laboratory tests on a variety of experimental chambers showed that this design gave consistent results without clogging the chamber screens.

---

[1] U.S. Fish and Wildlife Service, Suffolk, VA 23434.

ACKNOWLEDGMENTS

This project was supported in part by the U.S. Army Corps of Engineers, Waterways Experiment Station, Contract WESRF 82–145. Our thanks go to Dr. William Patrick, Louisiana State University, and Dr. Warren Wood, U.S. Geological Survey, who spent many hours discussing design and measurement problems and possible solutions.

CHAMBER CONSTRUCTION

The oxygen chambers[2] or reservoirs consisted of a 187-mm length of Johnson polyvinylchloride (PVC), 10-slot (0.25-mm opening), 41-mm outside diameter well screen capped on both ends (fig. 1) and connected to the surface by two copper access tubes. A small hole was drilled in the botton cap for drainage, and two small holes, approximately 3 mm in diameter, were drilled in the top cap for the copper access tubes. Two copper access tubes, 3-mm outside diameter and 1.65-mm inside diameter, were inserted through the upper cap. The length of the tubes depends upon the desired depth of installation. In the Great Dismal Swamp of Virginia and North Carolina, where root-zone oxygen was to be measured, water levels are high enough to require at least 310 mm of tubing above ground. The shorter tube was flared and fitted at the bottom of the upper cap and held in the chamber by a sleeve of Tygon tubing with 1.65-mm inside diameter supplemented with PVC glue. The longer tube extends to within 13 mm of the bottom of the chamber and was held in place by a loop in the tubing inside the cap and a Tygon sleeve supplemented with PVC glue outside the cap. Both caps were glued on the well screen with PVC glue. The outside of the chamber and the bottom of the drain hole were covered with a stainless steel wire cloth, mesh size 325.

The wire cloth was fastened to the well screen with a hot soldering iron which melts the plastic through the wire-cloth fibers. The two access tubes were each topped with a short piece of Tygon tubing closed by a plastic rachet tubing clamp. The installation depth is the distance between the center of the chamber and the ground surface. The volume of the chamber is estimated to be 160 mL.

CHAMBER INSTALLATION

A 51-mm diameter hole was augered with a hand auger to a depth of 95 mm more than the desired installation depth. The chamber was inserted, and the hole replaced in reverse order. Every attempt was made to minimize disturbances of the surrounding soil when repacking the soil material. Installation may be at any desired depth; chambers in the Dismal Swamp were placed at 310, 457, and 762 mm. Typically, two chambers were placed at each depth at each site. Table 1 shows the measurements made in the Great Dismal Swamp using duplicate installations at two depths on one transect on July 7, 1983. The mean difference in the dissolved oxgen of 10 duplicate samples is 0.2 mg/L, and the mean difference in oxygen in soil gas of 4 duplicate samples is 1.1 percent.

ANALYZER SYSTEM

Portable polarographic oxygen analyzers with oxygen electrodes were used for oxygen measurements. Because soil-gas measurements require a dry membrane, we used two oxygen analyzers and electrodes—one for gas measurements and the other for water measurements. A specially constructed cell of stainles steel with a gas inlet and outlet is employed for doing the soil-air measurements (Patrick, 1977). The cell is machined to thread onto the top of the oxygen electrode and was designed so that the internal volume of the cell is about 1 mL. An O-ring seal in the cell maintains the integrity of the air sample during contact with the membrane surface. Any battery-operated field oxygen meter capable of measuring oxygen in air and water can be used, but the cell must be custom fabricated to fit the electrode.

MEASURING OXYGEN

Before use, the oxygen meters were calibrated. The meter used for dissolved oxygen was calibrated using standard air calibration techniques. The gas meter was calibrated by drawing an air sample into the cell and setting the meter to 21-percent oxygen on the temperature scale. The zero oxygen point can be checked by drawing nitrogen through the cell. Experience indicates the 21-percent oxygen check should be done frequently in the field, both before and after measurements.

In the field, a plastic syringe with a short piece of flexible Tygon tubing and a plastic nozzle was attached

---

[2] The specifications of the oxygen chambers are intended to show their scale. Substitutions of similar, but not identical, material should pose no difficulty.

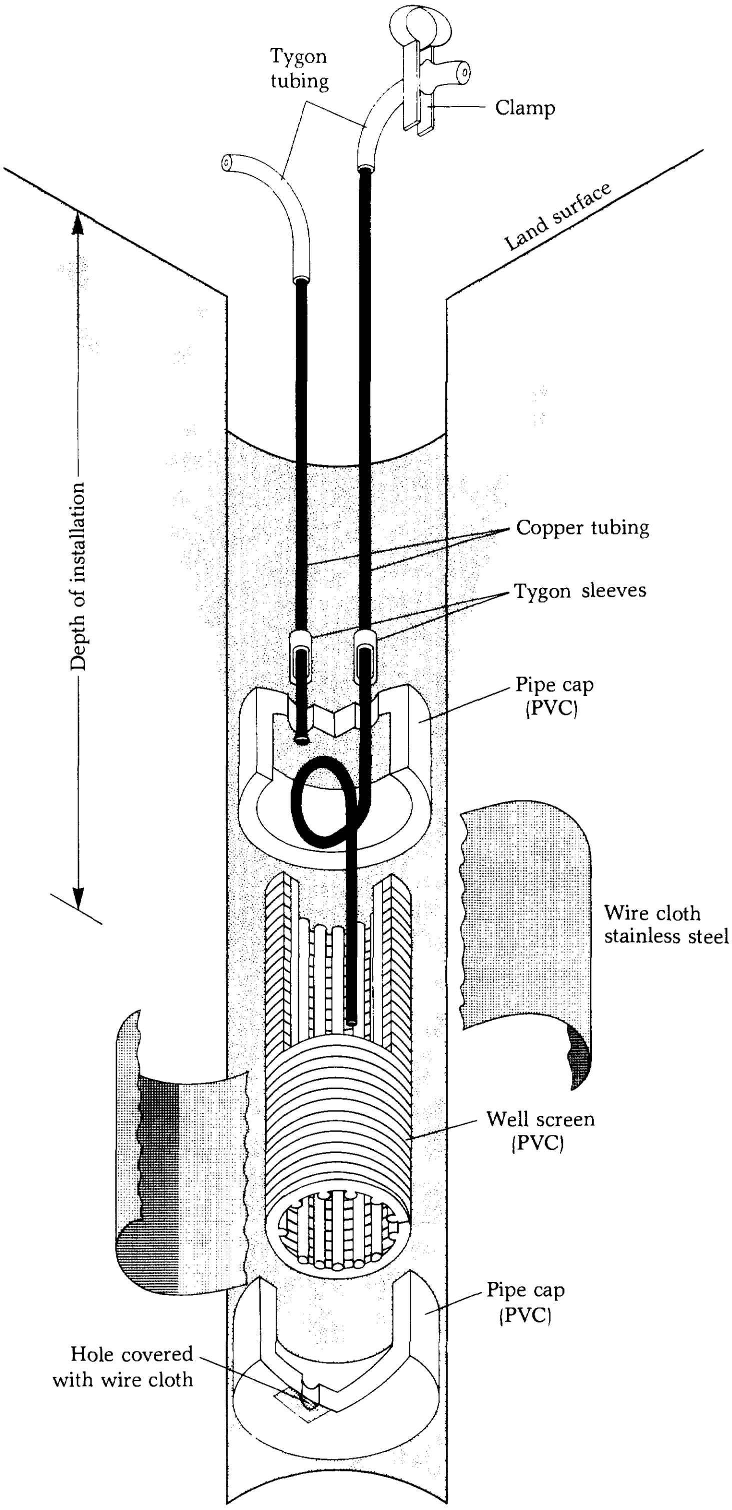


Figure 1. Details of oxygen chamber construction (exploded view from below).

Table 1. Oxygen measurements on the King Transect, Great Dismal Swamp, Virginia and North Carolina, July 7, 1983
[Two chambers are installed at each depth; at site 15, there are three chambers at 457 mm; n.d., no data obtained]

		Oxygen	
Site Number	Depth, in millimeters	Dissolved, in milligrams per liter	Soil gas, in percent
2	310	n.d.	18
	310	n.d.	18
	457	n.d.	18.5
	457	n.d.	17
10	310	n.d.	16
	310	0.9	n.d.
	457	0.6	n.d.
	457	0.7	n.d.
15	310	0.7	n.d.
	310	0.8	n.d.
	457	1.2	n.d.
	457	0.9	n.d.
	457	1.0	n.d.
20	310	n.d.	12
	310	n.d.	14
	457	1.0	n.d.
	457	1.0	n.d.
23	310	n.d.	12
	310	n.d.	13
	457	n.d.	15
	457	n.d.	n.d.
27	310	0.8	n.d.
	310	1.3	n.d.
	457	0.7	n.d.
	457	0.6	n.d.
30	310	1.0	n.d.
	310	0.9	n.d.
	457	1.3	n.d.
	457	1.1	n.d.
40	310	0.9	n.d.
	310	1.4	n.d.
	457	0.7	n.d.
	457	0.8	n.d.

to the short access tube, and a sample was withdrawn. Back pressure indicated that the chamber was filled with water rather than gas. To measure soil oxygen content above the water table, 60 mL of gas was withdrawn through the short copper access tube. The air in the syringe then was pushed slowly through the analyzer cell, and a reading was taken when the meter reading was steady. Because an appreciable vacuum sometimes was needed to withdraw gas from the chamber, the gas sample was not drawn directly through the analyzer cell to prevent changing the membrane calibration. Consecutive oxygen readings from the same chamber usually agreed within 2 percent. The total volume of the access tube and analyzer cell for a 762-mm-deep chamber is approximately 2.6 mL so that withdrawal of 60 mL insures that 96 percent of the gas passing through the cell is from the gas chamber. A reading can be taken in 2 to 3 minutes.

If the water table was above the chamber, the syringe was connected to the longer access tube, and a piece of flexible Tygon tubing containing flowing nitrogen was inserted in the short acess tube. Sixty milliliters of water were withdrawn and replaced by the nitrogen. A small hole in the nitrogen-supply tubing prevents excessive nitrogen pressure from entering the chamber during sampling. The nitrogen prevents any partial vacuum in the chamber. Withdrawing a sample without a simultaneous injection of nitrogen caused water outside the chamber to transport particulate material that clogged the fine screen.

After the sample was withdrawn, the short access tube was left open so that the nitrogen could escape as the chamber refilled. This may require several hours because of the low hydraulic conductivity of the surrounding soil. The water sample in the syringe was very carefully expressed through the Tygon tubing into the bottom of a 32-mL bottle, which contained a very small magnetic stirring rod, and was allowed to overflow. The head of the oxygen probe fits snugly into the top of the bottle, and the bottle is placed on a battery-operated magnetic stirrer. Oxygen measurements take 2 to 3 minutes.

When the water table is located near the midline of the chamber, it is possible to make both an air and water reading providing the air reading is done first.

CONCLUSION

This technique provides a fast, reliable method of performing a large number of oxygen measurements in the field. Oxygen can be measured in the root zone regardless of which phase, water or gas, is at the level of the chamber. In addition, water samples can be easily withdrawn from the chambers for measurement of other water-quality parameters such as pH.

REFERENCES CITED

Fox, R., and Rolfe, G. L., 1982, A method of collecting soil solutions from flooded soils: Soil Science Society of America Journal, v. 46, no. 6, p. 1332–1333.

Gill, C. J., 1970, Flooding tolerance of woody species—A review: Forestry Abstracts, v. 31, p. 671–688.

Patrick, W. H., Jr., 1977, Oxygen content of soil air by a field method: Soil Science Society of America Journal, v. 41, no. 3, p. 651–652.

Patrick, W. H., Jr., Delaune, R. D., and Engler, R. M., 1973, Soil oxygen content and root development of cotton in Mississippi River alluvial soils: Louisiana State University Agricultural Experiment Station Bulletin No. 673, 28 p.

Patrick, W. H., Jr., Turner, F. T., and Delaune, R. D., 1969, Soil oxygen content and root development in sugar cane: Louisiana State University Agricultural Experiment Station Bulletin No. 641, 20 p.

Robinson, F. E., 1957, A diffusion chamber for studying soil atmosphere: Soil Science, v. 83, p. 465–469.

Whitlow, T. H., and Harris, R. W., 1979, Flood tolerance in plants—A state-of-the-art review: U.S. Army Engineers Waterways Experiment Station Technical Report E–79–1, U.S. Army Corps of Engineers, Vicksburg, Mississsippi, 161 p.

Yamaguchi, M., Howard, F. D., Hughes, D. L., and Flocker, W. J., 1962, An improved technique for sampling and analysis of soil atmospheres: Soil Science Society of America, Proceedings, v. 26, p. 512–513.

A SYSTEM FOR MEASURING SURFACE RUNOFF AND COLLECTING SEDIMENT SAMPLES FROM SMALL AREAS

By John R. Gray *and* M. Peter deVries

Abstract

A system has been developed for measuring surface runoff and collecting water-sediment samples from small areas (plots) on a low-level radioactive waste disposal site in northwestern Illinois. Runoff from an 11-square-meter plot is routed through a Parshall flume. Peak discharge is computed from a peak stage measured in a flume stilling well and a stage-discharge relation for the flume. The flume discharges into a 20-liter primary collecting vessel. Runoff exceeding 16 liters is pumped from the primary vessel until 4 liters remain. Pumpage is routed through a cone-splitting chamber, which divides flow into 10 equal parts. One part is retained in addition to that stored by the primary vessel for subsequent measurement and sediment-sample collection. The device, called the dekaport divisor system, enables collection of reliable runoff and sediment yield data from small areas.

INTRODUCTION

Fractional hectare areas (plots) have been used in the United States since 1917 to measure soil and water losses due to rainfall and snowmelt. Most plot gages were designed and built by groups interested in specific problems; hence, a variety of equipment designs have evolved (see Mutchler, 1963, p. 1). This report describes the dekaport divisor system that was developed to obtain runoff and sediment-transport data at trench covers on a low-level radioactive waste disposal site near Sheffield in northwestern Illinois (Heim and Machalinski, 1980, p. 3–8). The system also enables the determination of rainfall-runoff relations when precipitation is measured.

Although many factors influenced the design of the system, the imposed absolute constraints on the type and capacity of flow measuring and sampling equipment used are as follows:

1. Access to the site is limited from 0800 to 1630 hours on weekdays. To collect data during nonaccess periods, an automated data-collection system was needed.
2. An anticipated brief duration of runoff and the need to avoid retarding runoff from the plot (such as with a hydraulic constriction to form a stable stage-discharge control) prevented the use of conventional stream-gaging techniques to meter flow (Rantz and others, 1982).
3. The site custodian preferred relatively small installations that required a minimum of excavation, which precluded the use of large flow collection tanks.
4. Land-surface slope downstream from site plots does not exceed 3 percent, which necessitates a pumping system as opposed to a gravity system to deliver plot runoff to a measuring device.
5. Distance from crests of selected trench covers to adjacent valleys is about 6 m. Flow converging at the base of this 6-m length emanates from about 11 m^2 of land surface. Hence, plots of about 11 m^2 in size were selected for study.

The design of the dekaport divisor system was influenced by sampling and measuring devices described by the U.S. Department of Agriculture (1979, p. 245–250), Hewlett (1979, p. 5–7), Mutchler (1963), and G. H. Leavesley (U.S. Geological Survey, oral commun., 1983). However, none of those devices were applicable directly at the Sheffield site.

DESIGN CRITERIA

A measuring and sampling system incorporating a flume, pump, flow splitter, and storage vessels was designed for use at study plots. Maximum volumetric capacity was selected based on the runoff from an 11-m^2 area that can be expected to result from the 24-hour-duration, 50-year rain for the region of 183 mm (Illinois State Water Survey, 1970, p. 5). The system can measure and sample runoff depths up to 195 mm (equal to a volume of 2,140 L).

The flume, pump, and flow splitter were selected for their ability to accommodate the peak discharge induced by the 1-hour duration, 100-year rain for the region. The rational formula was used with a runoff coefficient of 1.0 (100-percent runoff) and 84 mm of rain per hour on an 11-m^2 plot to compute a peak discharge of 0.25 L/s (Chow, 1964, chap. 14, p. 6–8). The system pumps at a rate of 0.32 L/s. The flume can accommodate flows under 0.5 L/s with minimal ponding upstream.

EQUIPMENT

The major components of the dekaport divisor system (fig. 1) are as follows:

1. A Parshall flume with a 76.2-mm throat, an attached stilling well, and sheet-metal wing walls extending 1 m upstream from the flume entrance.
2. A 20-L primary collecting vessel positioned beneath the flume outfall with upper and lower floats to operate pump-controlling switches.
3. A JABSCO pump powered by a 12-volt battery and operated by the float switches through a fuse-protected self-latching relay.
4. An intake pipe with a screened orifice.
5. A discharge hose.
6. A GEOTECH 10-port cone-splitting chamber with a sample tube (12.7-mm inside diameter, 0.75-m long) attached to one port.
7. A wind shield protecting the splitting chamber.
8. A 208-L auxiliary collecting vessel and lid with a hole to accommodate the sample tube.
9. A leveling bracket anchored to the auxiliary vessel lid supporting the splitting chamber base in a horizontal position.
10. A 20-L secondary collecting vessel inside the auxiliary vessel.
11. A partially buried gage shelter.

RUNOFF COLLECTION

Each plot is bordered by 100-mm-wide plastic edging buried on edge 50-mm deep to delineate drainage area while avoiding disruption of preexisting flow patterns. Surface runoff from either rainfall or snowmelt is routed by the edging and wing walls through the flume. The flume discharges into the primary collecting vessel in the gage shelter, where heavy sediments, if any, settle out. If volume of flow exceeds 4 L, a rise in the lower float trips one of the two switches required for pump activation.

When flow volume exceeds 16 L, a rise in the top float trips a second switch, closing the self-latching relay and activating the pump. The pump draws from the primary vessel through a screened intake orifice at 0.32 L/s. As the primary vessel is drained, the top-float switch opens, but the relay continues to transfer power to the pump through the self-latching mechanism. When the contents of the primary vessel falls to 4 L, the lower float drops, opens the switch, and stops the pump. The duration of the pump cycle is about 42 seconds, but it may be longer if runoff occurs concomitantly. The cycle repeats each time more than 16 L of runoff accrues in the primary vessel. Pumpage is routed by way of a discharge hose into the splitting chamber which divides flow into equal parts through 10 exit ports. Nine parts are automatically discarded downstream from the plot; the tenth passes through the sample tube into the auxiliary collecting vessel. The first 20 L of sample aliquot are stored within the secondary vessel. Further sample port discharge exceeds the secondary vessel's capacity and is contained by the auxiliary vessel.

FLOW MEASUREMENT

Upon cessation of runoff, aliquots may be in the secondary vessel or in both the secondary and auxiliary vessels, in addition to the part retained by the primary vessel. Runoff volume in the primary vessel is computed from a depth measurement and a depth-volume relation for the vessel. When the secondary vessel does not overfill, its contents also are quantified from a depth measurement and a depth-volume relation. When flow is retained in both the secondary and auxiliary vessels, total contents are measured by (1) removing the secondary vessel from the auxiliary vessel, (2) computing the volume of the aliquot removed with the secondary vessel, (3) computing the aliquot remaining in the auxiliary vessel based on a depth measurement and a depth-volume relation for the auxiliary vessel, and (4) adding the volumes of the two aliquots.

Runoff depth is determined as follows:

$$R = \frac{V_1 + K\,(V_2 + V_3)}{A},$$

where R is runoff depth, in millimeters:

V_1 is the runoff volume in the primary collecting vessel, in liters;

K is a factor expressing the sample port aliquot as a percentage of pumpage;

V_2 is the aliquot retained in the secondary vessel, in liters;

V_3 is the aliquot retained in the auxiliary vessel, in liters;

A is the area of the plot, in square meters.

Peak stage is determined by measuring the maximum height of crushed cork on a stick in the stilling well relative to the flume base. Peak discharge is computed from peak stage by using a published stage-discharge relation for the flume (Kilpatrick and Schneider, 1982, p. 15).

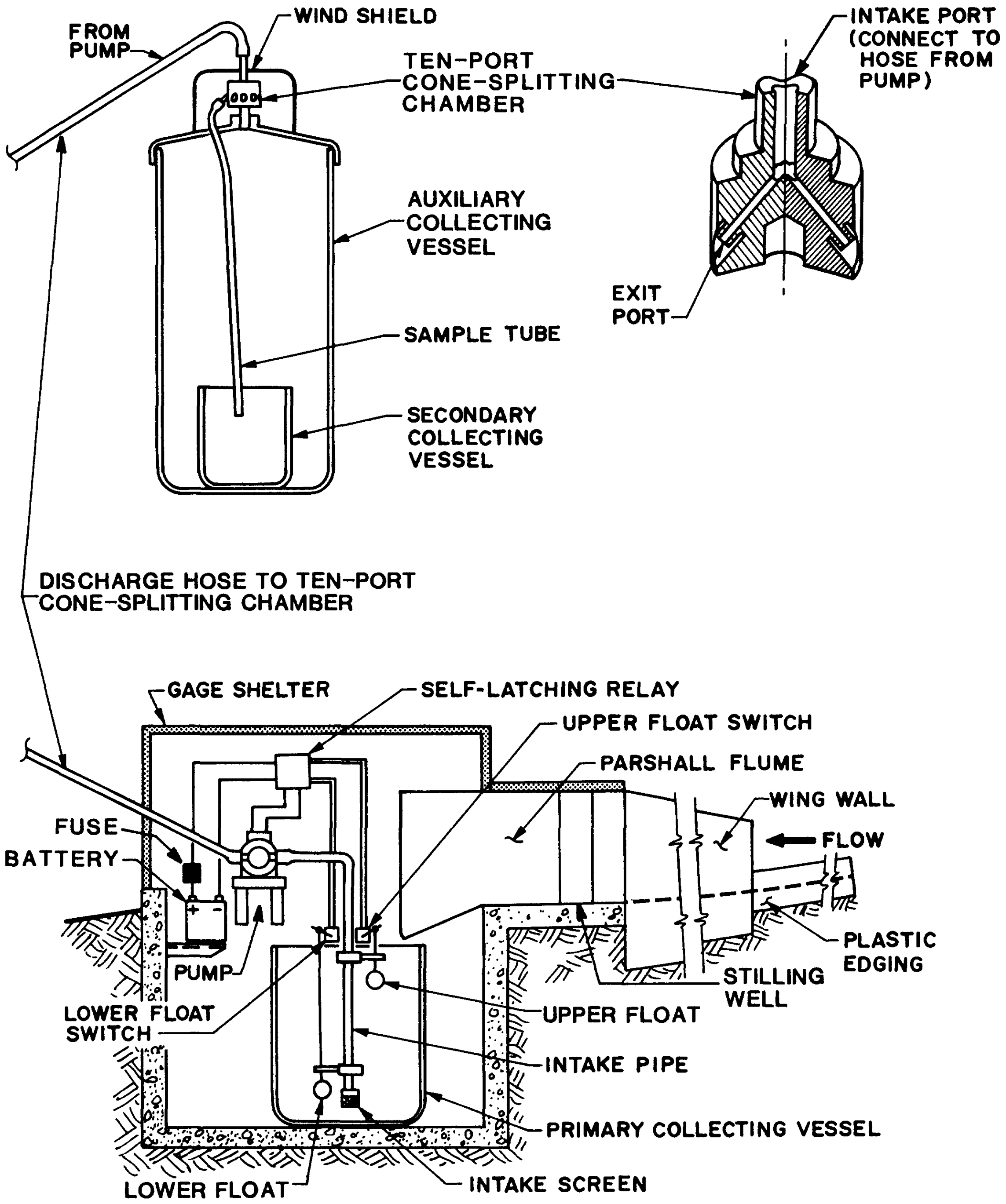


Figure 1. Dekaport divisor system for measuring surface runoff and collecting water-sediment samples from small areas.

Three dekaport divisor systems were tested at the Sheffield site to determine the K factor. After flushing tap water through the system, a known quantity of tap water (approximately 16 L) was added to the primary vessel. The pump then was operated until automatic shutoff occurred. Water remaining in the primary vessel was measured and subtracted from the initial volume to determine pumpage. The contents of the secondary vessel were measured and discarded following each trial. Results of each trial are shown in table 1.

A comparison of K values for each dekaport divisor system was made by calculating a percent error for each trial by the following equation:

$$E_i = \frac{\bar{x} - x_i}{\bar{x}} (100),$$

where E_i is the percent K error for the ith trial in relation to the mean K;

$\bar{x}$ is the mean K for the trials;

x_i is the K for the ith trial.

Excluding the error from the mean of -8.9 percent for

Table 1. Dekaport divisor system calibration tests for determination of K factor

Trial	Dekaport divisor system											
	A				B				C			
	Pumpage, in liters	Sample port aliquot, in liters	K factor, in percent	Percent error[1]	Pumpage, in liters	Sample port aliquot, in liters	K factor, in percent	Percent error[1]	Pumpage, in liters	Sample port aliquot, in liters	K factor, in percent	Percent error[1]
1	12.01	1.20	10.0	−1.9	13.82	1.36	9.8	+1.5	10.59	1.12	10.6	−8.9
2	12.01	1.22	10.2	−4.0	13.74	1.38	10.0	−.5	13.14	1.25	9.5	+2.0
3	12.18	1.21	9.9	−1.3	13.07	1.32	10.1	−.6	11.37	1.08	9.5	+2.0
4	12.50	1.25	10.0	−1.4	12.23	1.28	10.4	−4.2	12.21	1.16	9.5	+2.6
5	13.47	1.32	9.8	+.4	11.47	1.15	10.0	−.3	11.80	1.18	10.0	−3.5
6	12.01	1.19	9.9	−1.1	12.23	1.21	9.9	+1.1	12.04	1.15	9.6	+1.6
7	10.87	1.06	9.8	+.1	12.40	1.26	10.2	−1.6	10.62	1.02	9.6	+1.4
8	11.61	1.12	9.6	+2.1	13.74	1.36	9.9	+1.4	11.84	1.15	9.7	−.1
9	12.57	1.19	9.5	+3.5	11.94	1.17	9.8	+2.6	12.43	1.18	9.5	+2.7
10	12.63	1.20	9.5	+3.6	13.17	1.31	10.0	+.5	11.87	1.15	9.7	+.2
	Mean		9.8		Mean		10.0		Mean		9.7	
	Standard deviation		.24		Standard deviation		.19		Standard deviation		.35	
	Standard error of mean		.08		Standard error of mean		.06		Standard error of mean		.11	

[1] Percent error is calculated from

$$E_i = \frac{\bar{x}-x_i}{\bar{x}} (100),$$

where E_i is the percent K error for the ith trial in relation to the mean K;
$\bar{x}$ is the mean K for the trials; and
x_i is the K for the ith trial.

dekaport C, trial 1, the extreme in errors for all trials are +3.5 and −4.2 percent. A one-way analysis of variance showed no statistical difference between mean K factors computed for each system at the 95-percent confidence level. The mean K value of 9.83, from the 30 trials, is used for flow computations at each dekaport divisor system at the Sheffield site.

Sediment-Sample Collection

A sample of runoff is analyzed to determine sediment concentration and particle-size distribution. Results of concentration analyses are used with runoff depths to compute sediment yields. The particle-size distribution of sediment in runoff is indicative of the size distribution of surficial material and the ability of runoff to transport particles.

Procedures for sample collection depend on runoff volume. If runoff is confined to the primary vessel, a sample is obtained by collecting at least 0.3 L of the primary vessel's contents from a Survey cone splitter (R. F. Middleburg, U.S. Geological Survey, written commun., 1980). If runoff is retained in the secondary vessel or in both the secondary and auxiliary vessels, a single sample is obtained as follows: 10-percent of the primary vessel's contents is collected by passing the total contents through a Survey cone splitter and retaining the discharge from one port, the 10-percent split is combined with the contents of the secondary and auxiliary vessels, and the entire resulting volume is passed through the Survey cone splitter. A minimum split of 10 percent is available from the cone splitter; therefore, total volumes greater than 10 L may have to be split more than once to obtain a maximum 1-L sample.

Sediment yield is computed by the following equation:

$$S = RC\,(10^{-3}),$$

where S is sediment yield in grams per square meter;
R is runoff depth, in millimeters; and
C is sediment concentration, in milligrams per liter.

DISCUSSION AND CONCLUSION

Although the dekaport divisor system was developed in response to a specific problem, the design is readily adaptable for use in other runoff plot studies. For example, higher peak flows may be accommodated by connecting the primary vessel to another vessel by an overflow tube to provide additional storage capacity when discharge rate exceeds pumpage rate. Use of larger pumps, 10-port splitters, and auxiliary collectors would accommodate both greater runoff volumes and peak flows. If retention of more than 10 percent of runoff is desired, discharges from more than one exit port may be collected.

In many cases, knowledge of the temporal variability of runoff is desired. At the Sheffield site, the systems' self-latching relays are used to send signals to a data logger during pumpage, which occurs in response to accumulation of runoff in the primary vessel. Data from a nearby tipping-bucket rain gage then can be used with runoff data to assess rainfall-runoff relations for plots.

Dekaport divisor systems should be serviced following each occurrence of runoff. More than one occurrence can be accommodated by the system if criteria for maximum storage capacity and peak discharge are not exceeded; however, samples collected will represent the combined runoff. Volumes for each occurrence of runoff may be determined if relay operation is recorded.

Freezing temperatures will likely cause a malfunction in one or more subunits of the system. Dekaport divisor systems operated during freezing temperatures must be heated for proper operation.

A complete inspection of the system should be made periodically and should include

1. Checking contents of all vessels;
2. Removing insects and debris from the primary vessel;
3. Inspecting the edging and wing walls for void spaces caused by desiccation or collapse of surficial material;
4. Checking the stick in the flume stilling well for high-water marks;
5. Checking battery voltage;
6. Testing the pump and lubricating it, if necessary, to prevent seizure;
7. Ascertaining that the splitting-chamber base is horizontal; and
8. Inspecting the splitting chamber for obstructions (obstructions in the splitting chamber or in exit ports will likely alter the percentage of pumpage through the sample port).

Three dekaport divisor systems were installed at the site during April and May 1983. From May through October, only one rainstorm (July 30) produced more than 16 L of runoff from any plot. Two systems functioned properly during this storm; the third failed due to pump seizure. Both the effectiveness of pumphead lubricants and the availibility of pumps less prone to seizure are being reviewed.

Primary collecting vessels accumulate insects and animals, including mice, salamanders, and snakes. Coarse mesh screens have been fastened to flume outfall sections to reduce the accumulation of debris not associated with runoff.

Preliminary runoff and sediment-transport data indicate that yields from plots on trench covers are consistently lower than yields from larger (1.1-1.3 ha) surrounding gaged areas. The data also suggest that runoff from trench covers is less dependent on slope than on other factors, such as antecedent soil moisture conditions or the mechanical properties of the underlying soils. Data from plots with different slopes on a nearby undisturbed area show a more positive relation between slope and yields.

The dekaport divisor system was developed through trial and error for use on plots on and near trench covers at a low-level radioactive waste disposal site in Illinois. Experience indicates that, if designed, installed, and serviced properly, dekaport divisor systems should provide reliable runoff and sediment-transport data from small areas.

REFERENCES CITED

Chow, V. T., ed., 1964, Handbook of applied hydrology: New York, McGraw-Hill, 1,418 p.

Heim, G. E., and Machalinski, M. V., 1980, Characterization of existing surface conditions at Sheffield low-level waste disposal facility: U.S. Nuclear Regulatory Commission, NUREG/CR-2101, 177 p.

Hewlett, J. D., 1979, Forest water quality—An experiment in harvesting and regenerating Piedmont forest: Athens, University of Georgia, School of Forest Research, 22 p.

Illinois State Water Survey, 1970, Rainfall frequencies: Illinois State Water Survey Technical Letter 13, 5 p.

Kilpatrick, F. A., and Schneider, V. R., 1982, Use of flumes in metering discharge at gaging stations: U.S. Geological Survey Techniques of Water-Resources Investigations, Book 3, Chapter A14, 46 p.

Mutchler, C. K., 1963, Runoff plot design and installation for soil erosion studies: U.S. Department of Agriculture, ARS-41-79, 26 p.

Rantz, S. E., and others, 1982, Measurement and computation of streamflow: U.S. Geological Survey Water-Supply Paper 2175, v. 1 and 2, 630 p.

U.S. Department of Agriculture, Science and Education Administration, 1979, Field manual for research in agricultural hydrology: Agricultural Handbook, no. 224, p. 239-394.

GEOCHEMICAL STUDIES OF ORGANIC CARBON ASSOCIATED WITH VOLCANIC ASH FROM MOUNT ST. HELENS, WASHINGTON

By Wilfred E. Pereira *and* Colleen E. Rostad

Abstract

A volcanic ash sample obtained after the May 18, 1980, eruption of Mount St. Helens was found to contain significant amounts of organic carbon. Characterization of organic carbon using gas chromatography-mass spectrometry indicated the presence of several classes of compounds, including alkanes, hydroaromatic and aromatic hydrocarbons, fatty acids, aromatic acids, aldehydes, phenols, chlorinated aromatics, and tricyclic diterpenoids. The most probable source of these compounds is volatilization of plant and soil organic matter during the eruption, followed by sorption and transport on ash particulates. Evidence indicates that aromatic hydrocarbons are not products of pyrolysis of organic materials. Tricyclic diterpenoid compounds probably are precursors, intermediates, and end products in the diagenesis of abietic acid to retene in forest soils. A diagenetic scheme for conversion of abietic acid to retene is presented.

INTRODUCTION

Mount St. Helens, a 40,000-year-old volcano in southern Washington, erupted violently on May 18, 1980 (Mullineaux and Crandell, 1981). The volcano's last previous activity was in 1857, and, in 1975, Crandall and others (1975) predicted it would erupt before 2000.

Following several minor ash and gas eruptions, a hot lateral blast completely destroyed vegetation up to approximately 20 km north of the volcano. During the eruption, vast quantities of ash from the volcano were injected into the stratosphere. Although significant quantities of ash fell back to earth in the vicinity of the blast zone, prevailing winds transported the remainder of the ash eastward, resulting in ash deposition over large areas of Washington, Montana, and Idaho (fig. 1). Forests, vegetation, and soils in the immediate vicinity of the volcano were charred and pyrolyzed from the intense heat. Large areas of vegetation were buried under hot mudflows from melting glacial ice and snow, resulting in the in situ steam distillation of organic compounds derived from such wood constituents as lignins and tannins. The concentration of dissolved organic carbon (DOC) in surface waters near the volcano increased significantly as a result of destruction of the surrounding conifer forests (McKnight and others, 1982).

Initial studies of the ash were directed towards determination of its mineralogy and inorganic chemical composition (Hooper and others, 1980; Fruchter and others, 1980; and Taylor and Lichte, 1980). Column-leaching experiments in the U.S. Geological Survey's research laboratories indicated that aqueous leachates of volcanic ash contained significant concentrations of DOC–130 $\mu g/g$ (Taylor and Lichte, 1980). A preliminary investigation of the organic compounds associated with the ash revealed the presence of several classes of organic compounds (Pereira and others, 1980, 1982). It was presumed that large quantities of organic materials, derived from the surrounding vegetation and soils, pyrolyzed and vaporized during the eruption, and condensed on particulates in the ash cloud. Many of the organic compounds associated with the ash were readily leached by precipitation and found in surface waters near the volcano for at least two summers following the eruption (McKnight and others, 1982).

Ash samples collected at locations in Washington, Montana, and Idaho (fig. 1) all contained significant quantities of organic carbon (table 1). It was decided that a definitive chemical investigation of organic carbon in the ash should be conducted to determine its significance. A volcanic-ash sample collected near Richland, Washington, was chosen for analysis based on timeliness of sample collection, low probability of contamination, and availability of sufficient quantities. This report describes the investigation to determine the origin, chemical characterization, and geochemical significance of organic carbon associated with volcanic ash at Richland, Washington.

ACKNOWLEDGMENTS

The authors wish to acknowledge the gift of samples of retene, dehydroabietin, and dehydroabietic acid from Lawrence Lafleur, National Council of the Paper Industry for Air and Stream Improvement, Inc., Corvallis, Oregon. We wish to express our thanks to Georgia R. Mason (U.S. Geological Survey) for determining the organic-carbon content in ash samples.

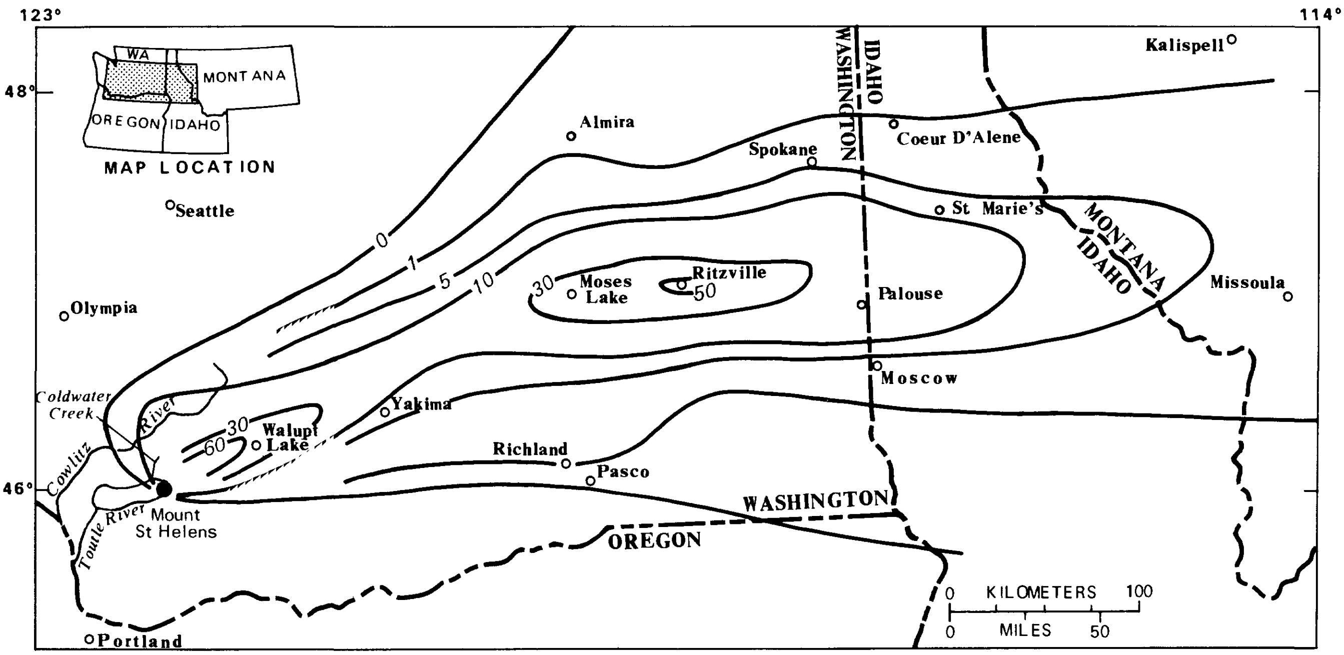


Figure 1. Thickness of ash deposited from the May 18, 1980, eruption of Mount St. Helens, shown by lines of equal uncompacted thickness, in millimeters. (Modified from Sarna-Wojcicki and others, 1980.)

Table 1. Organic carbon in volcanic ash from Mount St. Helens

Location	Organic carbon, in percent by weight
St. Maries, Idaho	0.05
Moscow, Idaho	.06
Palouse, Washington	.06
Ritzville, Washington	.07
Spokane, Washington	.07
Randle Ranger district, Washington	.10
Richland, Washington	.13
Richland, Washington	.14
Randle Ranger district, Washington	.14
Moses Lake, Washington	.14
Kalispell, Montana	.14
Coeur D'Alene, Idaho	.16
Missoula, Montana	.19
Almira, Washington	.22

METHODS

Sample Collection

A volcanic-ash sample was collected by Todd Hinkley (U.S. Geological Survey) at a site near Richland, Washington (fig. 1), on May 18, 1980. The site was approximately 225 km from the eruption zone. The sample was collected by sweeping ash into a sample container from such exposed metal surfaces as picnic tables where the probability of contamination was minimal.

Sample Preparation

A 20-g sample of the ash was extracted with benzene-methanol (2:1) in a Soxhlet apparatus for 20 hours. The extract was concentrated in a Kuderna-Danish apparatus to a volume of 4 mL. One milliliter of the concentrated extract was further concentrated in a stream of dry nitrogen (N_2) to a volume of 0.5 mL, then fractionated in a column containing 3 g of activated silica gel, to obtain an alkane fraction that eluted from the column in the first 10 mL of hexane. No further fractionation was done using silica gel. The hexane fraction was concentrated by evaporation in a stream of dry N_2 to a volume of approximately 100 μL. After addition of a solution of d_{10}-biphenyl as internal standard, the hexane fraction was analyzed for alkanes by gas chromatography-mass spectrometry (gc-ms). The remaining 3 mL of the concentrated extract was evaporated to dryness in a stream of dry N_2. The residue was methylated with an ether solution of diazomethane and evaporated in a stream of dry N_2 to a volume of approximately 100 μL. Following addition of a solution of d_{10}-biphenyl as internal standard, the methylated extract was analyzed by gc-ms.

A modified procedure was used for isolation of diterpenoid-resin acids and aromatic hydrocarbons. A 50-g sample of ash was extracted with a benzene-methanol mixture (2:1) in a Soxhlet apparatus for 24 hours. The extract was concentrated in a Kuderna-Danish apparatus to a volume of 1 mL; 0.5 mL of the concentrated extract was evaporated under a stream of dry N_2 to a volume of 0.1 mL and fractionated on a micro column containing 3 g of activated silica gel. The column was prewashed with two bed-volumes of hexane. Five fractions were collected with the following eluants: (1) 10 mL hexane, (2) 10 mL benzene, (3) 10 mL methylene chloride, (4) 10 mL methylene chloride-methanol (1:1), and (5) 10 mL methanol. Each fraction was evaporated in a stream of dry N_2 to a volume of approximately 100 μL. Fraction 1 containing the aliphatic hydrocarbons, fraction 2 containing the aromatic hydrocarbons, and fraction 4 containing the diterpenoid-resin acids were analyzed by capillary gc-ms. Diterpenoid-resin acids were esterified with diazomethane in ether-methanol solution prior to gc-ms analysis.

Instrumental Analysis

Instrumental analyses were performed on a Finnigan OWA 20 capillary-gas chromatography, mass-spectrometry system. The gc was equipped with a wall-coated open tubular fused-silica capillary column 30 m long by 0.26 mm inside diameter, coated with SE-54 or DB-5 (J & W Scientific). The linear velocity of helium (He) through the column was 29 cm/s; injections were made using the splitless-injection technique. The gc oven was held at 50°C for 4 minutes and programmed to increase at a rate of 6°C/min to a maximum of 300°C. One microliter of each sample extract was injected at 50°C. The vent valve was automatically opened at 45 seconds, and the filament and multiplier were automatically turned on at 240 seconds. Data acquisition began simultaneously with injection of the sample. The mass spectrometer was operated in the electron-impact mode using an ionizing voltage of 70 eV (electron-volts) and an ionization current of 250 μA (microamps). The instrument was scanned repetitively from 40 to 450 amu (atomic mass units) every 0.9 second.

RESULTS AND DISCUSSION

To study the nature of organic carbon associated with the ash, it was necessary to isolate and characterize the organic compounds using gc-ms. A mass chromatogram (mass charge 57) characteristic of alkanes is shown in figure 2. The chromatogram contains alkanes (n-C_{15} — n-C_{29}) with a pronounced odd-even predominance between C_{19} and C_{29}, indicating that these compounds were derived from higher plants (Giger and Schaffner, 1975). The chromatogram is unimodal, maximizing at n-C_{25}, indicating a single source for these compounds.

A reconstructed ion chromatogram of a methylated extract of volcanic ash is shown in figure 3. Organic compounds identified are listed by general class type in table 2, with their retention times, using d_{10}-biphenyl as the internal standard. Data in table 2 indicate the presence of several polycyclic aromatic hydrocarbons, notably alkylated phenanthrene derivatives. These compounds probably are derived from plant materials (Youngblood and Blumer, 1975). Other classes of compounds identified include fatty acids, dicarboxylic acids, phenolic acids, and aromatic aldehydes. Many of these compounds are derived from plant and soil organic matter (Schnitzer, 1978). Of special significance is the presence of the tricyclic diterpenoid-resin acid, methyldehydroabietate (compound VII, 12); the corresponding aldehyde, dehydroabietal (compound VIII, 5); and alcohol, dehydroabietol (compound III, 4). The presence of diterpene-resin compounds associated with

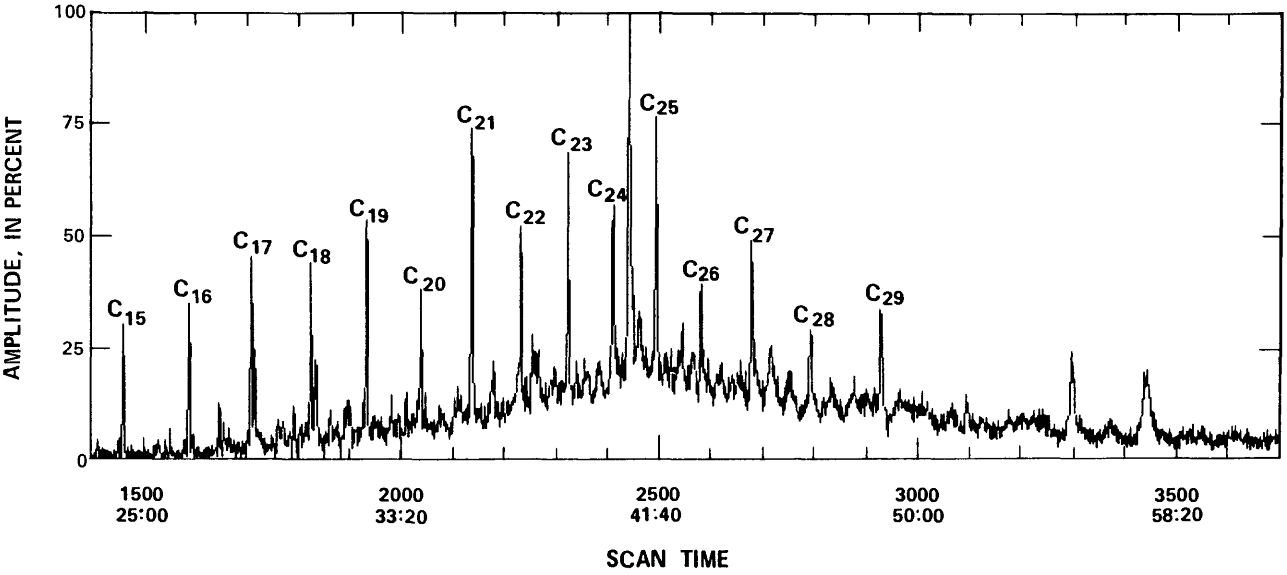


Figure 2. Mass chromatogram (mass charge 57) characteristic of alkanes in volcanic ash from Richland, Washington.

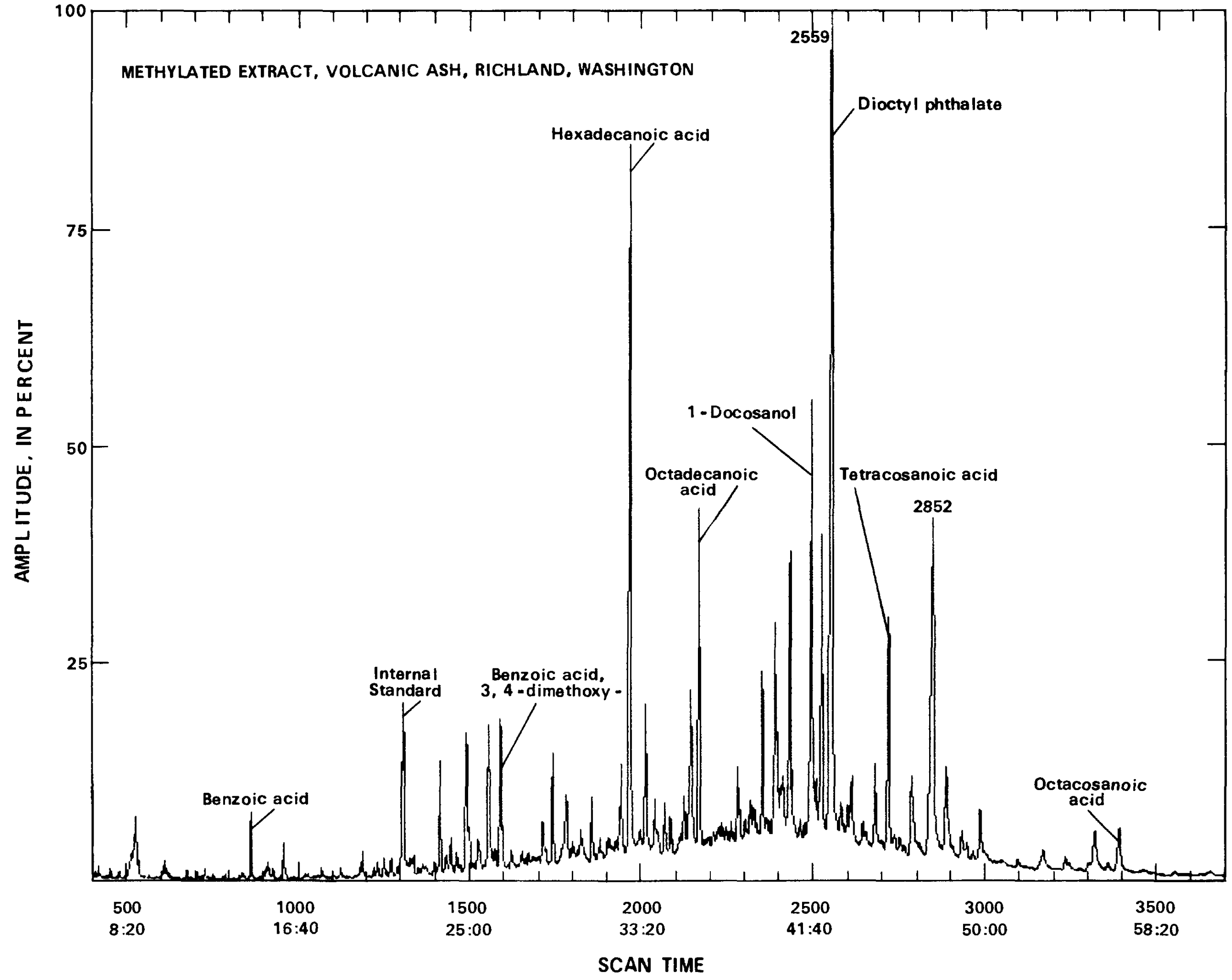


Figure 3. Reconstructed ion chromatogram (RIC) of a methylated extract of volcanic ash from Richland, Washington.

the ash indicates a source from higher terrigenous plants (Simoneit, 1977). These compounds probably are derived from coniferous species such as Douglas fir, which is the major tree species of the surrounding forests.

Several chlorinated species also were identified in the ash, including chlorinated derivatives of benzoic acid and three pentachlorobiphenyl isomers. These compounds could have been formed by pyrolysis of plant and soil organic matter, in the presence of inorganic chloride salts. Commercial polychlorinated biphenyl (PCB) formulations are known to contain complex mixtures of isomers of chlorinated biphenyl. The presence of only three pentachlorobiphenyl isomers indicates that these compounds could have been preferentially synthesized by a combustion process. However, the possibility of atmospheric contamination of the ash sample by PCB cannot be ruled out. Differential weathering and immobilization of the various PCB congeners appear to favor survival and propagation of pentachlorobiphenyl isomers (Fink, 1983). The chlorinated benzoic-acid isomers detected in the ash probably are biodegradation products of lesser chlorinated PCB's (Shiaris and Sayler, 1982).

Based on the evidence presented so far, the data indicate that organic compounds sorbed to the ash particulates probably originated from plant and soil organic matter. Having determined the origin and chemical nature of the organic carbon, it only remained to determine its geochemical significance. For this purpose, we focused our attention on two classes of compounds: cyclic terpenoids and hydroaromatic and aromatic hydrocarbons (Pereira and Rostad, 1983). These compounds were isolated by the modified procedure described in the sample-preparation scheme in the experimental section and analyzed by gc-ms. The compounds identified are listed in table 3, along with the gc-ms and retention index data. Structural formulas of these compounds are shown in figure 4. With the exception of the sesquiterpenoid cadalene (I), all other compounds listed in table 3 are cyclic diterpenoids or hydroaromatic and

Table 2. Organic compounds identified in volcanic ash from Richland, Washington

Compound	Relative retention time (RRT)
I. Alkanes:	
1. Pentadecane[1]	1.12
2. Hexadecane[1]	1.22
3. Heptadecane[1]	1.31
4. Octadecane[1]	1.40
5. Nonadecane[1]	1.48
6. Eicosane[1]	1.56
7. Heneicosane	1.63
8. Docosane[1]	1.71
9. Tricosane	1.78
10. Tetracosane[1]	1.84
11. Pentacosane	1.91
12. Hexacosane	1.97
13. Heptacosane	2.05
14. Octacosane[1]	2.13
15. Nanocosane	2.24
II. Aromatic and Polycyclic Aromatic Hydrocarbons:	
1. Benzene, 1-ethenyl-3, 5-dimethyl-	1.15
2. Naphthalene, 1,6-dimethyl-4-(1-methylethyl)-	1.30
3. Phenanthrene, methyl isomer	1.52
4. Naphthalene, 1-phenyl-	1.56
5. Phenanthrene, dimethyl isomer	1.62
6. Phenanthrene, trimethyl isomer	1.70
7. Phenanthrene, tetramethyl isomer	1.74
III. Alcohols:	
1. 2-Propanol, 1,3-dimethoxy-	0.37
2. 1,2-Propanediol, 3-methoxy-	.41
3. 3-Piperidinol, 1-ethyl-6-methyl-	.73
4. 1-Phenanthrenemethanol, 1,2,3,4,4a, 9,10,10a-octahydro-1,4a-dimethyl-7-(1-methylethyl)-	1.85
5. 1-Docosanol	1.91
IV. Fatty Acids:	
1. Pentanoicacid, 4-oxo-, methylester	.52
2. Octanoicacid, methylester[1]	.70
3. Nonanoicacid, methylester	.82
4. Decanoicacid, methylester[1]	.93
5. Undecanoicacid, methylester	1.04
6. Dodecanoicacid, methylester[1]	1.14
7. Tridecanoicacid, methylester[1]	1.24
8. Tetradecanoicacid, methylester[1]	1.33
9. Pentadecanoicacid, methylester[1]	1.42
10. Hexadecanoicacid, methylester[1]	1.51
11. Heptadecanoicacid, methylester[1]	1.58
12. 9-Octadecanoicacid, methylester	1.64
13. Octadecanoicacid, methylester[1]	1.66
14. Nonadecanoicacid, methylester[1]	1.73
15. Eicosanoicacid, methylester[1]	1.80
16. Heneicosanoic, methylester[1]	1.87
17. Docosanoicacid, methylester[1]	1.93
18. Tricosanoicacid, methylester[1]	2.00
19. Tetracosanoicacid, methylester	2.08
20. Hexacosanoicacid, methylester	2.28
21. Octacosanoicacid, methylester	2.59
V. Dicarboxylic Acids:	
1. Butanedioicacid, dimethylester[1]	.58
2. Hexanedioicacid, dimethylester[1]	.84
3. Octanedioicacid, dimethylester[1]	1.07
4. Nonanedioicacid, dimethylester[1]	1.17
VI. Ketones:	
1. 1H-Indene-1-one, 2,3-dihydro	.89
2. 1-Propanone, 1-phenyl	.97
3. Ethanone, 1-(4-methoxyphenyl)-	.97
4. 2,5-Cyclohexadiene-1,4-dione, 2,6-bis (1,1-dimethylethyl)-	1.10
5. 1H-Indene-1-one, 2,3-dihydro, 3,4, 7-trimethyl	1.18
6. Ethanone, 1-(3,4-dimethoxyphenyl)-	1.19
7. 1-Propanone, 1-(2,4-dimethoxyphenyl)-	1.28
8. 9H-Fluoren-9-one	1.36
9. 2-Heptadecanone[1]	1.48
VII. Aromatic Acids:	
1. Benzoicacid, methylester[1]	.66
2. Benzeneaceticacid, methylester[1]	.77
3. Benzoicacid, 2-hydroxy-, methylester	.79
4. Benzoicacid, 3-methyl-, methylester[1]	.80
5. Benzoicacid, 4-methyl-, methylester[1]	.81
6. Benzoicacid, methoxy-, methylester isomer	.96
7. Benzoicacid, methoxy-, methylester isomer	1.00
8. Benzoicacid, 3,4-dimethoxy-, methylester	1.22
9. 2-Naphthalenecarboxylicacid, methylester[1]	1.27
10. 2-Propenoicacid, 3-(3,4-dimethoxyphenyl)-, methylester	1.47
11. 1-Phenanthrenecarboxylicacid, 1,2,3,4,4a, 5,6,7,8,9,10,10a-dodecahydro-1,4a,-dimethyl-7-(1-methylethyl)-, methylester	1.81
12. 1-Phenanthrenecarboxylicacid, 1,2, 3,4,4a,9,10,10a-octahydro-1,4a-, dimethyl-7-(1-methylethyl)-, methylester	1.83
VIII. Aldehydes and Phenols:	
1. Benzaldehyde, 4-methoxy-	.86
2. Benzene, (trimethoxymethyl)-	.99
3. Benzaldehyde, 4-hydroxy-3-methoxy-	1.14
4. Benzaldehyde, 3,4-dimethoxy-	1.19

Table 2. Organic compounds identified in volcanic ash from Richland, Washington—Continued

Compound	Relative retention time (RRT)
5. 1-Phenanthrenecarboxaldehyde, 1,2, 3,4,4a,9,10,10a-octahydro-1,4a-, dimethyl-7-(1-methylethyl)-, methylester	1.78
IX. Chlorinated Aromatics:	
1. Benzoicacid, chloro-, methylester isomer	0.86
2. Benzoicacid, chloro-, methylester isomer	.88
3. Benzoicacid, 3,4-dichloro, methylester	1.03
4. Pentachlorobiphenyl isomer	1.67
5. Pentachlorobiphenyl isomer	1.73
6. Pentachlorobiphenyl isomer	1.76

[1] Identity confirmed by comparison of electron impact spectra and relative retention time with authentic standards.

aromatic hydrocarbons. Diterpenoids and sesquiterpenoids are important constituents of higher plant resins (Simonsen and Barton, 1961). Because their chemical structure can be correlated by way of a set of diagenetic changes to their source, these compounds are potential biological molecular markers (Simoneit, 1977; Simoneit and Mazurek, 1982).

Hydroaromatic and Aromatic Hydrocarbons

If forests, vegetation, and soils were pyrolyzed in the eruption zone, pyrolysis products, such as complex assemblages of polycyclic aromatic hydrocarbons (PAH's) characteristic of combustion processes (Lee and others, 1976; Laflamme and Hites, 1978), should be found sorbed to the ash particulates. Instead of complex assemblages of PAH's, only hydroaromatic and aromatic hydrocarbons listed in table 3 were identified. Three sets of information indicated these compounds were not products of combustion of organic matter: (1) combustion of organic materials results in a complex mixture of PAH's dominated by the unsubstituted species (Lee and others, 1977; Wakeham and others, 1980), lack of a complex assemblage of PAH's in the ash indicates that these compounds are not products of combustion of organic matter, (2) combustion of organic matter produces 4H-cyclopenta[def]phenanthrene (Lee and others, 1977; Wakeham and others, 1980), the ash did not contain this compound, and (3) incomplete combustion of organic materials containing nitrogen results in generation of azaarenes (Dong and

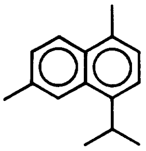
Table 3. Terpenoids and hydroaromatic and aromatic hydrocarbons associated with volcanic ash from Mount St. Helens
[ms, Mass spectrometry; RI, retention index]

Compound	Structure (fig. 4)	Molecular weight	Molecular formula	Retention index (sample)	Retention index (literature)[1]	Method of identification
Hydrocarbons:						
Cadalene	I	198	$C_{15}H_{18}$	1690	1689	ms,RI
Phenanthrene	II	178	$C_{14}H_{10}$	1792	1794	ms,RI[2]
Tetrahydroretene	III	238	$C_{18}H_{22}$	1871	-	ms
1-Methyl-phenanthrene	IV	192	$C_{15}H_{12}$	1942	1944	ms,RI[2]
Dehydroabietin	V	256	$C_{19}H_{28}$	2042	2040	ms,RI[2]
C_2-Phenanthrene	VI	206	$C_{16}H_{14}$	2066	-	ms
Dehydroabietane	VII	270	$C_{20}H_{30}$	2082	2078	ms,RI
Simonellite	VIII	252	$C_{19}H_{24}$	2156	2154	ms,RI
Retene	IX	234	$C_{18}H_{18}$	2245	2241	ms,RI[2]
Acids[3]:						
8-Abieten-18-oic acid	X	304	$C_{20}H_{32}O_2$	2022	-	ms
13-Isopropyl-5 α (H)-podocarpa-6,8,11,13-tetraen-16-oic acid	XI	298	$C_{20}H_{26}O_2$	2034	2027	ms,RI
Dehydroabietic acid	XII	300	$C_{20}H_{28}O_2$	2042	2036	ms,RI[2]
Aldehydes:						
Dehydroabietal	XIII	284	$C_{20}H_{28}O$	2320	-	ms
Alcohols:						
Dehydroabietol	XIV	286	$C_{20}H_{30}O$	2387	-	ms

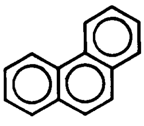
[1] Simoneit and Mazurek (1982).

[2] Retention index and mass spectrum confirmed with authentic standard.

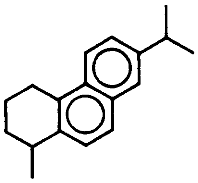
[3] Analyzed as the methyl esters (retention index versus alkanoic acid methyl esters).



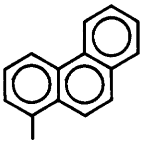
I. Cadalene, $C_{15}H_{18}$



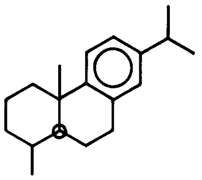
II. Phenanthrene, $C_{14}H_{10}$



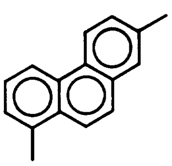
III. 1,2,3,4-tetrahydroretene, $C_{18}H_{22}$



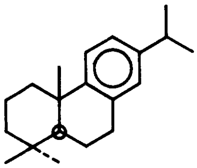
IV. 1-methylphenanthrene, $C_{15}H_{12}$



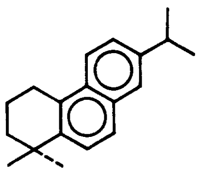
V. Dehydroabietin, $C_{19}H_{28}$



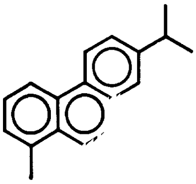
VI. Pimanthrene, $C_{16}H_{14}$



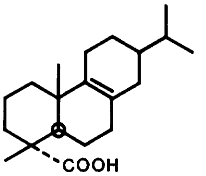
VII. Dehydroabietane, $C_{20}H_{30}$



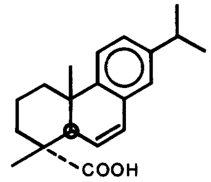
VIII. Simonellite, $C_{19}H_{24}$



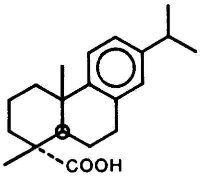
IX. Retene, $C_{18}H_{18}$



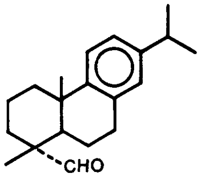
X. 8-abieten-18-oic acid, $C_{20}H_{32}O_2$



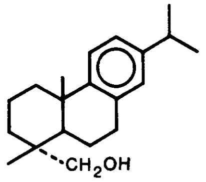
XI. 13-isopropyl-5α(H)-podocarpa-6,8,11,13-tetraen-16-oic acid, $C_{20}H_{26}O_2$



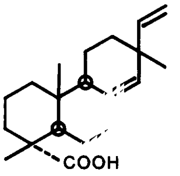
XII. Dehydroabietic acid, $C_{20}H_{28}O_2$



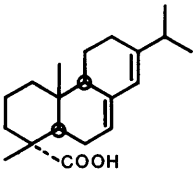
XIII. Dehydroabietal, $C_{20}H_{28}O$



XIV. Dehydroabietol, $C_{20}H_{30}O$



XV. Pimaric acid, $C_{20}H_{30}O_2$



XVI. Abietic acid, $C_{20}H_{30}O_2$

Figure 4. Structural formulas of terpenoids and hydroaromatic and aromatic compounds associated with volcanic ash from Mount St. Helens.

others, 1977), which were not detected in the ash sample providing further evidence against a combustion process. The evidence presented thus far indicates that thermal energy, generated during the eruption of Mount St. Helens, volatilized these compounds from forest soils but was insufficient for formation of a complex mixture of PAH's by pyrolysis of organic materials.

Three other compounds, cadalene (I), retene (IX), and dimethyl-phenanthrene, probably 1,7-dimethylphenanthrene or pimanthrene (VI), were identified in the ash. These compounds are diagenetic end-products of biogenic precursors. Cadalene probably is derived from isomers of cadinene or cadinol, which are constituents of essential oils of higher plants (Simonsen and Barton, 1961; Simoneit and Mazurek, 1982). Retene probably results from diagenetic aromatization of abietic acid (Simoneit, 1977; Laflamme and Hites, 1978; White and Lee, 1980), a diterpene resin acid found in conifer resins (Stonecipher and Turner, 1970). Retene has been reported in fossilized pine, pine-forest soils (Laflamme and Hites, 1978), and in aerosols sampled in the vicinity of conifer vegetation (Simoneit and Mazurek, 1982). Pimanthrene probably is derived by progressive aromatization of the resin acid, pimaric acid (XV) (Simoneit and Mazurek, 1982; Wakeham and others, 1980).

Several other possible intermediates in the diagenetic pathway of abietic acid also were identified, including simonellite (VIII), dehydroabietane (VII), dehydroabietin (V), and 1,2,3,4-tetrahydroretene (III). These compounds have been reported in a variety of environmental samples, including soils, sediments, coal extracts, and atmospheric aerosols (Simoneit, 1977; Simoneit and Mazurek, 1982; Laflamme and Hites, 1978; White and Lee, 1980; Wakeham and others, 1980; Swan, 1965).

Oxygenated Diterpenoids

Several oxygenated tricyclic diterpenoids also were identified in the ash. Dehydroabietic acid (XII) is a resin acid that occurs in coniferous wood species (Mahood and Rogers, 1975), conifer resin, and other higher plant resins and supportive tissue (Simoneit, 1977). It is a dehydrogenated product of abietic acid (XVI), a biogenic precursor of retene.

13-Isopropyl-5, a (H)-podocarpa-6,8,11,13-tetraen-16-oic acid (XI), also was identified in the ash. This compound has been reported in aerosols of the Western United States (Simoneit and Mazurek, 1982) and is a dehydrogenated product of dehydroabietic acid. Two other oxygenated species, dehydroabietal (XIII) and dehydroabietol (XIV), also were identified. The aldehyde dehydroabietal has been reported in Yosemite soil (Laflamme and Hites, 1978), and the corresponding alcohol dehydroabietol has been reported in effluents of mechanical pulping and debarking operations (Leach and others, 1977). Both compounds probably are reduction products of dehydroabietic acid.

Based on this suite of tricyclic diterpenoid compounds in the ash, including the biogenic precursor dehydroabietic acid, the diagenetic end-product retene, and several intermediates, sufficient geochemical evidence exists to link these compounds in the proposed diagenetic pathway outlined in figure 5. This pathway incorporates diagenetic pathways proposed by other workers (Simoneit and Mazurek, 1982; Laflamme and Hites, 1978; and Wakeham and others, 1980) for the conversion of abietic acid to retene.

Simonellite Pathway

This pathway involves successive reduction of dehydroabietic acid, by way of dehydroabietal, dehydroabietol, dehydroabietane, and simonellite to retene. These reactions probably occur under reducing conditions in forest soils.

Tetrahydroretene Pathway

This reaction pathway involves successive dehydrogenation and aromatization of abietic acid, by way of dehydroabietic acid, to 13-isopropyl-5μ (H) podocarpa-6,8,11,13-tetraen-16-oic-acid. Decarboxylation of this acid yields 1,2,3,4-tetrahydroretene, which can be dehydrogenated to yield retene. These reactions probably occur in aerobic zones of forest soils.

Dehydroabietin Pathway

These reactions involve decarboxylation of dehydroabietic acid to yield dehydroabietin, which undergoes successive dehydrogenations to yield retene, by way of 1,2,3,4-tetrahydroretene. These reactions also probably take place in aerobic zones of forest soils.

By far, the major components identified were dehydroabietic acid and retene with only trace quantities of the various intermediates. It is possible that many of these reactions are microbially mediated, probably taking place in microenvironments in the soil regardless of the redox conditions of the soil.

CONCLUSIONS

Results of this study demonstrated that the volcanic eruption of Mount St. Helens volatilized large quantities

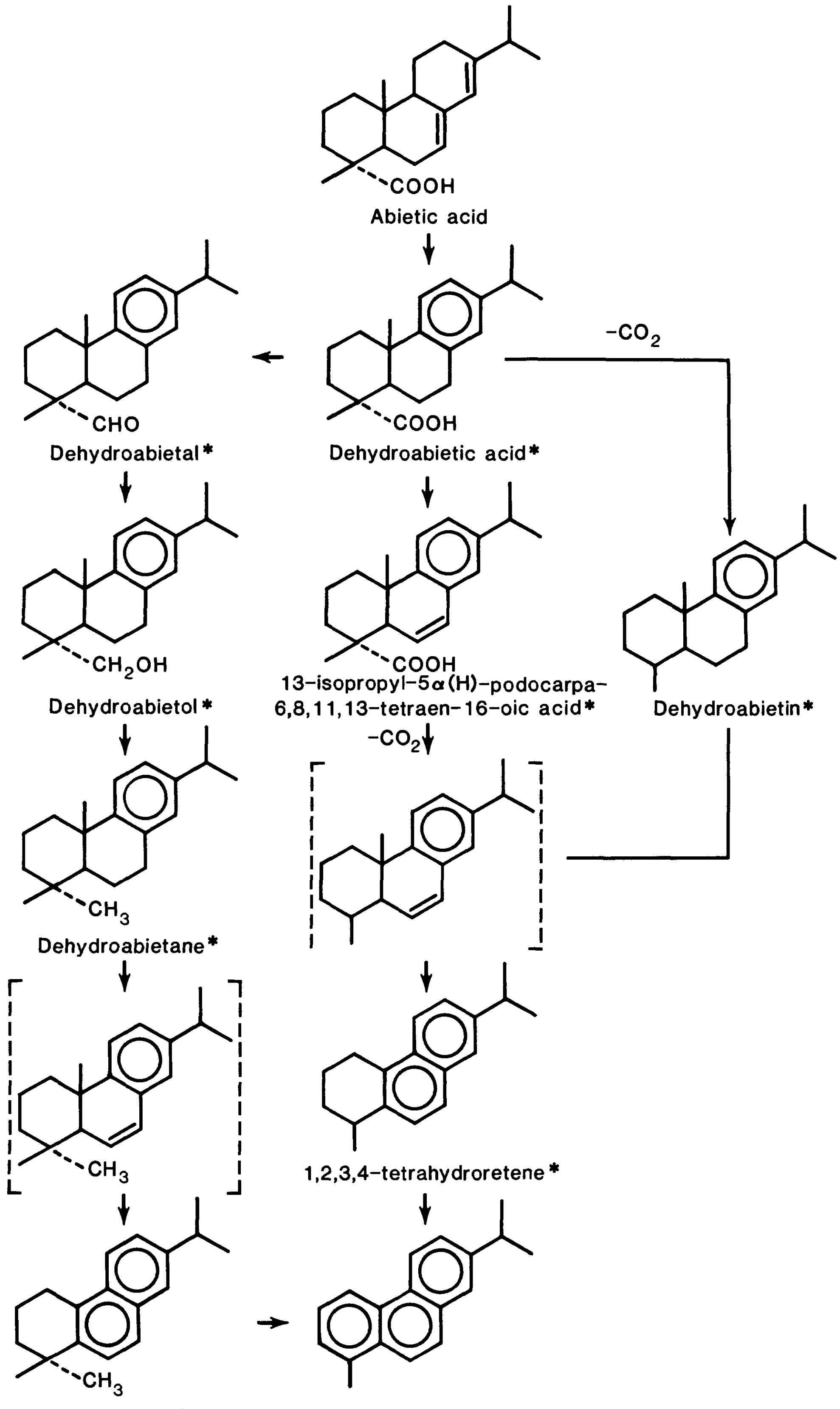


Figure 3. Proposed diagenetic pathway for conversion of abietic acid to retene. (Compounds enclosed in brackets are suggested intermediates; compounds with asterisks were identified in volcanic ash.)

of organic compounds from surrounding vegetation and soils. These volatile organic compounds condensed on ash particulates and were transported to areas remote from the eruption zone. A secondary source of these compounds probably was from atmospheric aerosols present in the vicinity of surrounding coniferous forests within the blast zone. Lack of complex assemblages of PAH's on ash particulates indicated that hydroaromatic and aromatic compounds identified were not of pyrogenic origin. Tricyclic diterpenoid compounds are important biological molecular markers; their presence in volcanic ash indicated that they are of biogenic origin. It is interesting to note that volcanic ash obtained after the eruption of El Chichon, Mexico, did not contain detectable quantities of PAH's or tricyclic diterpenoids (Garbarino, 1983). Absence of these compounds may be explained in terms of differences in vegetation and forest soils in the vicinity of El Chichon.

The May 18, 1980, eruption of Mount St. Helens provided a unique opportunity to study the geochemical diagenesis of abietic acid to retene in forest soils. Volatilization and sorption of these tricyclic diterpenoid compounds on volcanic ash is analogous to stop-action photograph, permitting the isolation of precursors, intermediates, and end-products of the reaction from a complex soil matrix, thereby allowing them to be studied in a matrix virtually free from interferences. Although the amount of organic material associated with volcanic ash may not be quantitatively significant in the global carbon budget, specific molecular-marker compounds, such as tricyclic diterpenoids, are useful as indicators of sources and important geochemical processes.

REFERENCES CITED

Crandell, D. R., Mullineaux, D. R., and Rubin, Meyer, 1975, Mount St. Helens volcano—Recent and future behavior: Science, v. 187, p. 438–441.

Dong, M. W., Locke, D. C., and Hoffmann, Dietrich, 1977, Characterization of azaarenes in the basic portion of suspended particulate matter: Environmental Science and Technology, v. 11, p. 612–618.

Fink, L. E., 1983, Comment on characterization of organic contaminants in environmental samples associated with Mount St. Helens 1980 volcanic eruption: Environmental Science and Technology, v. 17, p. 311–312.

Fruchter, J. S., Robertson, D. E., Evans, J. C., Olsen, K. B., Lepel, E. A., Laul, J. C., Abel, K. H., Sanders, R. W., Jackson, P. O., Wogman, N. S., Perkins, R. W, Van Tuyl, H. H., Beauchamp, R. H., Shade, J. W., Daniel, J. L., Erickson, R. L., Sehmel, G. A., Lee, R. N., Robinson, A. V., Moss, O. R., Briant, J. K., and Cannon, W. C., 1980, Mount St. Helens ash from the 18 May 1980 eruption: Chemical, physical, mineralogical, and biological properties: Science, v. 209, p. 1116–1125.

Garbarino, J. R., 1983, Comparative study of the organic and inorganic composition of El Chichon and Mount St. Helens ashes: Rocky Mountain Conference, 25th, Denver 1983, Proceedings, p. 62.

Giger, W., and Schaffner, C., 1975, Aliphatic, olefinic and aromatic hydrocarbons in recent sediments of a highly eutrophic lake, *in* Advances in organic geochemistry: International Meeting on Organic Geochemistry, 7th, Madrid, Spain, 1975, Proceedings, Empresa Nacional Adaro De Investigaciones, S.A., p. 375–439.

Hooper, P. R., Herrick, I. W., Laskowski, E. R., and Knowles, C. R., 1980, Composition of the Mount St. Helens ashfall in the Moscow-Pullman area on 18 May 1980: Science, v. 209, p. 1125–1126.

Laflamme, R. E., and Hites, R. A., 1978, The global distribution of polycylic aromatic hydrocarbons in recent sediments: Geochimica et Cosmochimica Acta, v. 42, p. 289–303.

Leach, J. M., Thakore, A. N., and Manville, J. F., 1977, Compounds toxic to fish in pulp mill waste streams: Progress in Water Technology, v. 9, p. 787–798.

Lee, M. L., Novotny, Milos, and Bartle, K. D., 1976, Gas chromatography—Mass spectrometric and nuclear magnetic resonance determination of polynuclear aromatic hydrocarbons in airborne particulates: Analytical Chemistry, v. 48, p. 1566–1571.

Lee, M. L., Prado, G. P., Howard, J. B., and Hites, R. A., 1977, Source identification of urban airborne polycyclic aromatic hydrocarbons by GC-MS and HRMS: Biomedical Mass Spectrometry, v. 4, p. 182–187.

McKnight, D. M., Pereira, W. E., Ceazan, M. L., and Wissmar, R. C., 1982, Characterization of dissolved organic materials in surface waters within the blast zone of Mount St. Helens, Washington: Organic Geochemistry, v. 4, p. 85–92.

Mahood, H. W., and Rogers, I. H., 1975, Separation of resin acids from fatty acids in relation to environmental studies: Journal of Chromatography, v. 109, p. 281–286.

Mullineaux, D. R., and Crandell, D. R., 1981, The eruptive history of Mount St. Helens, *in* Lipman, P. W., and Mullineaux, D. R., eds., The 1980 eruptions of Mount St. Helens, Washington: U.S. Geological Survey Professional Paper 1250, p. 3–15.

Pereira, W. E., and Rostad, C. E., 1983, Terpenoid marker compounds derived from biogenic precursors in volcanic ash from Mount St. Helens, Washington: Geochimica et Cosmochimica Acta, v. 47, no. 12, p. 2287–2291.

Pereira, W. E., Rostad, C. E., and Taylor, H. E., 1980, Mount St. Helens, Washington, 1980 volcanic eruption—Characterization of organic compounds in ash samples: Geophysical Research Letters, v. 7, p. 953–954.

Pereira, W. E., Rostad, C. E., Taylor, H. E., and Klein, J. M., 1982, Characterization of organic contaminants in environmental samples associated with Mount St. Helens 1980 volcanic eruption: Environmental Science and Technology, v. 16, p. 387–396.

Sarna-Wojcicki, A. M., Shipley, Susan, Waitt, R. B., Dzurisin, Daniel, Hays, W. H., Davis, J. O., Wood, S. H., and Bateridge, Thomas, 1980, Areal distribution, thickness, and volume of downwind ash from the May 18, 1980, eruption of Mount St. Helens: U.S. Geological Survey Open-File Report 80-1078, 15 p.

Schnitzer, Morris, 1978, Humic substances: Chemistry and reaction, *in* Schnitzer, Morris, and Kahn, S. U., eds., Soil organic matter: New York, Elsevier, p. 1-64.

Shiaris, M. P., and Sayler, G. S., 1982, Biotransformation of PCB by natural assemblages of freshwater microorganisms: Environmental Science and Technology, v. 16, p. 367-369.

Simoneit, B. R. T., 1977, Diterpenoid compounds and other lipids in deep-sea sediments and their geochemical significance: Geochimica et Cosmochimica Acta, v. 41, p. 463-476.

Simoneit, B. R. T., and Mazurek, M. A., 1982, Organic matter of the troposphere—II, Natural background of biogenic lipid matter in aerosols over the rural western United States: Atmospheric Environment, v. 16, p. 2139-2159.

Simonsen, Sir John, and Barton, D. H. R., 1961, The sesquiterpenes, diterpenes and their derivatives, *in* The Terpenes: Cambridge, Mass., The University Press, v. 3, 579 p.

Stonecipher, W. D., and Turner, R. W., 1970, Rosin and rosin derivatives: Encyclopedia of Polymer Science Technology, v. 12, p. 139-161.

Swan, E. P., 1965, Identity of a hydrocarbon found in forest soil: Forest Products Journal, v. 15, p. 272.

Taylor, H. E., and Lichte, F. E., 1980, Chemical composition of Mount St. Helens volcanic ash: Geophysical Research Letters, v. 7, p. 949-952.

Wakeham, S. G., Schaffner, C., and Giger, W., 1980, Polycyclic aromatic hydrocarbons in recent lake sediments—I, Compounds having anthropogenic origins: Geochimica et Cosmochimica Acta, v. 44, p. 403-413.

White, C. M., and Lee, M. L., 1980, Identification and geochemical significance of some aromatic components of coal: Geochimica et Cosmochimica Acta, v. 44, p. 1825-1832.

Youngblood, W. W., and Blumer, M., 1975, Polycyclic aromatic hydrocarbons in the environment—Homologous series in soils and recent marine sediments: Geochimica et Cosmochimica Acta, v. 39, p. 1303-1314.

ORGANOCHLORINE PESTICIDE AND POLYCHLORINATED BIPHENYL RESIDUES AT FOUR TROPHIC LEVELS IN THE SCHUYLKILL RIVER, PENNSYLVANIA

By James L. Barker

Abstract

Various biological components within four trophic levels of the Schuylkill River in eastern Pennsylvania were examined for organochlorine pesticide and polychlorinated biphenyl residues (PCB's) in 1980. Components examined were periphyton, green algae, macrophytes, snails, and whole bodies and fillets of nine common fish species.

Chlordane, dichlorodiphenyl trichloroethane (DDT) and its metabolites, dieldrin, and PCB's were detected at all trophic levels. Endrin and heptachlor epoxide were detected at all trophic levels except primary consumers (snails).

There is some evidence that these residues are being bioaccumulated in selected species at the higher trophic levels of the food web. The edible flesh of some fish, such as American eel and sunfish, contain concentrations of chlordane and PCB's that exceed U.S. Food and Drug Administration guidelines.

INTRODUCTION

The presence of toxic substances in fish of the Schuylkill River has become a major concern of local and State officials in recent years. Studies by Brezina and Arnold (1976) have indicated the presence of high concentrations of some pesticides and polychlorinated biphenyls (PCB's) in components of the Schuylkill River ecosystem, particularly fish. Subsequent studies of the water and bed sediments by the U.S. Geological Survey Schuylkill River Quality Assessment Project from 1978 to 1980 (Stamer and others, 1984) also have shown high concentrations of pesticides and PCB's in the bed material but relatively low concentrations (usually below detection limits) in the water. Several questions are raised: are the pesticides and PCB's being bioaccumulated by the fish? if there is evidence of bioaccumulation, at what trophic level(s) is it occurring? and do any of the fish harvested for consumption contain concentrations in their edible flesh that exceed current Food and Drug Administration guidelines?

This paper evaluates the potential for organochlorine pesticide and PCB residues to bioaccumulate in periphyton, algae, macrophytes, snails, and nine species of fish. Four trophic levels are represented: primary producers, primary consumers, secondary consumers, and tertiary consumers.

METHODS

Collection of Samples

Samples of assorted plant material, snails, and fish were collected at two sites at Reading and two sites about 96.5 km downstream at Philadelphia on August 19 and 20, 1980 (fig. 1). The Penn Avenue site, Reading (site 1), included that section of river from the U.S. Route 222 bridge upstream for 1,000 m. The South Street site, Reading (site 2), included that section of river from 1,000 to 2,000 m downstream from the U.S. Route 222 bridge. The Manayunk site, Philadelphia (site 3), included that section of river from the U.S. Route 1 bridge upstream to a point 1,500 m downstream of the Flatrock Dam. The Fairmount Pool site, Philadelphia (site 4), included that section of river from the downstream end of Peters Island upstream to Strawberry Bridge.

The plant material, consisting of periphyton, green algae (*Cladophera*) and macrophytes (*Potomogeton* sp.), and the snails were handpicked, placed directly into oven-fired wide-mouth glass jars, and held on ice until analyzed. Fish samples were collected by personnel of the Pennsylvania Fish Commission using electrofishing techniques. Whole small fish and fillets from each of the larger fish were wrapped in aluminum foil and transported on ice to the laboratory where they were frozen for later analysis. The nine species of fish collected for residue analysis included resident game fish, forage fish, and common rough fish. These species, in increasing trophic order, include assorted minnows (Cyprinidae), golden shiner (*Noteigonus crysoleucas*), white sucker (*Catostomus commersoni*), sunfish (*Lepomis* sp.), American eel (*Auguilla rostrata*), black crappie (*Pomoxis nigromaculatus*), smallmouth bass

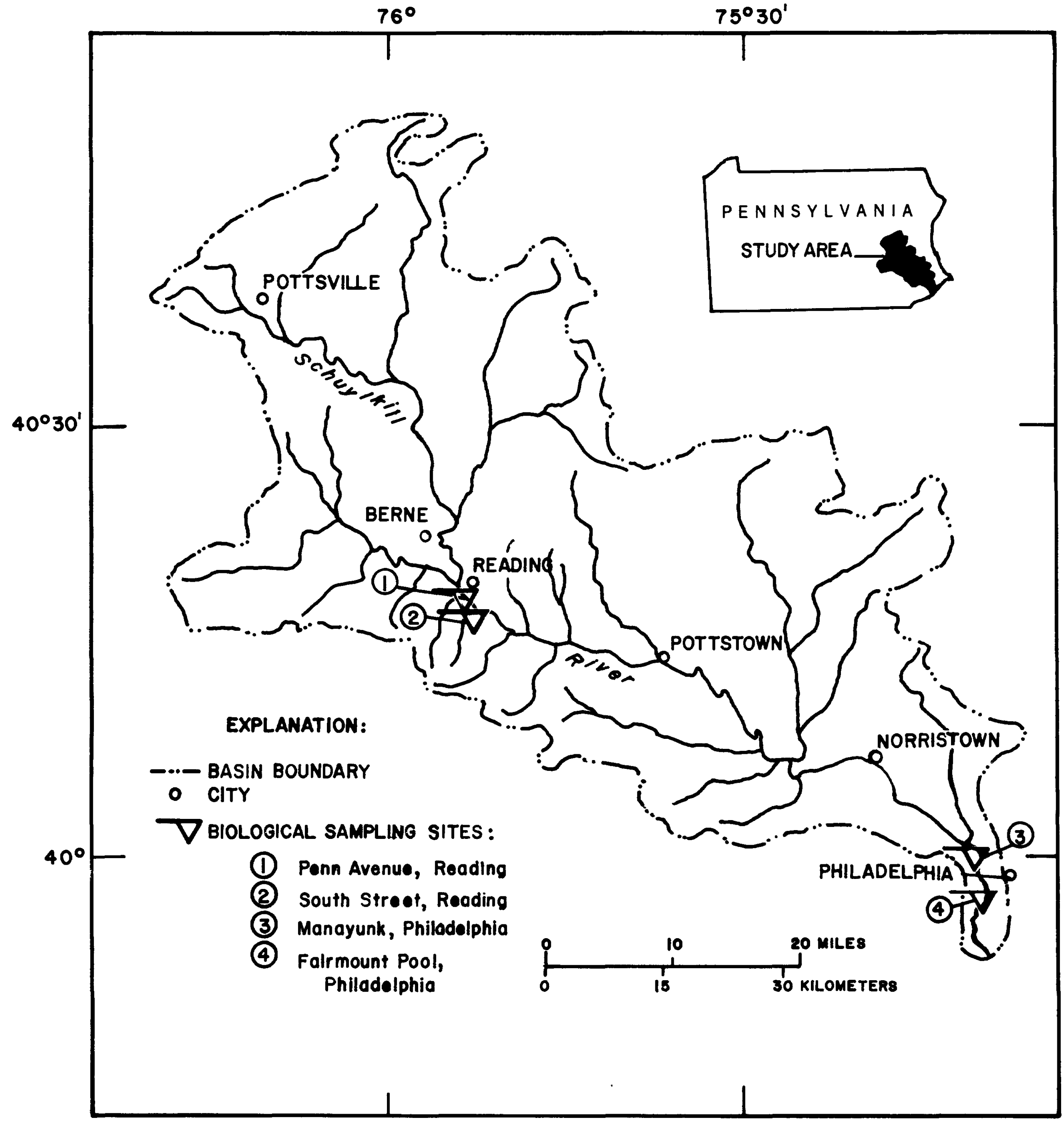


Figure 1. Location of sampling sites.

(*Micropterus dolomieui*), largemouth bass (*Micropterus salmoides*), and muskellunge (*Esox masquinongy*).

Residue Extraction and Analysis

Analyses for organochlorine residues in the tissue samples of whole small fish and fillets of large fish were performed at the U.S. Geological Survey Atlanta Central Laboratory according to the extraction procedures described by the U.S. Food and Drug Administration in *Pesticide Analytical Manual* (1972). Table 1 lists the limits of detection.

RESULTS AND DISCUSSION

Concentrations of residues in the biota were highest for PCB's, followed by chlordane, DDT and its metabolites, dieldrin, and endrin at all trophic levels and at all

Table 1. List of chlorinated hydrocarbon compounds analyzed for and their limits of detection in the biota

Compound	Detection limit (μg/kg)
Aldrin	0.1
Chlordane	.1
DDD	.1
DDE	.1
DDT	.1
Dieldrin	.1
Endosulfan	.1
Endrin	.1
Heptachlor epoxide	.1
Heptachlor	.1
Lindane	.1
Mirex	.1
Methoxychlor	.1
PCB's	1.0
PCN's	.1
Perthane	.1
Toxaphene	10.0

sampling stations. Both chlordane and DDT or its metabolites DDD and DDE were detected in 97 percent of the samples at concentrations as high as 1,100 and 500 μg/kg, respectively. Dieldrin was detected in 98 percent of the samples at concentrations as high as 180 μg/kg. PCB's were found in 100 percent of the samples analyzed at concentrations as high as 8,100 μg/kg. Highest concentrations of all residues were in the flesh of American eels. Table 2 summarizes the analytical results at each of the four sampling sites. Although analyses of the same species within a sample varied considerably, the concentrations probably reflect the potential of each organism and each trophic level to accumulate synthetic residues.

As reported in earlier studies by Brezina and Arnold (1976) and Stamer and others (1984), chlordane, dieldrin, DDT and its metabolites DDD and DDE, and PCB's are widespread throughout the lower Schuylkill River ecosystem. Table 3 lists the organochlorine residues analyzed for and present in the river. With a few exceptions, Stamer and others (1984) found that concentrations of organic residues in the Schuylkill River water were below detection limits. Trace quantities (0.3 μg/kg or less) of DDT and its metabolites, PCB's, and polychlorinated napthalenes (PCN's) were occasionally detected at Reading and Manayunk. They also found residues of PCB's, chlordane, DDT and its metabolites, and dieldrin to be concentrating in the river-bed sediments as summarized in table 4. PCB residues were highest followed by chlordane, DDT and its metabolites, and dieldrin.

Comparing the residues found in biota in 1980 with the results reported by Brezina and Arnold (1976) indicates PCB concentrations in fish flesh have not changed in 4 years. For example, in the reach downstream of Reading, they found concentrations of PCB's in carp to be as high as 7,500 μg/kg. A similar study by Hunter and others (1980a) indicates PCB and selected organochlorine residues in fish fillets from Lake Texoma are generally lower than those of the Schuylkill River. However, in another study conducted downstream of an industrial source, Hunter and others (1980b) found the PCB concentrations in fish fillets ranged from 120 to 2,800 μg/kg for carnivores and from 700 to 16,000 μg/kg for detritivores (primary consumers) and omnivores (secondary and tertiary consumers). These values were as high as or higher than those in the Schuylkill River.

Although somewhat difficult to evaluate because of small sample size and within-sample variability, the longitudinal distribution of organochlorine residues in the biota of the Schuylkill River is in general agreement with the distribution in the bed material, as determined by Stamer and others (1984); that is, PCB's are generally higher at upstream sites and chlordane and dieldrin are higher at downstream sites. An analysis of variance of the mean values for residues measured in white sucker, sunfish, American eel, and smallmouth bass shows no obvious trends. The results of the analysis of variance are summarized in table 5. For purposes of this analysis, the fish residues from the Reading and the Philadelphia sites were composited into two groups.

Evidence of bioaccumulation is suggested by the concentrations found in the different components of the ecosystem; for example, mean PCB concentrations are trace quantities in the river water, 152 μg/kg in the bed sediments (Stamer and others, 1984), 56 μg/kg in the primary producers, 125 μg/kg in the primary consumers, and 650 to 700 μg/kg in the secondary and tertiary consumers.

Concentration factors can be calculated by dividing the mean PCB concentrations of the sediment samples into the mean concentration of representative components of the various trophic levels. Concentration factors ranged from 0.4 for *Cladophora* to 18.4 for American eels. These concentration factors are very similar to the Pryor Creek data of Hunter and others (1980b).

The flesh of some fish samples contained residues that exceeded the Food and Drug Administration guidelines listed in table 6. Guidelines for chlordane were exceeded in American eels at all three sites downstream of Penn Avenue, Reading, and chlordane levels in sunfish and golden shiners exceeded guidelines at Manayunk and Fairmount Pool, Philadelphia, respectively. PCB levels in a 24-in American eel collected at

Table 2. Concentrations of organochlorine residues in aquatic organisms in the Schuylkill River, August 1980
[Concentrations are in micrograms per kilogram]

Organism	Number of fish analyzed	Number of of Analyses	Chlordane			DDT plus metabolites			Dieldrin			Endrin			PCB's		
			Max.	Mean	Std. dev.	Max.	Mean	Std. dev.	Max.	Mean	Std. dev.	Max.	Mean	Std. dev.	Max.	Mean	Std. dev.
Penn Street, Reading (river kilometer 121.3)																	
Potomogeton sp.		2	4.4	2.9	2.1	0.7	0.6	0.2	0.3	0.3	-	<0.1	<0.1	-	23	21	3.5
Snails[1] (small)		4	12	5.9	4.9	6.9	2.0	1.9	.7	.5	0.1	<.1	<.1	-	210	190	21
White suckers (12-15 in)	6	6	42	23	12	33	23	8.1	3.8	3.0	.7	.5	.3	.2	450	380	73
American eel (17-25 in)	6	6	270	180	69	390	280	120	56	35	20	19	9.2	7.5	8,100	3,700	2,300
Sunfish	5	4	94	39	44	100	31	49	21	9.1	10	<.1	<.1	-	1,400	620	660
Black crapple	5	3	11	9.5	1.3	8	6.7	1.2	1.4	1.1	.3	.2	.2	-	250	160	84
Smallmouth bass, Age I, II	8	2	14	13	.7	30	20	14	1.6	1.5	.2	2.3	1.3	1.5	140	130	9
Largemouth bass, Age II	2	1	6.2	6.2	-	7.6	7.6	-	.6	.6	-	<.1	<.1	-	130	130	-
South Street, Reading (river kilometer 119.7)																	
Cladophora		5	31	16	12	5.6	2.3	2.3	2.0	1.4	.4	<.1	<.1	-	99	85	13
Potomogeton sp.		3	4.1	2.7	2.3	1.1	.7	.6	.3	.3	-	<.1	<.1	-	35	32	4
Snails[1] (small)		2	18	12	8	3.0	2.7	.4	.8	.8	-	<.1	<.1	-	230	160	99
White suckers (12-15 in)	8	4	81	46	24	68	45	17	5.9	4.2	1.2	1.0	.6	.3	1,400	1,000	460
American eel (17-25 in)	4	4	470	360	130	500	290	140	180	99	71	8.7	5.0	3.9	3,500	2,600	700
Sunfish	4	2	130	71	87	78	65	19	8.3	7.2	1.6	<.1	<.1	-	1,300	940	550
Black crapple, Age II, III	15	5	100	39	44	59	25	28	12	4.1	5	3.6	.8	1.6	2,100	590	850
Smallmouth bass, Age I, II	7	2	6.6	6.1	.8	7	7	.6	1.5	1.0	.7	.2	.1	.1	250	210	65
III	1	1	5.2	5.2	-	4.8	4.8	-	1.0	1.0	-	.2	.2	-	170	170	-

Table 2. Concentrations of organochlorine residues in aquatic organisms in the Schuylkill River, August 1980—Continued

Organism	Number of fish analyzed	Number of Analyses	Chlordane			DDT plus metabolites			Dieldrin			Endrin			PCB's		
			Max.	Mean	Std. dev.	Max.	Mean	Std. dev.	Max.	Mean	Std. dev.	Max.	Mean	Std. dev.	Max.	Mean	Std. dev.
Manayunk, Philadelphia (river kilometer 22.9)																	
Cladophora		4	18	15	5	6.1	2.9	2.2	3.0	2.1	1	<0.1	<0.1	-	40	31	7
Snail[1] (small)		2	13	11	3	5.9	4.1	2.6	1.7	1.5	.3	<.1	<.1	-	85	76	13
Snail[1] (large)		1	18	18	-	1.5	1.5	-	1.3	1.3	-	<.1	<.1	-	90	90	-
Minnows	Many	1	140	140	-	21.4	21.4	-	14	14	-	0.4	0.4	-	700	700	-
Golden shiners	Many	1	100	100	-	22.9	22.9	-	8.1	8.1	-	.4	.4	-	810	810	-
White suckers (12–15 in)	8	7	130	89	35	50	22	14	11	6.9	2.9	.4	.1	0.2	1,100	840	450
American eel (17–25 in)	2	2	1,100	590	770	260	140	170	110	59	75	0.3	0.2	0.2	3,900	2,100	2,500
Sunfish	>9	7	320	150	99	120	49	38	28	16	11	2.0	.6	.6	1,700	890	530
Black crapple																	
Age II, III	6	2	14	12	3	11	7	5	2.0	1.0	1.4	<.1	<.1	-	64	42	31
Smallmouth bass,																	
Age I, II	2	2	38	28	14	11	11	0.2	2.1	2.1	-	.3	.2	.1	190	170	33
III	1	1	25	25	-	7.7	7.7	-	0.7	0.7	-	.1	.1	-	230	230	-
IV	1	1	53	53	-	32	32	-	2.1	2.1	-	.5	.5	-	570	570	-
Muskellunge,																	
Age VI	1	4	100	70	31	46	32	13	9.1	5.6	3.1	.5	.4	.2	810	520	240
Fairmount Pool, Philadelphia (river kilometer 16.4)																	
Periphyton		1	8.2	8.2	-	11.5	11.5	-	2.6	2.6	-	.5	.5	-	70	70	-
Minnows	Many	1	79	79	-	31	31	-	7.2	7.2	-	<.1	<.1	-	230	230	-
Golden shiners	Many	1	350	350	-	75	75	-	3.1	3.1	-	<.1	<.1	-	1,400	1,400	-
White suckers (12–15 in)	1	1	57	57	-	37	37	-	4.5	4.5	-	<.1	<.1	-	330	330	-
American eel (17–25 in)	4	4	1,000	440	390	330	220	110	120	38	52	5.9	2.2	2.6	3,700	2,000	1,200
Sunfish	<7	6	230	130	71	300	97	110	29	18	11	.1	<.1	-	1,200	590	370
Smallmouth bass,																	
Age I, II	6	3	33	26	6	12	9	3	4.1	3.1	.9	.2	.1	.1	210	180	34
III	1	1	15	15	-	1.4	1.4	-	.6	.6	-	.1	.1	-	320	320	-
Largemouth bass,																	
Age II	1	1	15	15	-	13	13	-	1.9	1.9	-	<.1	<.1	-	160	160	-

[1] Goniobasis.

Table 3. Summary of trace organochlorine residues analyzed for and identified in the Schuylkill River ecosystem

	Water	Bed sediment	Primary producers	Primary consumers	Secondary consumers	Tertiary consumers
Aldrin	---	---	---	---	---	---
Chlordane	---	X	X	X	X	X
DDD	---	X	X	X	X	X
DDE	---	X	X	X	X	X
DDT	X	X	X	X	X	X
Dieldrin	---	X	X	X	X	X
Endosulfan	---	---	---	---	---	---
Endrin	---	---	X	---	X	X
Heptachlor epoxide	---	---	X	---	X	X
Heptachlor	---	---	---	---	---	---
Lindane	---	---	---	X	---	---
Mirex	---	---	---	---	---	---
Methoxychlor	---	---	---	---	---	---
PCB's	X	X	X	X	X	X
PCN's	X	---	---	---	---	---
Perthane	---	---	---	---	---	---
Toxaphene	---	---	---	---	---	---

Table 4. Concentrations of trace organic substances contained in 38 samples of river-bed sediments collected from the Schuylkill River, Philadelphia, November-December 1979

[Data modified from Stamer and others (1984). Concentrations are in micrograms per kilogram]

Constituent	Mean	Minimum	Maximum	Range
Chlordane	24	0	57	57
DDD	4.3	0	11	11
DDE	8.2	.6	24	23.4
DDT	5.5	.4	32	31.6
Dieldrin	1.8	0	7.9	7.9
PCB's	152	22	320	298

Table 5. Summary of analyses of variance test for significance of concentrations found in fish at Reading and Philadelphia sites

[NS, no significant difference; DS, Philadelphia sites greater; and US, Reading sites greater]

Compound	White sucker, 1,16 degrees of freedom	Sunfish, 1,17 degrees of freedom	American eel, 1,14 degrees of freedom	Smallmouth bass, 1,8 degrees of freedom
Chlordane	DS	DS	DS	DS
DDT plus metabolites	NS	NS	US	DS
Dieldrin	DS	DS	NS	NS
PCB's	NS	NS	US	NS

Table 6. U.S. Food and Drug Administration guidelines for the human consumption of edible fish flesh

Compound	Concentration (μg/kg)
Chlordane	300
DDT plus metabolites	5,000
Dieldrin	300
Endrin	300
Heptachlor epoxide	300
PCB's	5,000

Penn Avenue, Reading, exceeded the guideline. However, numerous individuals from all four sites contained residues of PCB's in excess of the proposed 2,000-μg/kg Food and Drug Administration guideline. It is believed that species of fish such as American eels and shiners tend to accumulate higher concentrations of organic compounds because of a higher lipid content in their tissue (Brezina and Arnold, 1976). As pointed out by Phillips (1978), age, sex, sex cycle, and diet as well as lipid content and weight are related to PCB concentration in various organisms.

SELECTED REFERENCES

Brezina, E. R., and Arnold, M. V., 1976, Levels of PCB and other chlorinated hydrocarbons in fishes from selected Pennsylvanian waters: Pennsylvania Department of Environmental Resources, Bureau of Water Quality Management, Publication No. 46, 20 p.

Frank, Richard, Braun, H. E., Holdrinet, Micheline, Dodge, D. P., and Nepszy, S. J., 1978, Residues of organochlorine insecticides and polychlorinated biphenyls in fish from lakes Saint Clair and Erie, Canada, 1968-76: Pesticides Monitoring Journal, v. 12, no. 2, p. 69-80.

Goerlitz, D. F., and Brown, Eugene, 1972, Methods for analysis of organic substances in water: U.S. Geological Survey Techniques of Water Resources Investigations, Book 5, Chapter A3, Part II, 40 p.

Henderson, D., Inglis, A., and Johnson, W. L., 1971, Organochlorine insecticide residues in fish—Fall 1969: Pesticides Monitoring Journal, National Pesticides Monitoring Program, v. 5, no. 1, p. 1-11.

Henderson, D., Johnson, W. L., Inglis, A., 1969, Organochlorine insecticide residues in fish: Pesticide Monitoring Journal, National Pesticides Monitoring Program, v. 3, no. 3, p. 145-171.

Hunter, R. G., Carroll, J. H., and Randolph, J. C., 1980a, Organochlorine residues in fish of Lake Texoma, October 1979: Pesticide Monitoring Journal, v. 14, no. 3, p. 102-107.

Hunter, R. G., Randolph, J. C., and Carroll, J. H., 1980b, Polychorinated biphenyls in the sediments and fish of an Oklahoma stream: Environmental Pollution, Series B: Chemical and physical, v. 1, no. 3, July-September 1980, p. 233-240.

Klaassen, H. E., and Kadoum, A. M., 1975, Insecticide residues in the Tuttle Creek Reservoir, Kansas—1970-71: Pesticide Monitoring Journal, v. 9, no. 2, p. 89-93.

Nadeau, R. J., and Davis, R. P., 1974, Investigation of polychlorinated biophenyls in the Hudson River (Hudson Falls-Ft. Edward area): U.S. Environmental Protection Agency Report, 39 p.

Phillips, D. J. H., 1978, Use of biological indicator organisms to quantitate organochlorine pollutants in aquatic environments: A review: Environmental Pollution, v. 16, p. 167-230.

Spagnoli, J. J., and Skinner, L. C., 1977, PCB's in fish from selected waters of New York State: Pesticides Monitoring Journal, v. 11, no. 2, p. 69-87.

Stamer, J. K., Yorke, T. H., and Patterson, G. L., 1984, Distribution and transport of trace substances in the Schuylkill River basin from Berne to Philadelphia, Pennsylvania: U.S. Geological Survey Water-Supply Paper 2256 [in press].

U.S. Food and Drug Administration, 1972, Pesticide analytical manual: U.S. Department of Health and Human Services, v. 1, Sec. 211.14, Washington, D.C.

Veith, G. D., DeFoe, D. L., and Bergstedt, B. V., 1979, Measuring and estimating the bioconcentration factor of chemicals in fish: Journal of Fisheries Research Board, Canada, v. 36, p. 1040-1048.

A SOLUTION-CHEMISTRY MODEL OF THE INTERFERENCE OF CADMIUM-CARBONATE PRECIPITATION IN THE DETERMINATION OF CATION-EXCHANGE SEPARATION FACTORS

By Ronald L. Miller, David B. Grove, *and* Kenneth G. Stollenwerk

Abstract

A computer model combining the equilibria for cadmium-calcium ion exchange and precipitation of cadmium carbonate simulates experimentally determined sorption curves. Results show that carbon dioxide in air and carbonates in sand samples and reagents may interfere with the determination of cation-exchange separation factors because of cadmium-carbonate precipitation. The magnitude of this interference depends on solution pH and ionic strength. When precipitation of cadmium carbonate is not considered, calculated values of cation-exchange separation factors appear several orders of magnitude greater than their correct values.

INTRODUCTION

Recent interest in the subsurface storage of wastes has created a need to evaluate containment practices and to predict the possible movement of toxic substances that may be released to the environment. Quantitative techniques to predict the movement and concentration changes of contaminants in the subsurface have been described by Grove (1977), Bredehoeft and Pinder (1973), and Konikow and Grove (1977); the importance of ion-exchange reactions related to these predictions is well known (Rubin and James, 1973; Grove, 1976). Inclusion of such chemical reactions into predictive equations requires accurate knowledge of mass-action equilibrium constants that are necessary to describe the process.

When measuring cation-exchange separation factors for metal ions on soils, care is needed to avoid precipitation reactions which compete with cation-exchange processes. This is true especially when carbonates or sulfide ions can be dissolved from air (CO_2,H_2S), from soil, or where they are present in reagents. (A list of definitions of symbols can be found at the end of this paper.) Many anions may form precipitates that interfere in cation-exchange determinations; these anions include chlorides ($AgCl$, Hg_2Cl_2, $PbCl_2$); sulfates ($BaSO_4$); phosphates (Ag_3PO_4, $Ca_3(PO_4)_2$, $Ca_5(PO_4)_3(OH)$, $FePO_4$, Hg_2HPO_4); carbonates (Ag_2CO_3, $FeCO_3$); and sulfides (Ag_2S, CuS, HgS, PbS). Many minimally soluble hydroxides and oxides also are potential interferences.

The ion-exchange reaction:

$$Cd^{+2} + \overline{Ca^{+2}} \rightleftarrows \overline{Cd^{+2}} + Ca^{+2}, \qquad (1)$$

that describes cadmium exchanging for calcium in a calcium-saturated soil can be quantitized by the cation-exchange separation factor, S, (Helfferich, 1962):

$$\alpha = \frac{(\overline{Cd^{+2}}\text{meq/g})\ (Ca^{+2}\text{meq/L})}{(Cd^{+2}\text{meq/L})\ (\overline{Ca^{+2}}\text{meq/g})}, \qquad (2)$$

where the superscript bar denotes a concentration associated with the soil phase.

Initial attempts to determine this separation factor were confounded by erratic results. Chemical reactions continued for more than 1 hour and varied with soil-to-water ratios and indicated what processes other than equilibrium-controlled ion exchange were occurring.

Experiments were devised to test the hypothesis that precipitation of cadmium carbonate ($CdCO_3$) was a competing reaction. This report presents the results of these experiments and the effect of this competing chemical reaction on calculation of cation-exchange separation factors. A computer model is used to demonstrate the agreement between theory and experimental results for simultaneous precipitation and cation-exchange equilibria.

EXPERIMENTAL

Materials

The soil material used was an acid-washed and sieved sand from the Lubbock, Texas, area. The sand passed a 500-μm sieve and was retained by a 420-μm sieve. The sand had a surface area of 0.5 m^2/g (four-point BET gas adsorption) and consisted of particles that were ellipsoidal to spherical. The sand was predominantly quartz, with some plagioclase and hornblende.

The cadmium chloride ($CdCl_2 \cdot 2\ 1/2\ H_2O$) was Matheson, Coleman, and Bell reagent ACS crystals. The calcium chloride ($CaCl_2 \cdot H_2O$) and calcium hydroxide [$Ca(OH)_2$] were Baker-analyzed reagents. Cadmium and calcium solutions were acidified with ultrapure nitric acid after collection from the reaction vessels and sand columns. Calcium solutions were spiked with a lanthanum chloride-hydrochloric acid solution (Skougstad and others, 1979) before analysis to eliminate interferences. Sulfuric acid used to titrate for carbonate and bicarbonate was standardized against Baker-analyzed reagent, primary standard potassium biphthalate.

Apparatus

Cadmium- and calcium-ion concentrations were analyzed with a Perkin-Elmer 305 atomic-absorption spectrophotometer using direct methods (aspirate solution without extraction). An Orion Model 701 pH meter and an Orion pH electrode were used for all pH measurements.

Some samples were equilibrated by using a Burrel wrist-action shaker, elevated to permit samples to be immersed in a Forma Scientific 2095 bath and circulator at 25°C. Other samples were equilibrated under a nitrogen atmosphere at ambient temperature (20°-25°C), using a magnetic stirrer.

Procedures

Several experimental configurations were used. The first set of experiments (with carbonates) was performed without special care, which allowed exposure to atmospheric carbon dioxide. For these experiments, 1 g of sand was equilibrated with 25 mL of solution at 25°C for 120 min with a wrist-action shaker.

A second set of experiments (few carbonates) received special care to decrease the quantity of carbonates in the reaction vessel. Reagents were prepared fresh under a nitrogen atmosphere. Nitrogen gas was first bubbled through 25 mL of solution for at least 30 minutes from pH 4 to 5. The pH was adjusted, 1 g of sand was added, and the sand-water mixture gently stirred for 120 min, all under a nitrogen atmosphere. At the end of the experiment, pH was measured under the nitrogen atmosphere to avoid the effects of carbon dioxide. Actual carbonate concentration of the solutions was not determined in either of the above experiments.

In a third experiment, four solutions, varying in pH and carbonate concentration, were equilibrated with sand. These four solutions were titrated for carbonate species, so a solubility product for $CdCO_{3(s)}$ could be obtained: consequently, the experimental data could be compared to model predictions.

For all these experiments, pH was adjusted to values between 5 and 9 with either calcium hydroxide solution or acetic acid. Initial cadmium concentration was 300 μg/L and initial calcium concentration varied with the quantity of calcium hydroxide solution required to adjust pH.

Cation-exchange capacity was determined by a sodium-saturation procedure, at pH values ranging from 4.96 to 9.08, according to published procedures (Black and others, 1965, method 57-3.2).

COMPUTER PROGRAM

Chemical Reactions

Theoretical ion-exchange separation factors were calculated from mass-balance relationships. Chemical reactions assumed to affect the concentrations of cadmium in these experiments, in addition to their equilibrium constant expressions, are listed in table 1. In addition to ion-exchange, precipitation, and dissolution reactions, they include carbonate, hydroxide, and acetate and chloride ion-pair formation.

The Debye-Huckel equation was used to calculate activity coefficients. CaX_2 and $CaHCO_3^+$ were assumed to be the major ionic strength determining species, where X is the sum of acetate and chloride ions. An approximate effective ion radius of 0.4 nm was chosen (Meites, 1963) to represent all ions with a charge of ± 1 in the system; a radius of 0.5 nm was chosen to represent all ions with a charge of ±2. One activity coefficient was calculated for all ± 1 ions, and another was calculated for all ±2 ions. Uncharged species were given an activity coefficient of 1.

From these reactions, the ionic strength and activity coefficients of the +1 ions and +2 ions were calculated according to Meites (1963) as follows:

$$\mu = 3[Ca^{+2}]\ , \quad (3)$$

$$\gamma_1 = \text{antilog}\ [(-0.511\sqrt{\mu})/(1 + 1.3\sqrt{\mu})]\ , \quad (4)$$

$$\gamma_2 = \text{antilog}\ [(-0.2044\sqrt{\mu})/(1 + 1.6\sqrt{\mu})]\ . \quad (5)$$

The complexes of cadmium with chloride and acetate ions were considered as one complex with a formation constant of $10^{1.4}$ because chloride and acetate were not measured individually and their formation constants are similar, that is, $10^{1.5}$ for cadmium carbonate and $10^{1.3}$ for acetate.

Table 1.—Chemical reactions used in model

Reaction	Equilibrium-constant expression	Value of equilibrium constant at 25° C
$H_2O \rightleftarrows H^+ + OH^{1}$	$K_w = a_{H^+} \cdot a_{OH^-}$	[1]1.00×10^{-14}
$Cd^{+2} + \overline{Ca^{+2}} + \rightleftarrows \overline{Cd^{+2}} + Ca^{+2}$	$\alpha = \dfrac{[\overline{Cd^{+2}}]\,[Ca^{+2}]\,\gamma_2}{[Cd^{+2}]\,\gamma_2\,[\overline{Ca^{+2}}]}$	$1.3259 \cdot pH - 5.9265$ (this paper, eq.6)
$H_2CO_3^* \rightleftarrows H^+ + HCO_3^-$	$K_1 = \dfrac{(a_{H^+})\,[HCO_3^-]\,\gamma_1}{[H_2CO_3^*]}$	[1]4.446×10^{-2}
$HCO_3^- \rightleftarrows H^+ + CO_3^{-2}$	$K_{2^-} = \dfrac{(a_{H^+})\,[CO_3^{-2}]}{[HCO_3^{-1}]\,\gamma_1}$	[1]4.688×10^{-11}
$Ca^{+2} + CO_3^- \rightleftarrows CaCO^0_{3(aq)}$	$K_{f,CaCO^0_{3(aq)}} = \dfrac{[CaCO_3^0]}{[Ca^{+2}]\,\gamma_2\,[CO_3^{-2}]\,\gamma_2}$	[1]1585
$Ca^{+2} + HCO_3^- \rightleftarrows CaHCO_3^+$	$K_{f,CaHCO_3^+} = \dfrac{[CaHCO_3^+]\,\gamma_1}{[Ca^{+2}]\,\gamma_2\,[HCO_3^-]\,\gamma_1}$	[1]18.2
$Ca^{+2} + CO_3^{-2} \rightleftarrows CaCO_{3(s)}$	$K_{sp,CaCO^3(s)} = [Ca^{+2}]\,\gamma_2\,[CO_3^{-2}]\,\gamma_2$	[1]4.57×10^{-9}
$Cd^{+2} + X^- \rightleftarrows CdX^+$	$K_{f,CdX^+} = \dfrac{[CdX^+]\,\gamma_1}{[Cd^{+2}]\,\gamma_2\,[X^-]\,\gamma_1}$	[2]25
$Cd^{+2} + OH^- \rightleftarrows CdOH^+$	$K_{f,CdOH^+} = \dfrac{[CdOH^+]\,\gamma_1}{[Cd^{+2}]\,\gamma_2\,a_{OH^-}}$	[3]3.89×10^4
$Cd^{+2} + 2OH^- \rightleftarrows Cd(OH)^0_{2(aq)}$	$K_{f,Cd(OH)^0_{2(aq)}} = \dfrac{[Cd(OH)^0_{2(aq)}]}{[Cd^{+2}\,\gamma_2\,a^2_{OH^-}}$	[3]8.51×10^8
$Cd^{+2} + CO_3^{-2} \rightleftarrows CdCO_{3(s)}$	$K_{sp,CdCO_{3(s)}} = [Cd^{+2}]\,\gamma_2\,[CO_3^{-2}]\,\gamma_2$	7.2×10^{-13} (this paper)
$Cd^{+2} + 2OH^- \rightleftarrows Cd(OH)_{2(s)}$	$K_{sp,Cd(OH)_{2(s)}} = [Cd^{+2}]\,\gamma_2\,a^2_{OH^-}$	[3]2.2×10^{14}

[1]Stumm and Morgan (1970).
[2]Meites (1963).
[3]Rubin (1974).

A cation-exchange capacity and a cadmium-calcium separation factor also are required for the computer program. Both values were experimentally determined to be linear functions of pH, from 6.0 to 9.06. Linear-regression lines with the 95-percent confidence interval, calculated according to Snedecor and Cochran (1967, p. 154), are shown in figure 1 for the cation-exchange capacity and in figure 2 for the cation-exchange separation factor.

Equations of these regression lines are given as

$$CEC = 0.000144\ pH + 0.00357, \tag{6}$$

and

$$\alpha = 1.33\ pH - 5.93. \tag{7}$$

This separation factor was experimentally determined in the absence of any precipitation reactions, by decreasing the cadmium- and carbonate-activity products well below the cadmium carbonate solubility product.

Assumptions

Several assumptions made to simplify computations are as follows:

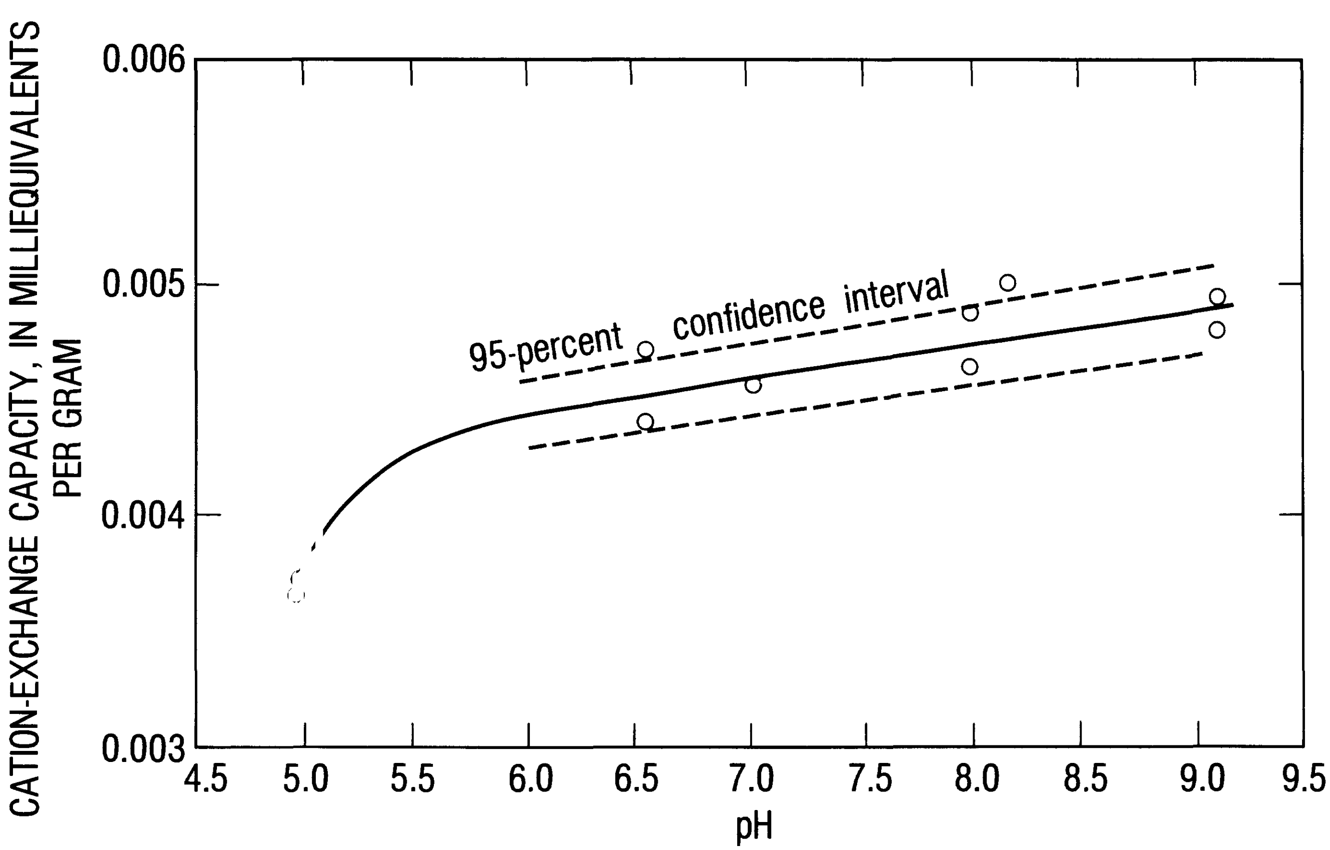


Figure 1. Cation-exchange capacity of sand sample versus pH.

1. Only Cd^{+2} was involved in the cation-exchange reaction. This assumption is not true at large pH values, but it was made because the + 2 charge of Cd^{+2} would compete strongly with the + 1 charge on the $CdOH^{+}$ complex, and $[CdOH^{+}]$ did not equal $[Cd^{+2}]$ until about pH 9.4. Also, there was no way to separately measure the species $[Cd^{+2}]$ and $[CdOH^{+}]$. Only the sum of these two species at cation-exchange sites could be calculated.
2. The variation of CEC and α with pH was linear for within the range of interest, which involved an extrapolation for a range of 1 pH unit (9.06–10.0). These regression lines are shown in figures 1 and 2.
3. All cation-exchange sites were occupied initially by Ca^{+2}; after equilibration, only Ca^{+2} and Cd^{+2} were present on these sites. Consequently, it was assumed that

$$\overline{Ca^{+2}} = CEC - \overline{Cd^{+2}} \, . \tag{8}$$

4. The computer model ignored the effects of the electrical double-layer ion concentration at the water-surface interface. It used only the equilibria for the bulk solution and a simple cation exchange equilibrium between Cd^{+2} and Ca^{+2}.
5. Only four cadmium and two calcium complexes were used; the model did not include the effects of organic or inorganic complexing agents that may have dissolved from the sand.

Computer model results

For initial cadmium, calcium, carbonate, and X concentrations, sand weight, and solution volume, the pH was fixed, and the calculations were performed assuming equilibrium for cation exchange and precipitation of $CdCO_{3(s)}$. After a stable mathematical solution was achieved, the pH was incremented, and results were calculated for the new pH. In this manner, data for a graph of cadmium lost from solution (and suspension) versus pH were obtained.

RESULTS AND DISCUSSION

As calculated from equation 7, actual separation factors ranged from 2.0 to 6.0 for pH values of 6 through 9. When $CdCO_3$ precipitation was not accounted for or assumed to be part of the ion-exchange reaction, erroneously large values of the separation factor are calculated from laboratory data. To illustrate this problem, an apparent cation-exchange separation factor (α_{app}) was defined that took into account cadmium removed from

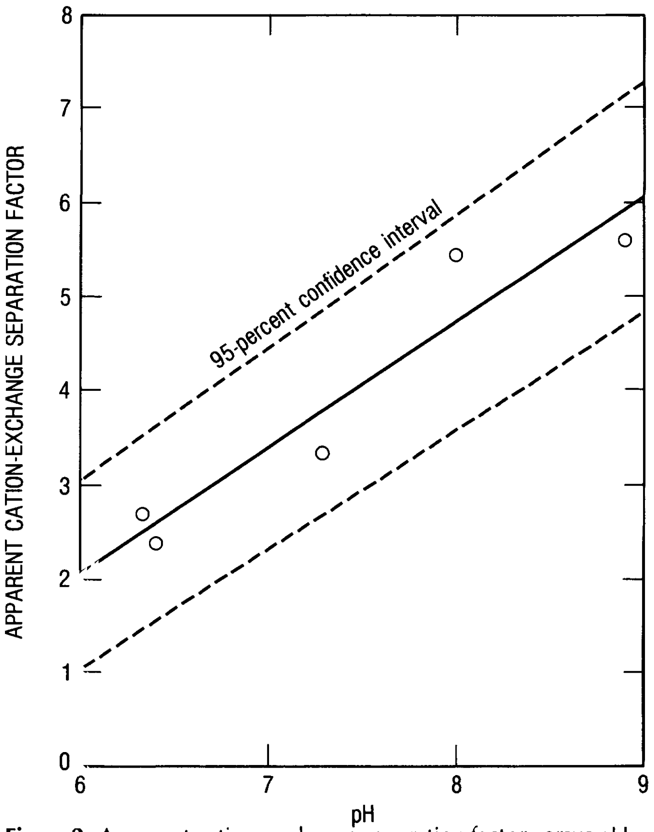


Figure 2. Apparent cation-exchange separation factor versus pH.

solution by both cation exchange and precipitation. These experimentally determined α_{app} for small and moderate concentrations of carbonate in solution are plotted in figure 3. The curve labeled "Experimental, with carbonates" was obtained with no attempt made to eliminate atmospheric carbon dioxide from the solutions. The curve labeled "Experimental, few carbonates" was obtained under a nitrogen atmosphere, with special care being taken to decrease carbonates to a minimum. For a given pH, a decrease in α_{app} was measured in the batch experiments conducted under a nitrogen atmosphere compared to air. This decrease in α_{app} resulted from the smaller carbonate concentration that resulted in less $CdCO_3$ precipitation.

When the curves generated by the computer model were compared (fig. 3), the effect of $CdCO_3$ precipitation on α_{app} also was evident. These effects were indicated by solid-line curves for various total initial concentrations, ranging from 1×10^{-5} to 1×10^{-2} mol/L of carbonate species. When $CO_{3\,T,\,init.}$ was decreased to 1×10^{-5} mol/L, the solubility product for $CdCO_3$ (7.2×10^{-13}) was not exceeded, and the model considered only cation exchange. Once the solubility product for $CdCO_3$ was exceeded that is, $CO_{3\,T,\,init.} = 1 \times 10^{-3}$ mol/L, a slight increase in pH could cause a significant increase in α_{app}. In many natural waters, pH and carbonate concentration are large enough to result in $CdCO_3$ precipitation. Thus, the mechanism for cadmium removal from solution could erroneously be interpreted as ion exchange.

The approximate match of the model results for $CO_{3\,T,\,init.} = 1 \times 10^{-4}$ mol/L with the "Experimental, with carbonates" curve (fig. 3) presumably resulted because the concentration for that experiment happened to contain about 1×10^{-4} mol/L carbonates. Precipitation of $CdCO_3$ at pH >9 was indicated by the upswing in the experimental curve for few carbonates. This upswing indicated a $CO_{3\,T,\,init.}$ between 1×10^{-4} and 1×10^{-5} mol/L.

The value of α_{app} was very sensitive to pH and to the final cadmium concentration. Because soluble cadmium decreased with increasing pH, and the resulting analytical error at small cadmium concentrations became large, the error in α_{app} increased rapidly with pH as indicated by the error bars for each data point ("Experimental, with carbonates").

It is important to note that when $CaCO_{3(s)}$ formation was included in the model calculations, the apparent cation-exchange separation factors obtained were much smaller because of the removal of carbonate as $CaCO_{3(s)}$ (data not shown). It is believed that $CaCO_{3(s)}$ formation was slow compared to the formation of $CdCO_{3(s)}$ and might be neglected during these 2-hour experiments.

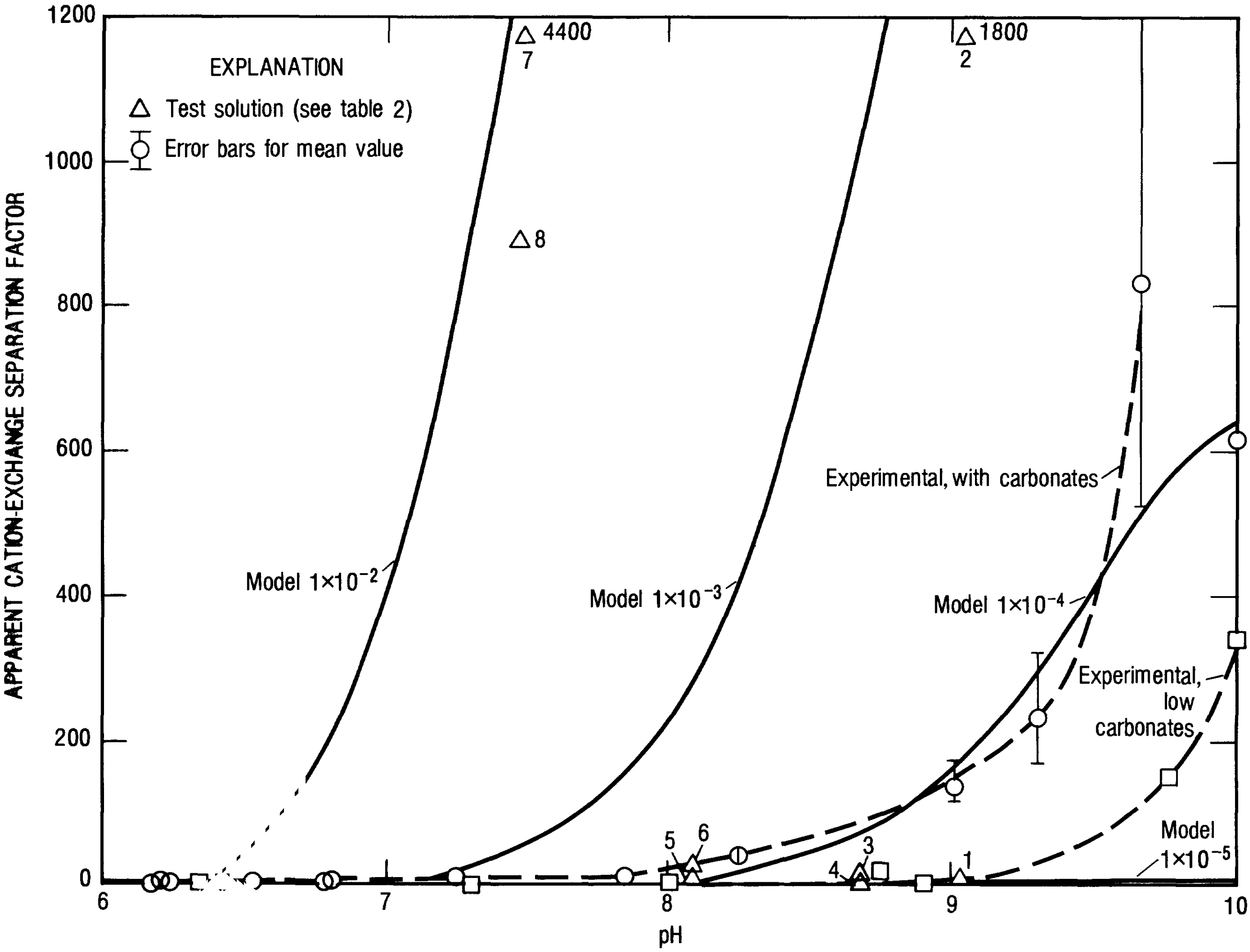


Figure 3. Apparent ion-exchange separation factor versus pH. All values represent total initial carbonate concentrations, in miles per liter.

This assumption was reasonable according to Pytkowicz's (1965) observation for sea water, a suggestion by Hanshaw and others (1966) for ground water, and the work of Mercado and Billings (1975) for ground water. In addition, the solubility product for $Cd(OH)_2$ was never exceeded at such small cadmium concentrations.

Results of the batch experiments also are shown in figure 3; these experiments were conducted to determine how well the model predicted experimental results. The pH and carbonate concentration were determined carefully for four experimental solutions (table 2, experimental 1, 3, 5, 7); these values were then used in the model (table 2, model 2, 4, 6, 8) to calculate α_{app}. The four paired sets of data (1, 2), (3, 4), (5, 6), and (7, 8) were plotted in figure 3. A significant correlation between experimental data and model calculations is indicated if the data points for each set plot near each other. Data points 3, 4 and 5, 6 indicated a significant correlation between experimental data and model calculations; also, a reasonable agreement between data points 7, 8 was evident. The model did not predict the experimental α_{app} for data point 1, probably because the experiment was not at equilibrium with respect to $CdCO_3$.

The same data presented in figure 3 also is presented in figure 4 but in a different manner. The percent loss of cadmium from solution was plotted versus pH. Solid lines represent the model-predicted values, and dashed lines represent a fit through experimental points. The "Experimental, few carbonates" curve showed the expected shift to the right compared to the "Experimental, with carbonates" curve when the quantity of carbonates available to precipitate cadmium was decreased. The effect that the large analytical error had on α_{app} (fig. 3) at small cadmium concentrations became almost insignificant in calculating error bars for percent cadmium loss from solution (fig. 4).

The model calculation, $CO_{3\,T,\,init.} = 1 \times 10^{-5}$ mol/L, showed that a maximum of 20 percent cadmium was removed by cation exchange. Increasing the $CO_{3\,T,\,init.}$ to

1×10^{-3} mol/L resulted in precipitation of $CdCO_3$, and almost 100-percent removal of cadmium at pH 8.3.

The four sets of numbered test points (table 2) also were plotted in figure 4. There is significant correlation between data points 3, 4 and 7, 8. Lesser correlation between experimental and model data is shown by data points 5, 6; there is no correlation between data points 1, 2.

The family of curves produced by the model when $CO_{3\,T,\,init.}$ was fixed at 1×10^{-4} mol/L and $Cd_{T,\,init.}$ was

Table 2. Key to test data points shown in figures 3 and 4

Data point	pH	Source	Time, in hours	Total analytical concentration of carbonate, in moles per liter	Apparent cation-exchange separation factor	Cadmium loss, in percent
1	9.03	Experimental	2.0	8×10^{-4}	6.9	22.0
2	9.03	Model	-	8×10^{-4}	1,800	97.5
3	8.68	Experimental	4.5	4×10^{-5}	13	45.1
4	8.68	Model	-	4×10^{-5}	12	42.0
5	8.08	Experimental	4.5	4×10^{-4}	8.5	42.5
6	8.08	Model	-	4×10^{-4}	25	66.4
7	7.46	Experimental	2.5	8×10^{-2}	4,400	98.9
8	7.46	Model	-	7×10^{-2}	900	95.4

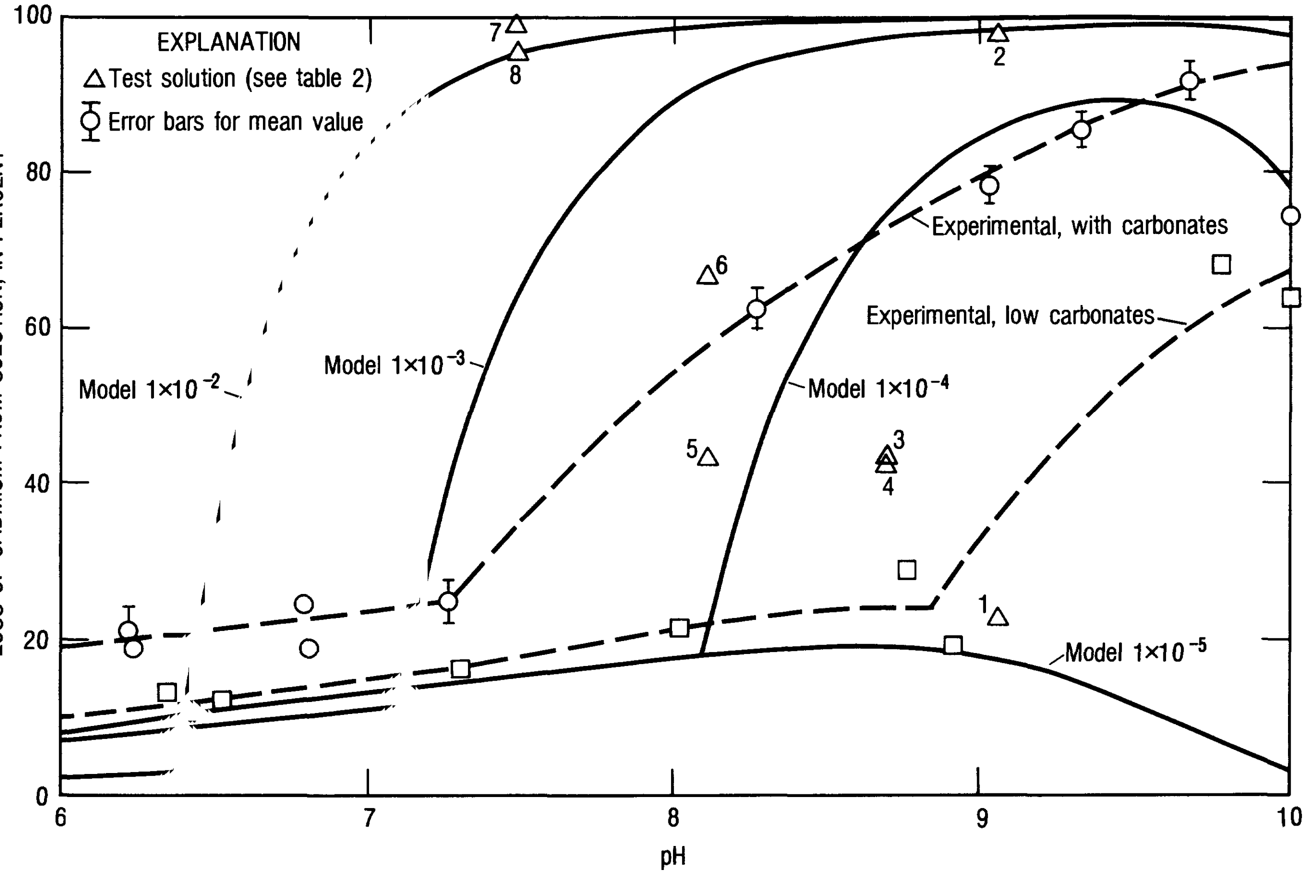


Figure 4. Experimental and theoretical percentage of cadmium lost from solution versus pH for various initial carbonate concentrations. All values represent total initial carbonate concentrations, in moles per liter.

varied from 300 to 1,200 μg/L is shown in figure 5. As expected, increasing the concentration of cadmium resulted in greater precipitation of $CdCO_3$ and more cadmium being removed from solution.

The mechanism of cadmium exchange was investigated by spiking a sand-water mixture that had been previously stirred for 1,011 minutes. The experiment proved that the predominant reaction was cadmium exchanging with calcium. The ratios of milliequivalents-per-liter change during the 60 minutes when the cadmium was allowed to react is shown in table 3. These ratios indicated that, at pH near 7, simple cation exchange was the predominant mechanism rather than an exchange with hydrogen ions that might have occurred in the presence of hydrous iron and manganese oxides.

Care needs to be taken when conducting experiments where precipitation of slightly soluble carbonate minerals could occur. Carbonate contamination of the experimental solutions in this study could come from the following sources:

1. Significant concentrations of carbonates were solubilized when acid-washed sand was shaken with deionized water for several days in the absence of air. Carbonate concentrations exceeding 2.4×10^{-4} mol/L were measured with a soil to water ratio of 1:5. This potential probably was not fully realized during the short time (120 minutes) of the batch experiments.
2. Carbonate contamination of the reagents was a possibility but was unquantified.
3. Carbonate contamination of solutions by carbon dioxide from the air. In the experiments, the air-to-water ratio was about 5:1 in stoppered reaction vessels. The carbon dioxide in this air could result in a potential contribution of 6×10^{-5} mol/L of carbonates. This source of contamination is pH dependent.

As shown by data in figure 3, preparing the reagent solutions and conducting the experiment under a nitrogen atmosphere significantly decreased the carbonate contamination from carbon dioxide.

CONCLUSIONS

Precipitation of $CdCO_3$ is a potential source of interference in attempts to determine cation-exchange separation factors. The magnitude and effect of this interference depends on the chemistry of each individual system and the time needed to attain equilibrium.

A simple computer model that involved only bulk-solution chemistry and cation-exchange reactions

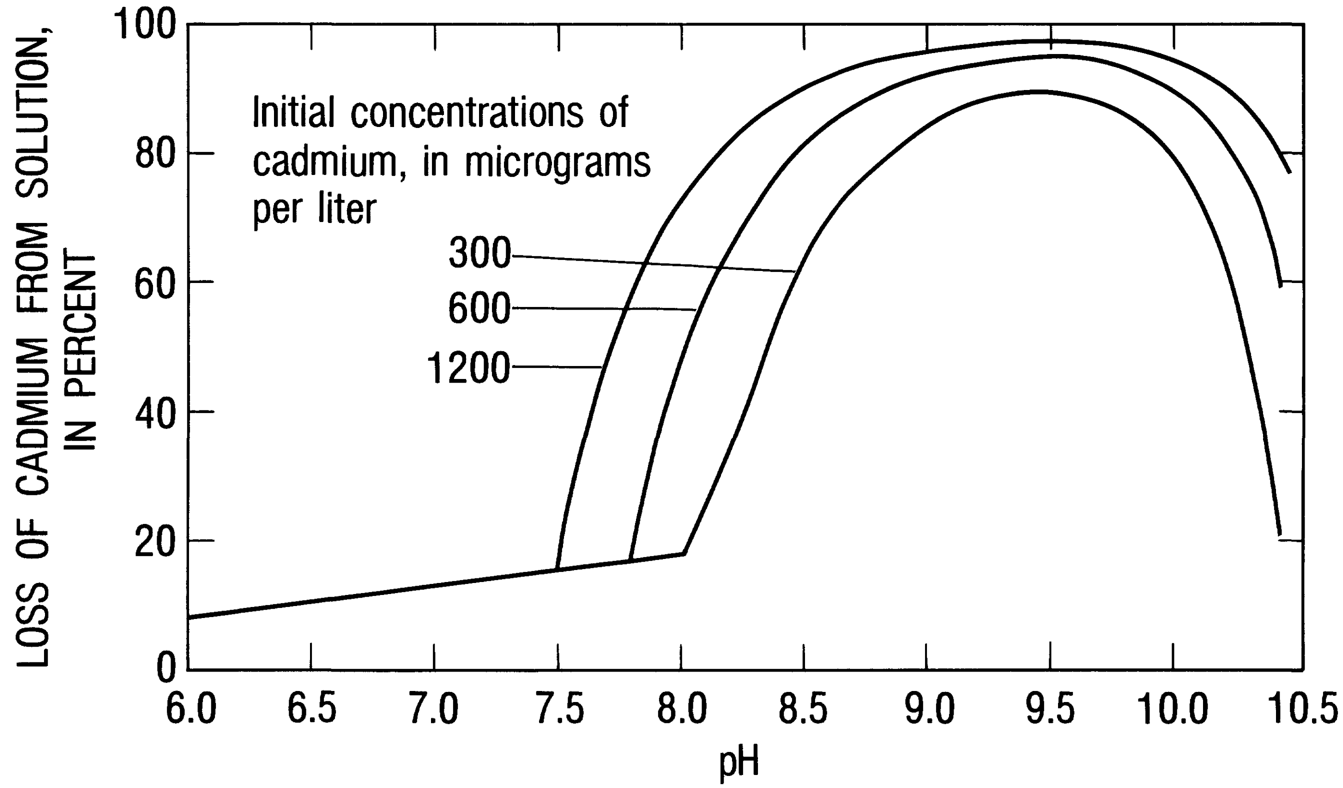


Figure 5. Theoretical percentage of cadmium lost from solution versus pH for various initial cadmium concentrations. Initial total carbonate concentration was 1×10^{-4} mol/L.

Table 3. Comparison of ratios of milliequivalents per liter exchanged during a 60-minute reaction period
[Initial pH value was 7.06; final was 6.84. Initial cadmium concentration was 14 mg/L. Δ = change in concentration]

Species	Simple cation exchange	
	Expected	Observed
$\Delta Cd/\Delta Ca$	− 1.00	− 1.3
$\Delta H_+/\Delta Cd$	0	-4.6×10^{-7}
$\Delta HCO_3^-/\Delta Cd$	0	+ .08
$\Delta HCO_3^-/\Delta Ca$	0	− .1

simulated batch experiments reasonably well. Although a simple approach cannot be expected to include all competing reactions of a real soil-water system, it still can be useful in modeling more complicated flowing systems, such as laboratory columns and aquifers.

DEFINITIONS

meq	milliequivalents
mol	mole
μ	ionic strength
γ_1	activity coefficient of ± 1 charged ions
γ_2	activity coefficient of ± 2 charged ions
[ ]	concentration in terms of activity
α	cation-exchange separation factor
α_{app}	apparent cation-exchange separation factor
CEC	cation-exchange capacity
ACS	American Chemical Society
a	activity
K_w	Dissociation constant of water
K_{sp}	solubility product
K_f	formation constant
K_1	first dissociation constant
K_2	second dissociation constant
pH	negative logarithm of the hydrogen ion activity
H_2O	water
H^+	hydrogen ion
OH^-	hydroxide ion
Cd^{+2}	cadmium ion
Ca^{+2}	calcium ion
$H_2CO_3^*$	sum of carbonic acid and aqueous carbon dioxide
HCO_3^-	bicarbonate ion
CO_3^{-2}	carbonate ion
$CaHCO_3^+$	calcium bicarbonate ion
$CaCO^0_{3(aq)}$	aqueous calcium carbonate
$CaCO_{3(s)}$	solid calcium carbonate
X^-	chloride plus acetate ion
$CdOH^+$	cadmium hydroxide ion
$Cd(OH)^0_{2(aq)}$	aqueous cadmium hydroxide
$Cd(OH)_{2(s)}$	solid cadmium hydroxide
$CdCO_{3(s)}$	solid cadmium carbonate
$CO_{3\,T,\,init.}$	initial total carbonate concentration
$Cd_{T,\,init.}$	initial total cadmium concentration

REFERENCES CITED

Black, C. A., and others, 1965, Methods of soil analysis, chemical and micro-biological properties: American Society of Agronomy, Inc., Agronomy series no. 9, part 2, p. 771-1572.

Bredehoeft, J. D., and Pinder, G. F., 1973, Mass transport in flowing ground water: Water Resources Research, v. 9, no. 1, p. 194-210.

Grove, D. B., 1976, Ion exchange reactions important in ground water quality models, *in* Saleem, Z. A., ed., Advances in groundwater hydrology: American Water Resources Association, p. 144–152.

______1977, The use of Galerkin finite-element methods to solve mass-transport equations: U.S. Geological Survey Water-Resources Investigations 77–49, 55 p.

Hanshaw, B. B., Back, William, and Rubin, Meyer, 1966, Carbonate equilibria and radiocarbon distribution related to ground water flow in the Floridan limestone aquifer: Symposium, Dubrovnik, Yugoslavia, IASH published proceedings, no. 74, v. 2, p. 601-614.

Helfferich, Friedrich, 1962, Ion exchange: New York, McGraw-Hill, 624 p.

Konikow, L. F., and Grove, D. B., 1977, Derivation of equations describing solute transport in ground water: U.S. Geological Survey Water-Resources Investigations 77-19, 30 p.

Meites, Louis, 1963, Handbook of Analytical Chemistry (1st ed.): New York, McGraw-Hill, 1782 p.

Mercado, A., and Billings, G. K., 1975, The kinetics of mineral dissolution in carbonate aquifers as a tool for hydrological investigations, I, Concentration-time relationships: Journal of Hydrology, v. 24, p. 303-331.

Pytkowicz, R. M., 1965, Rates of inorganic calcium carbonate nucleation: Journal of Geology, v. 73, no. 1, p. 196–199.

Rubin, A. J., 1974, Aqueous-environmental chemistry of metals: Ann Arbor, Michigan, Ann Arbor Science, 390 p.

Rubin, Jacob, and James, R. V., 1973, Dispersion-affected transport of reacting solutes in saturated porous media: Galerkin method applied to equilibrium-controlled exchange in unidirectional steady water flow: Water Resources Research, v. 9, no. 5, p. 1332-1356.

Skougstad, M. W., Fishman, M. J., Friedman, L. C., Erdmann, D. E., and Duncan, S. S., (eds.), 1979, Methods for determination of inorganic substances in water and fluvial sediments: U.S. Geological Survey Techniques of Water-Resources Investigations, Book 5, Chapter A-1, 626 p.

Snedecor, G. W., and Cochran, W. G., 1967, Statistical Methods (6th ed.): The Iowa State University Press, 593 p.

Stumm, Werner, and Morgan, J. J., 1970, Aquatic chemistry: New York, Wiley-Interscience, 583 p.

CONFIDENCE LIMITS FOR DETERMINING CONCENTRATION OF TRACER PARTICLES IN SEDIMENT SAMPLES

By Carl F. Nordin, Jr., *and* Paul W. Mielke, Jr.[1]

Abstract

Tracer-particle techniques often are used in sediment transport studies. The concentration of tracers is estimated by counting the number of tracer particles X in a sample of size n. The sample concentration, $\hat{C} = X/n$, is an estimate of the concentration of C of the population from which the sample was drawn. In this report, the confidence limits for the sample concentrations are derived under the assumption that each particle in the sample has the probability of being a tracer equal to C.

INTRODUCTION

Tracer-particle techniques have the potential for wide applications in sediment-transport studies. The techniques may be used to determine bed-material and bed-load discharge, to estimate the rates of dispersion of particles, and to measure the mean velocities of various sizes of particles (Rathbun and Nordin, 1971). Radioactive tracers often were used in earlier applications; they have the distinct advantage that their distributions can be determined in situ with radiation detection equipment (Hubbell and Sayre, 1964). However, because environmental regulations make it difficult to introduce radioactive materials into rivers, fluorescent tracers generally are used.

In fluorescent tracer applications, it is necessary to sample through the depth of moving sediments and to determine the concentration of marked particles in the samples. The sample concentration, $\hat{C}$, is an estimate of the the concentration C of the population from which the sample was taken. The purpose of this report is to derive confidence limits for sample concentrations.

THEORY

Suppose that tracer particles are introduced, either as an instantaneous point or line source, or as a continuous source through some feed system, into a flowing stream that is transporting sediment particles with properties similar to the properties of the tracer particles. Downstream of the introduction point, a quantity of moving sediment with a concentration C of tracer particles is collected. The concentration, C, which is the ratio of the number of tracer particles to the total number of particles in the mixture, may vary from negligible quantities to about 0.5. Thus, in 1 kg of fine sand, the number of tracer particles may range upward to several million.

Usually, it is not practical to count all the tracer particles in a mixture to determine C. Instead, one will estimate C by analyzing a subsample of n particles with X tracers, $\hat{C} = X/n$. The question arises, what should be the number n to insure that the estimated concentration $\hat{C}$ is within some prescribed percentage of the true concentration C at a given confidence level? Knowing n, the expected value of X, E {X}, can be computed from the relation E {X} = nC.

We assume that the sample is well mixed. Thus, in an independent sample of size n, each particle has the probability C of being a tracer particle.

The answer to this question is formulated in the following manner. Consider the constants α and β, and C specified, with $0<\alpha<1$, $0<\beta<1$, and $0<C<1$. It then needs to be determined for what value of n the following relation will hold:

$$P\left[1-\alpha<\frac{\hat{C}}{C}<1+\alpha\right]=1-\beta\ , \qquad (1)$$

where P denotes probability.

If the sample is well mixed, X is a random variable that follows the binomial distribution (see, for example, Feller, 1957, p. 136):

$$P[X=x]=\binom{n}{x}C^{x}(1-C)^{n-x},\ x=0,\ 1,\ \ldots,\ n. \qquad (2)$$

For large n, X is approximately distributed as the normal distribution with mean nC and variance nC(1 − C) (Feller, 1957, p. 168–173),

$$X\left(\overset{d}{=}\right)N[nC,\ nC(1-C)]\ . \qquad (3)$$

---

[1] Colorado State University, Fort Collins, CO 80521.

where $\left(\overset{d}{=}\right)$ denotes approximately distributed according to, and

N denotes normal distribution.

Therefore,

$$\frac{\hat{C}}{C} = \frac{X}{nC} \left(\overset{d}{=}\right) N \left[1, \frac{1-C}{nC}\right] \tag{4}$$

Consider now a standardized normal variable, z, with zero mean and unit variance, $z \overset{d}{=} N\ (0,\ 1)$, where $\overset{d}{=}$ denotes distributed according to. Then let

$$P(z > \xi) = \beta/2. \tag{5}$$

where ξ is a real number, $-\infty < \xi < +\infty$.
With β specified, values of ξ can be obtained directly from a table of the standardized normal variable. Applying equation 5 to equation 4 yields

$$P(1-\alpha < \frac{\hat{C}}{C} < 1+\alpha) = 1-\beta$$

$$(=)\ P\left(1 - \xi\sqrt{\frac{1-C}{nC}} < \frac{\hat{C}}{C} < 1 + \xi\sqrt{\frac{1-C}{nC}}\right). \tag{6}$$

From equation 6,

$$n(=)\left(\frac{\xi}{\alpha}\right)^2 \frac{1-C}{C}, \tag{7}$$

$$E\{X\} = nC\ (=)\left(\frac{\xi}{\alpha}\right)^2 (1-C)\ . \tag{8}$$

From equations 7 and 8, values of n and the expected values of X can be computed for any values of α, β, and C.

DISCUSSION OF RESULTS

Equations 7 and 8 for $\beta = 0.1$ and for several values of α are plotted on figure 1. For dilute concentrations, say below 0.1, n varies inversely with concentration, and the expected number of tracer particles, E {X} is nearly a constant.

Families of curves similar to those in figure 1 for any values of β can easily be plotted to assist in sample analysis and in estimating confidence intervals of the concentrations determined by analysis. For example, suppose 10^4 particles are to be counted. From figure 1, it is seen that the estimated concentration, C, will be within 40 percent of the true concentration in 9 of 10 samples on the average only if the concentration is greater than 2×10^{-3}. For more dilute concentrations, a larger number of particles must be counted to obtain the same accuracy of concentration estimates.

Usually, one is interested in particle velocities or in transport and dispersion rates as functions of particle size. If so, the sample is sieved into narrow size classes, and the tracer particles are counted in each size class. In this case, it is more convenient to work with concentration on a weight basis, because the weight of the total sample analyzed in each size class (equivalent to n, total number of particles) is easily determined. X is converted to a weight basis by weighing a known number of particles in each of several narrow sieve-size ranges and by plotting the number of particles per gram against the geometric mean sieve diameter. The relation between diameter and number of particles per gram for quartz tracer particles used by Rathbun and others (1971) is shown in figure 2. As expected, the number of particles per gram varies inversely with approximately the square of the particle diameter. Because the relationship will vary somewhat, depending on particle densities and shape factors, curves should be prepared for each tracer material used.

REFERENCES CITED

Feller, William, 1957, An introduction to probability theory and its applications (2d ed.): New York, John Wiley & Sons, Inc., 461 p.

Hubbell, D. W., and Sayre, W. W., 1964, Sand transport studies with radioactive tracers: American Society of Civil Engineers Proceedings, v. 90, no. HY 3, p. 39–68.

Rathbun, R. E., Kennedy, V. C., and Culbertson, J. C., 1971, Transport and dispersion of fluorescent tracer particles for the flat-bed condition, Rio Grande conveyance channel, near Bernardo, New Mexico: U.S. Geological Survey Professional Paper 562-I, 56 p.

Rathbun, R. E., and Nordin, C. F., 1971, Tracer studies of sediment transport processes: American Society of Civil Engineers Proceedings, v. 97, no. HY 9, p. 1305–1316.

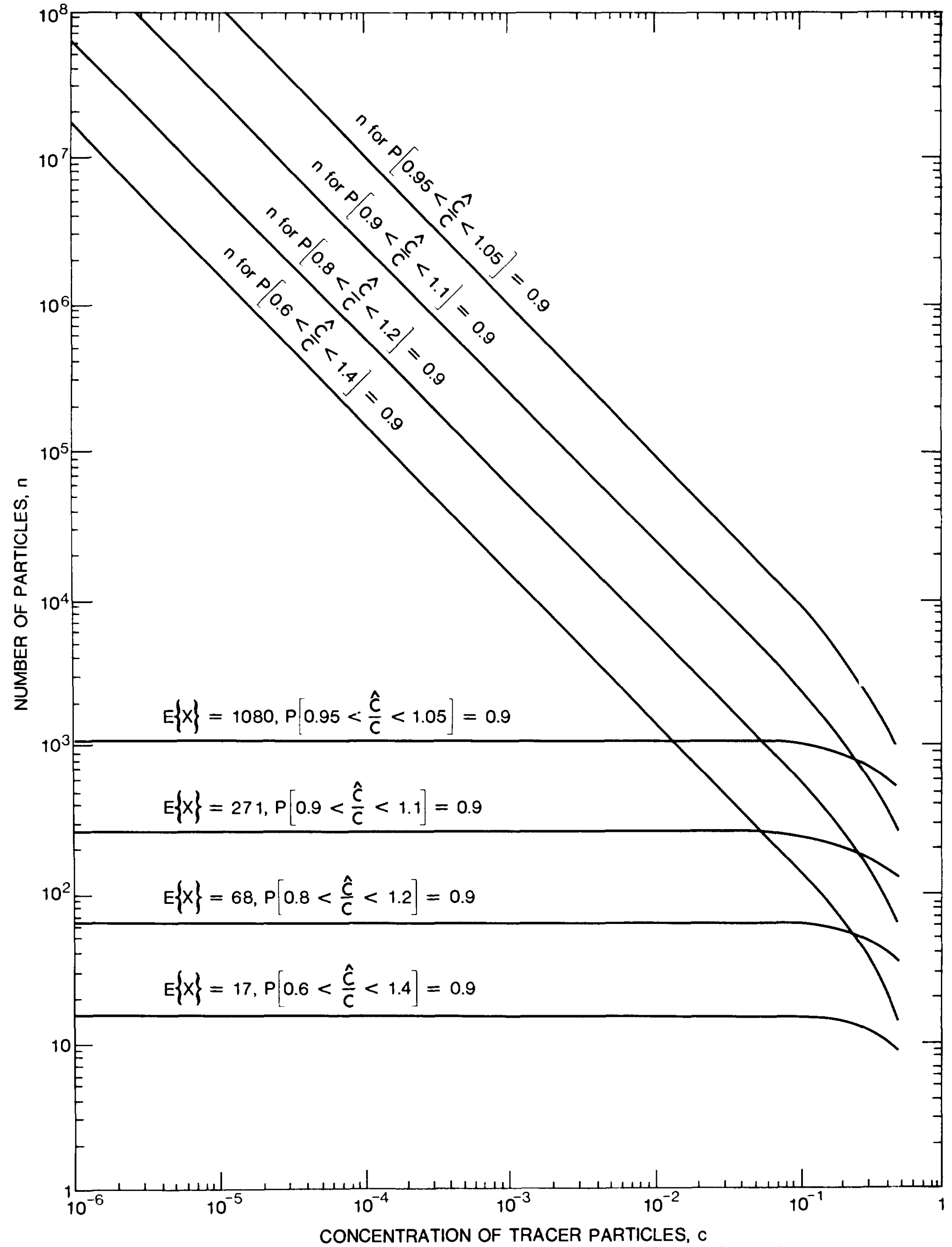


Figure 1. Total number of particles, n, and expected number of tracer particles, {E}X, as a function of concentration, C.

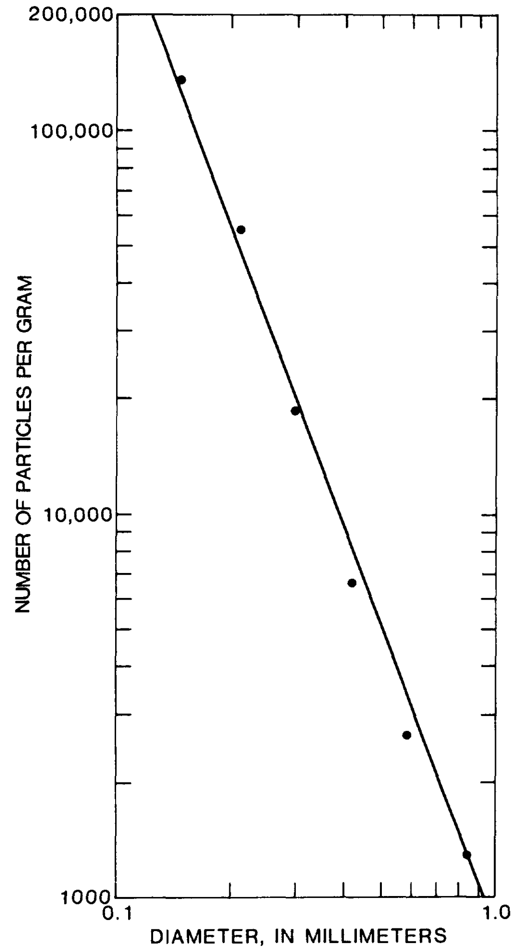


Figure 2. Relation between diameter and number of particles per gram for quartz tracer particles used by Rathbun and others (1971).

DETERMINATION OF AQUATIC HUMIC SUBSTANCES IN NATURAL WATERS

By E. M. Thurman

Abstract

Aquatic humic substances in 50-milliliter samples are measured at the microgram-per-liter level following desorption of the adsorbed humic material from a macroporous resin with 0.1 normal sodium hydroxide. The resulting eluate is quantified by measuring dissolved organic carbon. The method is quantitative, rapid, simple, and inexpensive.

INTRODUCTION

Aquatic humic substances are an important constituent of the dissolved organic carbon (DOC) in water and account for 30 to 50 percent of the DOC. Some researchers hypothesize that humic substances, originating in the soil and sediments of a watershed, are leached by subsurface drainage and surface flow (Wetzel, 1975; Beck and others, 1974; Wilson and Weber, 1977). Also, terrestrial vegetation is an important source for colored organic acids in water (Thurman and Malcolm, 1981a). Humic substances are known to complex trace metals and are implicated in the solubilization of hydrophobic organic compounds, including some pesticides and hydrocarbons (Schnitzer and Khan, 1972). The study of sources of dissolved humic substances and their role in transport of trace metals and hydrophobic organic solutes is difficult without a convenient, accurate assay for aquatic humic substances.

Present assays for aquatic humic substances include (1) tannins and lignin (a part of humic substances), which are determined by a colorimetric procedure (American Public Health Association and others, 1980), (2) color, which is determined by measuring absorbance at 400 nm and relating this to humic concentration (Gjessing, 1976), (3) fulvic acid, tannins, and lignins, which are determined by using visible and ultraviolet absorbance measurements of natural waters (Lawrence, 1980), (4) humic acid, which is determined by a colorimetric procedure using liquid extraction into isoamyl alcohol (Martin and Pierce, 1971), and (5) humic substances, which are determined by liquid extraction of ion pairs quantified by spectrometric measurements (Eberle and Schweer, 1974). None of these methods determine the quantity of organic carbon that is aquatic humic substances. Rather, the methods measure a characteristic of the organic matter, such as color or phenol content.

This paper presents a simple, quantitative assay for aquatic humic substances based on adsorption chromatography on XAD resins. The adsorbed substances are eluted with a basic solution and quantified by DOC. This paper also addresses the semantic question, What are aquatic humic substances? Because no known structure for aquatic humic substances and no reagent labeled aquatic humic substances exist, there is no simple answer to this question. First, to evaluate an assay method for aquatic humic substanes, one needs to define aquatic humic substances and to relate this definition to soil humic substances. Second, one needs to show that this method measures this defined substance to some degree of accuracy and precision. The method presented here only validly measures "aquatic humic substances," which are defined as follows:

Aquatic humic substances are colored, polymeric acids isoloated from water on XAD resins; these nonvolatile organic substances range in molecular weight from 500 to more than 5,000 (Thurman and others, 1982); they are derived from plant, soil, and aquatic processes; their elemental composition is approximately 52-percent carbon, 4- to 5-percent hydrogen, 35- to 40-percent oxygen, 1- to 2-percent nitrogen, and less than 1-percent sulfur and phosphorous; and their major functional groups include carboxylic acids, phenolic hydroxyls, and hydroxyls.

This operational definition of aquatic humic substances is related to the isolation procedure (Thurman and Malcolm, 1981b), which was developed during the last decade. With the development of macroporous resins during the late 1960's and early 1970's, Riley and Taylor (1969) and Mantoura and Riley (1975) were able to isolate successfully aquatic humic substances by adsorption onto XAD resins. During the late 1970's, Aiken and others (1979) examined the mechanisms of adsorption of humic substances onto various XAD resins and reached the conclusion that the acrylic ester copolymer, XAD–8, was best suited for efficient adsorption and elution of aquatic humic substances. Thurman and Malcolm (1981b) extended these studies to the development of a procedure for the isolation of gram quantities of aquatic humic substances with XAD-8 resin. Therefore, the operational definition of aquatic humic substances includes the isolation prodcedure on XAD resins.

How does the definition of aquatic humic substances compare with the term "humic substances" used by soil scientists and used to define dissolved organic matter in water (aquatic humic substances)? Because the definition of humus originated in the soil literature, this is an important question. Humic substances are defined as the organic matter extracted from soil by 0.1 normal sodium hydroxide (0.1*N*NaOH). The fraction that precipitates in acid is humic acid, and the fraction that remains in solution is fulvic acid (Schnitzer and Khan, 1972). This definition is too general to compare with the operational definition of aquatic humic substances. Therefore, the best comparison is among the general chemical characteristics of humic substances from soil and water.

The comparison of soil and aquatic humic substances shows them to be similar. Both are polymeric, colored acids with comparable molecular weights. Their elemental composition is similar, as is their functional group analysis. This does not prove that humic substances from soil and water are the same; it merely demonstrates that their general chemical characteristics are similar (Thurman and Malcolm, 1981a). Determining the sources of humic substances in water remains an important research problem, which is still under investigation.

Therefore, the assay presented here for aquatic humic substances measures polymeric organic acids with the general characteristics of humic substances from soil. Also, the assay measures the amount of carbon in the aquatic humic fraction. For these reasons, this assay is a valid measure of aquatic humic substances in natural waters.

ACKNOWLEDGEMENTS

I wish to thank my colleagues Ronald Malcolm, George R. Aiken, Harold A. Stuber, Jerry A. Leenheer, and Steve Wilson for their help and review of theory and manuscript.

ASSAY FOR AQUATIC HUMIC SUBSTANCES

Range of Application

The assay for aquatic humic substances may be applied directly to water samples when concentrations of aquatic humic substances range from 50 μg C/L to 20 mg C/L (carbon per liter). If the concentration of humic substances is more than 20 mg C/L, the sample is diluted to this concentration with distilled water. If the concentration of humic substances is less than 50 μg C/L, the carbon analyzer will not reliably measure the concentration of carbon in the eluate. However, the concentrations of humic substances in natural waters generally are more than 50 μg C/L—concentrations of humic substances in ground waters range from 50 to 200 μg C/L (Thurman, 1984a); concentrations in snowmelt waters are 50 μg C/L or more (Thurman, 1984b); concentrations in sea water range from 100 to 250 μg C/L (Stuermer and Harvey, 1977); concentrations in most surface waters range from 100 μg C/L to 4 mg C/L (Thurman, 1984b); and concentrations in drainage from wetlands, such as bogs, marshes, and swamps, range from 10 to 100 mg C/L (E. M. Thurman, unpub. data). Thus, the assay is applicable for most natural waters.

Summary of Method

Aquatic humic substances are concentrated from 50 mL of water on a macroporous adsorbent, XAD-8, at pH 2.0. A 25-cm column of resin is eluted with 0.1 *N* NaOH, and the eluate is quantified by DOC. Influent, effluent, and eluate DOC's are measured; thus, the percentages of DOC adsorbed onto the column and eluted from the column are measured. Aquatic humic substances are the DOC eluted from the column. A diagram of the microcolumn is shown in figure 1.

Interferences

Suspended organic matter will foul the resin and bias the determination. Therefore, filter the water sample prior to analysis using the method described by Malcolm and McKinley (1972).

A few samples will form organic precipitates when they are acidified to pH 2.0; this is due to the presence of humic acid. Care needs to be taken that these precipitates are slurried and pumped into the column.

DOC from the resin, in concentrations of as much as 0.5 mg C/L, will contaminate the samples. Therefore, it is critical to follow the resin cleanup procedure to minimize this contamination, especially if the concentrations of aquatic humic substances are less than 200 μg C/L. Also, the carbon contamination from pump tubing needs to be checked with the eluting solvent, sodium hydroxide. Generally, contamination of organic carbon from the tubing is less than 0.5 mg C/L.

Low-molecular-weight acids (for example, fatty acids), which are nonhumic substances, are concentrated with humic substances, if their capacity factor k′, is

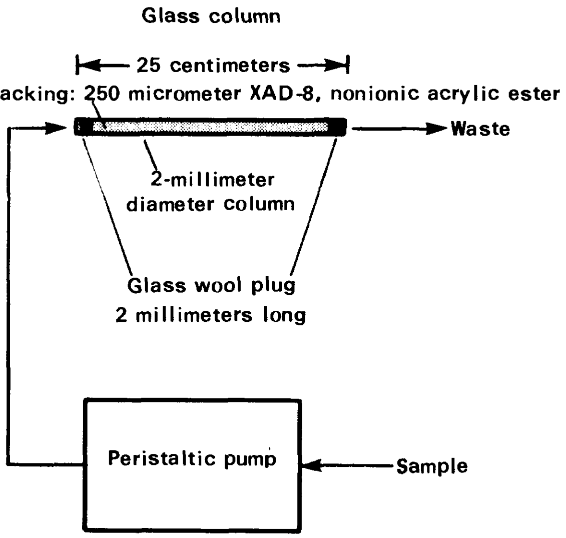


Figure 1. Diagram of sample flow through microcolumn of XAD-8.

within the range of concentration of the resin (see "Discussion of Adsorption of Humic Substances"). Typically, simple fatty acids and phenols occur in water in microgram-per-liter concentrations (Williams, 1961; Slowey and others, 1962; Lamar and Goerlitz, 1963; Hullett and Eisenreich, 1979; Barcelona and others, 1980), and humic substances are the major acidic component. Therefore, these nonhumic acids usually cause only a minor error in the assay, approximately 5 percent or less of the acidic components.

However, in waters polluted by man, such as sewage effluents, the amount of organic acids present would interfere with the humic substances determination. In this instance, fatty acids would contribute from microgram to milligram amounts of organic carbon. In a previous study, fatty acids contributed 15 percent of the carbon present in the humic substances fraction (Thurman and Malcolm, 1979). This probably represents the maximum interference by low-molecular-weight acids.

Column Preparation

The resin, XAD-8, obtained from Rohm and Haas, Philadelphia, is a spherical packing sized to 250 μm by dry screening. Prior to column packing, clean the resin with successive treatments of 0.1 *N* NaOH for 5 days. During this period, the concentration of DOC of the cleansing solution decreases from 1,000 to 10 mg C/L. Next, extract the resin in a soxhlet with hexane, methanol, acetonitrile, and methanol, for 24 hours each. After this extensive cleanup, pack the resin into a 0.2- by 25-cm glass column that has a 2-mm length of glass wool in one end. After filling the tube, seal the column with another 2-mm length of glass wool.

After dry packing the column, wet it with methanol. When the air has been displaced from the column, pump distilled water through the column until the concentration of DOC decreases to 0.5 mg C/L, determined on a Beckman 915 carbon analyzer (oxidative combustion and infrared detection), a Technicon analyzer, or comparable instrument. At this point, clean the column three times with 0.1 *N* NaOH and 0.1 *N* hydrochloric acid (HCl) alternating between the two solvents. Now the column is ready for use. It is *important* that the resin is cleaned with a basic and acidic solution just prior to use.

Procedure

Collect the samples in organic-free glass containers. Filter 51 mL of sample through a 0.45-μm silver membrane filter (Malcolm and McKinley, 1972) or equivalent filter. Chill the samples to 4°C for sample preservation.

Take a 1-mL aliquot of sample for DOC analysis. Preclean the column with three cycles of 0.1 *N* NaOH and 0.1 *N* HCl just prior to pumping the sample into the column. Determine blank carbon anaylsis on the final NaOH rinse. Leave the column saturated with 0.1 *N* HCl. Acidify 50 mL of sample to pH 2.0 with concentrated HCl, and pump it into the column with a peristaltic pump at a flow rate of 1.0 mL/min (fig. 1). Save the 50 mL of effluent that passes the column for DOC analysis. The colored organic acids will adsorb at the top of the column. Now back elute the column with the eluant of 0.1 *N* NaOH at a rate of 0.2 mL/min. Approximately 1 mL of solution is pushed ahead of the NaOH front. Discard; there should be virtually no aquatic humic substances in this fraction. As the pH starts to increase from 2.0 (monitored with pH paper), change the eluate to distilled water because sufficient basic solution is present to elute the organic acids. Then collect 0.9 mL of eluate in a 1.0-mL volumetric flask, and add 0.1 mL of concentrated phosphoric acid to acidify the sample. Determine the DOC on original sample, effluent, and eluate.

Calculations and Precision

The difference between the DOC of the influent and effluent reflects the amount of adsorbed carbon on the XAD resin. The organic matter that adsorbs on the XAD resin is called the hydrophobic fraction (Leenheer and Huffman, 1976). The DOC of the NaOH eluate is the hydrophobic acid fraction (Leenheer and Huffman, 1976). This fraction contains the aquatic humic substances (approximately 90–100 percent of the DOC of the eluate, as discussed earlier in the section on "Interferences"). Therefore, aquatic humic substances are calculated from the following equation:

AHS = (NaOH eluate in mg C/L) (volume of eluate in liters)/ (volume of sample in liters),

where AHS is aquatic humic substances.

Carbon analysis of the eluate limits the method's precision to ± 2 percent. This is the principal analytical error along with the blank from the resin column in NaOH, typically 0.5 mg C/L. This resin blank adds another 1-percent error for most natural waters. The final error is due to nonhumic substances that may vary from 1 to 5 percent of the total hydrophobic fraction. These errors give a final precision of 4 to 8 percent for the concentration of aquatic humic substances in water. This precision range is as good as the measurement of the original DOC of the sample which is ± 0.1 mg C/L at 2.0 mg C/L determined using a Technicon DOC analyzer (E. M. Thurman, unpub. data). Multiple analyses of humic substances in tap water gave a precision of ± 6 percent as shown in the following section.

Recovery and Comparison of Method

The concentration of aquatic fulvic acid determined by the XAD-8 method and a color method (Gjessing, 1976; Eberle and Schweer, 1974; Martin and Pierce, 1971), and the gravimetrically determined value, which is the weighed-out value of fulvic acid from each of the 10 samples of ground waters, rivers and lakes, and wetlands, are compared in table 1. The color method is based on an average gram-extinction coefficient at 400 nm. Because humic substances from different sources vary in their molar-extinction coefficient, the results obtained with this method will vary. The average deviation from the gravimetric value for the color method for the 10 samples in table 1 was 39 percent. This is a combination of variation in gram-extinction coefficients and absorbance measurements. The average deviation from the gravimetric value for the XAD-8 method was 6.2 percent. This deviation is caused by a combination of variation in the percentage of carbon in humic substances and variation in DOC determinations. Thus, the XAD-8 method gives more accurate values than does the color method.

DISCUSSION OF ADSORPTION OF HUMIC SUBSTANCES

Because the adsorption of humic substances is discussed in the previous reports of Mantoura and Riley (1975), Thurman and others (1978), Aiken and others (1979), and Leenheer (1981), only a review of important adsorption theory will be given here. The resin adsorbs by the hydrophobic effect, and aqueous solubility is used to estimate concentration factors. Thurman and others (1978) found that solubility could be related to k'

Table 1. Comparison of concentration of fluvic acid determined by XAD-8 method and color methods
[Data in milligrams per liter fluvic acid]

Sample	Color method	XAD-8 method	Gravimetric value
Ground Waters:			
Denver, Colo.	0.07	0.48	0.40
Yuma, Ariz.	.88	2.0	2.0
Miami, Fla.	8.4	16.0	16.5
Rivers and Lakes:			
Brainard Lake (Ward, Colo.)	1.6	1.8	2.0
Hawaii stream (Hawaii, Hawaii)	2.1	1.9	2.0
Yampa River (Yampa, Colo.)	2.1	2.0	2.0
Shawsheen River (Mass.)	4.7	3.9	4.0
Wetlands:			
Suwannee River (Fargo, Ga.)	59.0	59.0	60.0
Thoreau's bog (Concord, Mass.)	104.0	56.0	60.0
Hawaii marsh (Hawaii, Hawaii)	26.0	13.0	15.0
Average percent deviation	39.0	6.2	0.0

Standard solutions of fluvic acid were made up of 10 samples from various origins and determined by the color method (Gjessing, 1976; Eberle and Schweer, 1974) with an average gram-extinction coefficient of 4.47 and by the XAD-8 method with an average carbon concentration of 52 percent.

of the solute retained. Solubility was quantitatively related to k′ by an empirical equation:

$$\log k' = 1.78 - 0.52 \log \text{molar solubility}.$$

Thus, if the solubility of the solute is known, k′ may be estimated to a first approximation by this equation.

It is apparent that the solubility of the solute controls its k′ for the resin. The ionic character of the solute will increase solubility and decrease k′; therefore, acidic, organic solutes adsorb when protonated and elute when ionic. When the ratio of functional groups to carbon atoms is approximately 1:12, even ionic solutes are retained by the resin. For these reasons, organic acids, such as the humic substances, need to be adsorbed at an acidic pH. Humic substances, with a ratio of one carboxyl group to six carbon atoms, elute efficiently with a basic solution. When the functional groups ionize, the humic substances have no affinity for the resin. Elution efficiency is further improved by back elution of the column.

Adsorption of organic solutes onto the resin is a type of frontal chromatography, that is, solutes are adsorbed continuously while water is pumped through the column. The equation that relates k′ to the volume of sample is

$$2V_0(1 + k') = V_{50},$$

where V_0 is the void volume of the column (0.65 × bed volume), and

V_{50} is the volume of sample passed through the column when 50 percent of the solute is retained on the resin.

This equation quantifies the relationship between percentage solute-retention, volume of sample, and column volume. This V_{50} is not the same as V (one-half). V is the volume passed through the column when the concentration leaving the column is one-half of the concentration entering the column. The term V commonly is used in liquid chromatography to measure k′. For example, the assay presented here uses a 50-mL sample and a column of 1-mL bed volume. The capacity factor at 50 percent retention is calculated,

$$2(0.65)(1 + k') = 50,$$
$$k' = 37.5.$$

Therefore, 50 percent of the solutes with a capacity factor of 37.5 are retained. Thus, k′ is defined as the mass of solute on the resin per mass of solute in the water phase. As an example of what k′ = 37.5 means: A three-carbon acid such as proprionic acid has a k′ of 13, butyric acid with four carbons has a k′ of 39, and valeric acid with five carbons has a k′ of 100. Thus, a k′ of 37.5 would retain 50 percent of the butryic acid in the sample or 50 percent of another solute with similar solubility.

The k′ of humic substances ranges from 50 to more than 100 (Aiken and others, 1979), but this range of k′ is dependent on the structure of the aquatic humic substances. Solubility factors, such as functional groups, aromaticity, and carbohydrate content, decrease the k′ and the affinity of the resin for the humic substances.

Because of these factors, k′ for humic substances ranges from 0 to 1,000 in natural samples (E. M. Thurman, unpub. data). In spite of many different capacity factors of aquatic humic substances for the resin, the method is an effective tool to measure and compare the amount of aquatic humic substances in water. In practice, this method removes 40 to 60 percent of the DOC of most waters and approximately 85 to 100 percent of the visible color or absorbance at 400 nm.

APPLICATIONS

This method has been used successfully on samples from an alpine watershed in Colorado to determine the input of hydrophobic acids (chiefly aquatic humic substances) to the watershed from the surrounding terrain. Concentrations of aquatic humic substances as small as 50 μg C/L were detected. The method works best when the concenration of aquatic humic substances or hydrophobic acids is greater than 0.3 mg C/L. At the concentration of 50 μg C/L, the eluate is 50 times greater, or 2.5 mg C/L. At this concentration, a Technicon carbon analyzer was used; care was taken to assure blank concentrations of 0.5 mg C/L in the NaOH eluate.

Small concentrations of humic substances have been found in snowmelt (50–100 μg C/L) and in pristine alpine streams (0.3 mg C/L or more of aquatic humic substances). At concentrations as low as these, the eluate DOC is 15 mg C/L, which is substantially greater than resin blanks of 0.5 mg C/L and is in the range of the Beckman 915 carbon analyzer.

There are a few other examples of the usefulness of the assay for aquatic humic substances. This method has been used to concentrate and measure the amounts of colored organic acids in the leachates of plants in an alpine bog, a primary source of organic acids in some watersheds. Soil and sediment leachates may be examined by this technique to measure the amount of humic substances leached by water from these sources.

REFERENCES CITED

Aiken, G. R., Thurman, E. M., Malcolm, R. L., and Walton, H. F., 1979, Comparison of XAD macroporous resins for the concentration of fulvic acid from aqueous solution: Analytical Chemistry, v. 51, p. 1799-1803.

American Public Health Association, American Water Works Association, and Water Pollution Control Federation, 1980, Standard methods for the examination of water and wastewater (15th ed.): Washington, D.C., American Public Health Association, 1134 p.

Barcelona, M. J., Liljestrand, H. M., and Morgan, J. J., 1980, Determination of low molecular weight volatile fatty acids in aqueous samples: Analytical Chemistry, v. 52, p. 321-325.

Beck, K. C., Reuter, J. H., and Perdue, E. M., 1974, Organic and inorganic geochemistry of some coastal plain rivers of the southeastern United States: Geochimica et Cosmochimica Acta, v. 38, p. 341-364.

Eberle, S. B., and Schweer, H. K., 1974, Determination of humic acid and lignosulfonic acid in water by means of liquid-liquid extraction: Vom Wasser, v. 41, p. 27-44.

Gjessing, E. T., 1976, Physical and chemical characteristics of aquatic humus: Ann Arbor, Ann Arbor Science, 120 p.

Hullett, D. A., and Eisenreich, S. J., 1979, Determination of free and bound fatty acids in river water by high performance liquid chromatography: Analytical Chemistry, v. 51, p. 1953-1960.

Lamar, W. L., and Goerlitz, D. F., 1963, Characterization of carboxylic acids in unpolluted streams by gas chromatography: Journal of American Water Works Association, v. 55, p. 797-802.

Lawrence, J., 1980, Semiquantitative determination of fulvic acid, tannin, and lignin in natural water: Water Research, v. 14, p. 373-377.

Leenheer, J. A., 1981, A comprehensive approach to preparative isolation and fractionation of dissolved organic carbon from natural wastes and wastewaters: Environmental Science and Technology, v. 15, p. 578-587.

Leenheer, J. A., and Huffman, E. W. D., Jr., 1976, Classification of organic solutes in water by using macroreticular resins: U.S. Geological Survey Journal of Research, v. 4, p. 737-751.

Malcolm, R. L., and McKinley, P. W., 1972, Collection and preservation of water samples for carbon analysis, *in* Goerlitz, D. F., and Brown, Eugene (eds.), Methods for analysis of organic substances in water: U. S. Geological Survey Techniques of Water-Resources Investigations, Supplement I to Book 5, Chapter A3, 6 p.

Mantoura, R. F. C., and Riley, J. P., 1975, The analytical concentration of humic substances from natural waters: Analytica Chimica Acta, v. 76, p. 97-106.

Martin, D. F., and Pierce, R. H., Jr., 1971, A convenient method of analysis of humic acid in fresh water: Environmental Letters, v. 1, p. 49-52.

Riley, J. P., and Taylor, D., 1969, The analytical concentration of traces of dissolved organic materials from sea water with Amberlite XAD-1 resin: Analytica Chimica Acta, v. 46, p. 307-309.

Schnitzer, Morris, and Khan, S. U., 1972, Humic substances in the environment: New York, Marcel Dekker, Inc. 319 p.

Slowey, J. F., Jerffrey, L. M., and Hood, D. W., 1962, The fatty acid content of ocean water: Geochimica et Cosmochimica Acta, v. 26, p. 607-616.

Stuermer, D. H., and Harvey, G. R., 1977, The isolation of humic substances and alcohol-soluble organic matter from seawater: Deep-Sea Research, v. 24, p. 303-309.

Thurman, E. M., 1984a, Humic substances in ground water, *in* McKnight, D. M., Aiken, G. R., Wershaw, R. L., McCarthy, P., eds., Humic substances in water and soil: International Conference on Humic Substances in Water and Soil, 1st Proceedings, Wiley & Sons (in press).

______1984b, Organic geochemistry of natural waters: The Hague, Martinus Nijhoff (in press).

Thurman, E. M., and Malcolm, R. L., 1979, Concentration and fractionation of hydrophobic organic acid constituents from natural waters by liquid chromatography: U.S. Geological Survey Water-Supply Paper 1817-G, 16 p.

______1981a, Abstract no. 7, symposium on humic substances in coal, soil and aquatic environments: American Chemical Society Meeting, March 1981, 1 p.

______1981b, Preparative isolation of aquatic humic substances: Environmental Science and Technology, v. 15, p. 463-466.

Thurman, E. M., Malcolm, R. L., and Aiken, G. R., 1978, Prediction of capacity factors for aqueous organic solutes adsorbed on a porous acrylic resin: Analytical Chemistry, v. 50, p. 775-779.

Thurman, E. M., Wershaw, R. L., Malcolm, R. L., and Pinckney, D. J., 1982, Molecular size of aquatic humic substances: Journal of Organic Geochemistry, v. 4, p. 27-35.

Wetzel, R. G., 1975, Organic carbon cycle and detritus, *in* Limnology: Philadelphia, W. B. Saunders Co., p. 583-621.

Williams, P. M., 1961, Organic acids in Pacific Ocean waters: Nature, v. 189, p. 219-220.

Wilson, S. A., and Weber, J. H., 1977, A comparative study of number-average dissociation-corrected molecular weights of fulvic acids isolated from water and soil: Chemical Geology, v. 19, p. 285-293.

EVOLUTION OF THE USE OF CHANNEL CROSS-SECTION PROPERTIES FOR ESTIMATING STREAMFLOW CHARACTERISTICS

By Kenneth L. Wahl

ABSTRACT

Channel dimensions have proven to be valid indicators of streamflow characteristics. Use of channel geometry requires that a relation be defined between the desired flow characteristic and stream-channel size based on data at gaging stations; estimates of flow characteristics then can be made at ungaged sites by obtaining measurements of the channel dimensions. Regional analyses of these relations have been made in many Western States and in some Eastern States by the U.S. Geological Survey. These analyses are summarized, and some results are compared. Three reference levels have been used to define the channel dimensions.

The principal differences between the channel-geometry approach and conventional approaches using basin characteristics are that the ungaged site must be visited to measure the channel size before an estimate can be made and that some field training is required before an individual can identify the channel reference level.

Variability between channel measurements by trained individuals increases the error of estimates over the standard error of estimate defined during calibration. The increase is dependent on the variability in channel type, but extremely variable conditions could increase a calibration error of 42 percent to an application error of 55 percent.

INTRODUCTION

Engineers and hydrologists frequently are required to estimate flow characteristics at ungaged sites. Conventional techniques have used relations between flow characteristics and physical characteristics of drainage basins, such as drainage area, to transfer information to ungaged sites. However, flow characteristics in arid and semiarid regions generally are only poorly related to size of drainage basin. Relations between flow characteristics and stream-channel size offer a promising alternative.

That streams are the authors of their channels has long been recognized; however, methods of quantifying the interrelation between flow characteristics of rivers and channel size have developed only in recent years. The regime concept, as originated by Kennedy (1895) and Lindley (1919) and discussed by Leliavsky (1955) for canals in India and Pakistan, gave empirical relations for the hydraulic properties of stable canals. This concept, however, was not extended to natural rivers in the United States until half a century later.

The initial impetus for the studies of canals stemmed from the desire for improved design techniques. Similarly, the early work in rivers was oriented toward expressing channel dimensions as functions of a formative or dominant discharge. In recent years, efforts have focused on using dimensions of the stream channel as indices of flow characteristics, particularly flood-frequency characteristics. These approaches are not unrelated; however, the latter approach does not require definition of a dominant discharge.

The purposes of this report are to examine the evolution of our understanding of relations between dimensions of river channels and discharge characteristics, to summarize the regional relations that have been developed, and to examine the sources of error. The focus will be on attempts to use these relations as tools in estimating flow characteristics of rivers, with emphasis on flood characteristics, rather than on use of the information in channel design. Consequently, the regime concept as it relates to canals will be considered only in relation to its bearing on rivers. Because of the emphasis on regional relations, the "at-a-station" variation of hydraulic geometry exponents (Leopold and Maddock, 1953) is not included.

HYDRAULIC GEOMETRY APPROACH

A channel is considered to be in regime if it can accommodate its flow for one or more years without a net change in hydraulic characteristics (Blench, 1969). Within that period, scour or deposition may occur, in either the lateral or vertical direction, as long as they are transient phenomena.

The morphology of regime canals has been the subject of many investigations since Kennedy stated his empirical equation of non-scouring velocity for canals of Punjab in 1895 (Leliavsky, 1955). The basic principle generally was not applied to rivers in the United States, however, until Leopold and Maddock (1953) reported their analysis of the relationships between hydraulic properties of the cross-section and river discharge. They theorized that the hydraulic geometry of river channels in approximate equilibrium could be expressed as exponential functions of discharge such that

$$W = aQ^b, \tag{1}$$

$$D = cQ^f, \tag{2}$$

$$V = kQ^m, \tag{3}$$

where W is width, D is mean depth, V is mean velocity, Q is discharge, and a, c, k, b, f, and m are numerical constants.

The numerical constants for the above relations were developed empirically from data collected on rivers representing a variety of hydrologic conditions. Mean annual discharge was used as the independent variable because it provided a discharge of approximately the same frequency throughout the area of investigation, thus permitting comparison between relations. The values of the exponents b, f, and m were relatively constant, and the average values agreed quite closely with previously defined values for regime canals. The coefficients a, c, and k, however, varied among river systems.

Leopold and Maddock (1953) were not the first to apply the regime concept to rivers, although their analysis was one of the first to gain wide acceptance. In 1935, Gerald Lacey extended his earlier empirical equations for Punjab canals by including limited data for rivers from the United States, Europe, and Punjab (Mahmood and Shen, 1971); however, he grouped river data by discharge and used averages. Pettis (1937) independently developed similar regime equations based on natural streams in the Miami River basin of Ohio. Pettis' relations were intended for use in river channelization, therefore, his discharge was a flood discharge, apparently near bankfull (Pettis, 1937, p. 150).

In 1947, S. I. Rybkin (Kondrat'ev and others, 1962) developed a set of relations based on rivers in the upper Volga and Oka basins, U.S.S.R. These relations were in terms of long-term average discharge and river gradient but contained a modulus term that permitted computation of the hydraulic properties for discharges other than the long-term mean. Rybkin's hydraulic-geometry variables, like those of Leopold and Maddock (1953), were properties at the particular discharge rather than dimensions based on a specific feature of the channel. In 1950, S. T. Altunin (Kondrat'ev and others, 1962) confirmed that the general regime equation for width with $b = 0.50$ was valid for rivers of central Asia. He also concluded that the coefficient, a, varied with slope to the -0.20 power. Whether the width used in Altunin's analysis is based on a specific channel feature is not clear, but Kondrat'ev and others (1962) give some insight with the observation, ". . .(Altunin's) formulas are true only for a certain channel-forming discharge, whose value is taken as that of discharges with a 10 to 20 percent reliability [sic, probability]. These discharges are usually accommodated within the height of the channel edges."

While furthering the state of knowledge, most of the preceding studies, including the 1953 work of Leopold and Maddock, were of limited practical value because the hydraulic-geometry variables used were those of specific discharges and could not be identified with recognizable channel features. Thus, Wolman's (1955) analysis of the Brandywine Creek drainage in Pennsylvania, in which he related hydraulic geometry to bankfull discharge, was significant. In addition, he analyzed the hydraulic-geometry relationships with flows of 50-, 15-, and 2-percent duration. The recurrence interval of flows exceeding bankfull on Brandywine Creek ranged between 1 and 3 years and averaged 2.2 years.

Although simple in concept, bankfull stage may be interpreted in a number of different ways, each associated with different values of width and depth and yielding a different bankfull discharge. Williams (1978) gave a comprehensive review of definitions of bankfull stage. He identified and discussed 11 definitions that have been used by investigators. But even when guided by a single definition, he found (Williams, 1978, p. 1141), "Bank-full discharge does not have a common recurrence frequency among the rivers studied, and the discharge corresponding to the 1.5-year recurrence interval in most cases does not represent the bank-full discharge."

Most investigations of hydraulic geometry after Wolman's (1955) were directed at one or more of the following problems: (1) physically identifying bankfull stage, (2) determining the significance (such as the recurrence interval) of bankfull discharge, (3) determining the exponents in the hydraulic-geometry equations either theoretically or empirically for a specific region or channel type, or (4) application of the concept to solve practical problems. Excepting the theoretical analyses, many studies involve several of the classifications. The hydraulic-geometry exponents for selected empirical and theoretical studies are summarized in table 1.

DISCHARGE RELATED TO CHANNEL DIMENSIONS

Ideally, a channel feature used as an index to discharge should be a unique, recognizable feature of the channel. It should also be active, that is, free to adjust to changes in the flow regime. These considerations, and a need for a reconnaissance technique to estimate discharge characteristics at ungaged sites, led to the recent attempts to relate an active, within-channel feature

Table 1. Exponents of discharge in regime equations for width (b), depth (f), and velocity (m)

Region and source	b	f	m	Discharge
Empirical studies				
Indian canals and rivers (Mahmood and Shen, 1971)	0.50	0.333	0.167	Equilibrium
Miami River, Ohio (Pettis, 1937)	.50	.30	.20	Bankfull
Volga and Oka basins, US.S.R. (Kondrat'ev and others, 1962)	.57	.22	.21	Mean annual
Midwest United States (Leopold and Maddock, 1953)	.50	.40	.10	Do.
Brandywine Creek, Pennsylvania (Wolman, 1955)	.58	.40	.02	2 percent duration
Ephemeral streams in southwest (Leopold and Miller, 1956)	.50	.30	.20	Mean annual
Rivers in England and Wales (Nash, 1959; Nixon, 1959)	.53	.27	.20	Bankfull
Appalachian streams (Brush, 1961)	.55	.36	.09	Do.
Canada rivers, Colorado canals (Kellerhals, 1967)	.50	.40	.10	3- to 5-year flood
Illinois Rivers (Stall and Fok, 1968)	.48	.36	.16	Of measurement
Average for Alaska rivers (Emmett, 1972)	.50	.35	.15	Bankfull
Rivers in central Idaho (Emmett, 1975)	.54	.34	.12	Do.
Colorado gravel bed streams[1] (Andrews, 1984)	.480	.374	.146	Do.
Theoretical approaches				
Leopold and Langbein (1962)	.55	.36	.09	
Langbein (1964, 1965)	.50	.37	.13	
Ackers (1964)	.53	.35	.12	
Engelund and Hansen (1967)	.525	.317	.158	
Joering and Preul (1973)	.50	.375	.125	
Smith (1974)	.6	.3	.1	
Li and others (1976)	.46	.46	.08	

[1] Average of values for thick and light bank vegetation.

to discharge characteristics. The approach was apparently first suggested by W. B. Langbein (U. S. Geological Survey, written commun., 1966).

The concept as well as the feature differed from the earlier work. With the bankfull-stage concept, the emphasis had been on relating the bankfull channel properties (dependent variables) to some formative or dominant discharge (independent variable). Langbein instead suggested relating empirically the average annual discharge, as the dependent variable, to dimensions of recognizable active features of the channel, as the independent variables. This permits estimates of the discharge characteristic to be made at ungaged sites on the basis of channel dimensions. The approach infers that the discharge characteristic to be estimated is related directly to the formative discharge of streams in the area of investigation but does not require identification of that formative discharge.

Several reference levels have been used; the levels referred to in this paper are the section defined by within-channel bars, the active channel section, and the main-channel section (see fig. 1). Regional investigations by hydrologists of the U.S. Geological Survey are summarized in table 2 by the reference level used. Those studies and other investigations are discussed in the sections that follow.

Within-Channel Bars

Langbein (written commun., 1966) suggested a reference level defined by the tops of point bars meeting these conditions: (1) the highest bed forms the particles of which are subject to annual sediment movement and (2) the lowest prominent bed forms. He also noted that the reference level could be related to vegetation zones if (1) the channel below the reference level generally is free of nonaquatic vegetation, (2) the zone between the tops of the bars and the flood plain is occupied by annuals (forbs and grasses), and (3) the true flood plain is occupied by shrubs. This section has been described in more detail by Moore (1968), Hedman (1970), and Hedman and others (1972).

Early studies using the in-channel bar feature defined relations only for mean annual flow. More recent investigations also have defined relations for floods of selected frequency. Relations between the 10-year flood and width between in-channel bars are compared for selected studies in figure 2.

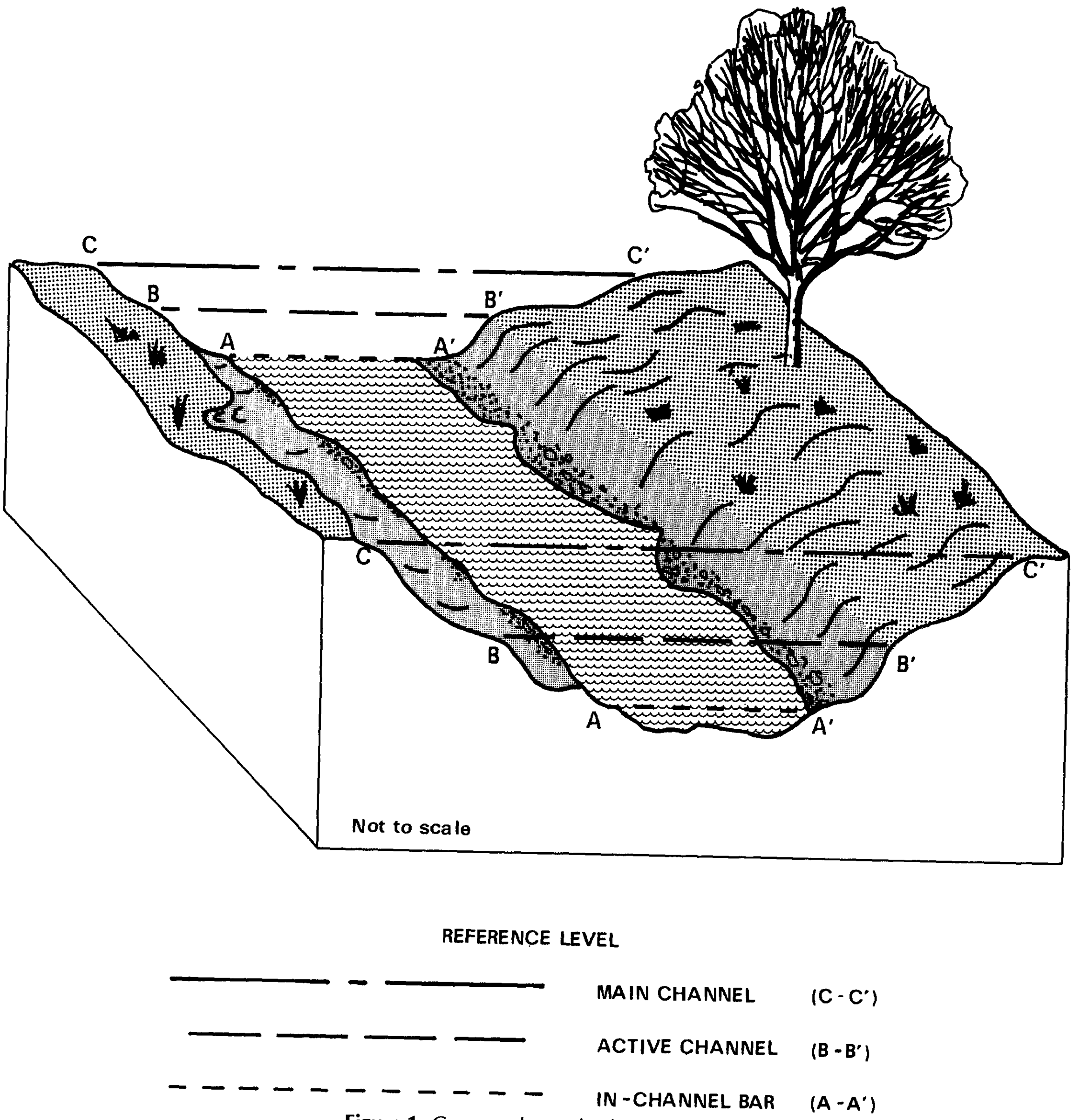


Figure 1. Commonly used reference levels.

The first published analysis using the within-channel feature was that by Moore (1968) for streams in Nevada. He graphically related mean annual discharge to the width and average depth of the channel cross section defined by the tops of the channel bars and gave separate results for perennial and ephemeral streams.

In a related study, Hedman (1970) equated mean annual flow of 48 California streams to the dimensions of the cross section defined by the within-channel bars. Like Moore (1968), he developed separate relations for ephemeral (20 sites) and perennial (28 sites) streams.

Kopaliani and Romashin (1970) analyzed relations between the "flood-channel" width and the 2-year flood for rivers in western Georgia, U.S.S.R. Based on their description of the flood channel, the width used seems to be compatible with the in-channel feature treated in this section: "The flood channel is that part of the valley which is systematically flooded by high water and within which sediments are continuously redistributed so that there is no vegetation. On mountain rivers it is a wide gravelly-bouldery strip, which dries out during the low-water period. Its relief consists of gentle mobile placer deposits of the side-bar or midstream-bar type." In a logarithmic plot relating 2-year flood and flood-channel width, the data separate into three distinct, but parallel, groups. In order of decreasing discharge for a given width, they were braided reaches, reaches with midchannel and side-channel bars, and meandering

Table 2. Summary of regional analyses by the U.S. Geological Survey

Region and reference level used	Characteristic used	
	Mean annual flow	Flood-flows
In-Channel Bar Section:		
Nevada (Moore, 1968)	X	--
Coastal and southern California (Hedman, 1970)	X	--
Kansas (Hedman and Kastner, 1972)	X	--
Colorado, perennial streams (Hedman and others, 1972)	X	X
Nevada (Moore, 1974)	--	X
Utah (Fields, 1975)	X	X
Missouri River basin[1] (Hedman and Kastner, 1977)	X	X
Active-Channel Section:		
Kansas (Hedman and others, 1974)	X	X
New Mexico (Scott and Kunkler, 1976)	--	X
Missouri River basin[1] (Hedman and Kastner, 1977)	X	X
Western United States (Hedman and Osterkamp, 1982)	X	X
Kansas, regulated streams (Osterkamp and Hedman, 1981)	X	--
Ohio (Webber and Roberts, 1981)	--	X
Tennessee, Cumberland Plateau (Glazzard, 1981)	X	X
Missouri River basin (Osterkamp and Hedman, 1982)	X	X
Southeastern Montana[2] (Omang and others, 1983)	X	X
Northeastern and western Montana[2] (Parrett and others, 1983)	X	X
Main-Channel Section:		
Western Mountain areas (Riggs, 1974)	--	X
Wyoming (Lowham, 1976)	X	X
Idaho, Owyhee County (Riggs and Harenberg, 1976)	--	X
Idaho (Harenberg, 1980)	--	X
Southeastern Montana[2] (Omang and others, 1983)	X	X
Northeastern and western Montana[2] (Parrett and others, 1983)	X	X

[1] Includes both the in-channel bar and active-channel sections.

[2] Includes both the active-channel and main-channel sections.

reaches. Although they were defining width as a function of discharge (and gradient), this writer deduced a relation of

$$Q = aW^{1.5} \qquad (4)$$

from a plot of their data. This general relation would apply to all three groups, but the constant of proportionality, a, would vary; average standard error of estimate (graphical) would be in the range of 30 to 40 percent.

Equations for estimating mean annual flow from channel geometry in Kansas were developed by Hedman and Kastner (1972). They used the within-channel bar feature and gave separate results for perennial and ephemeral streams.

One of the first studies to relate flood characteristics to channel dimensions in the United States was done by Hedman and others (1972). They related mean annual discharge and 2-, 5-, 10-, 25-, and 50-year flood peaks to width and mean depth of the within-channel cross section for perennial streams in Colorado. The standard errors of estimate for their flood equations ranged from about 30 to 45 percent and were significantly less than comparable conventional relations between flood characteristics and basin characteristics. Including mean depth and drainage area in the equations did not significantly decrease the standard errors, nor did the use of a second-degree polynominal.

DeWalle and Rango (1972) used data from 27 small basins (19.59–303.44 acres) in Maryland, New Hampshire, New Jersey, Pennsylvania, Vermont, and West Virginia to develop linear relations between the logarithms of mean annual flood and properties of the channel cross section. Their channel width was defined as "... the horizontal distance from the top of the lowest bank to the opposite bank wall." The description seems to be consistent with that of the within-channel bar based on their statement "... the more obvious upper banks which may be associated with a discharge

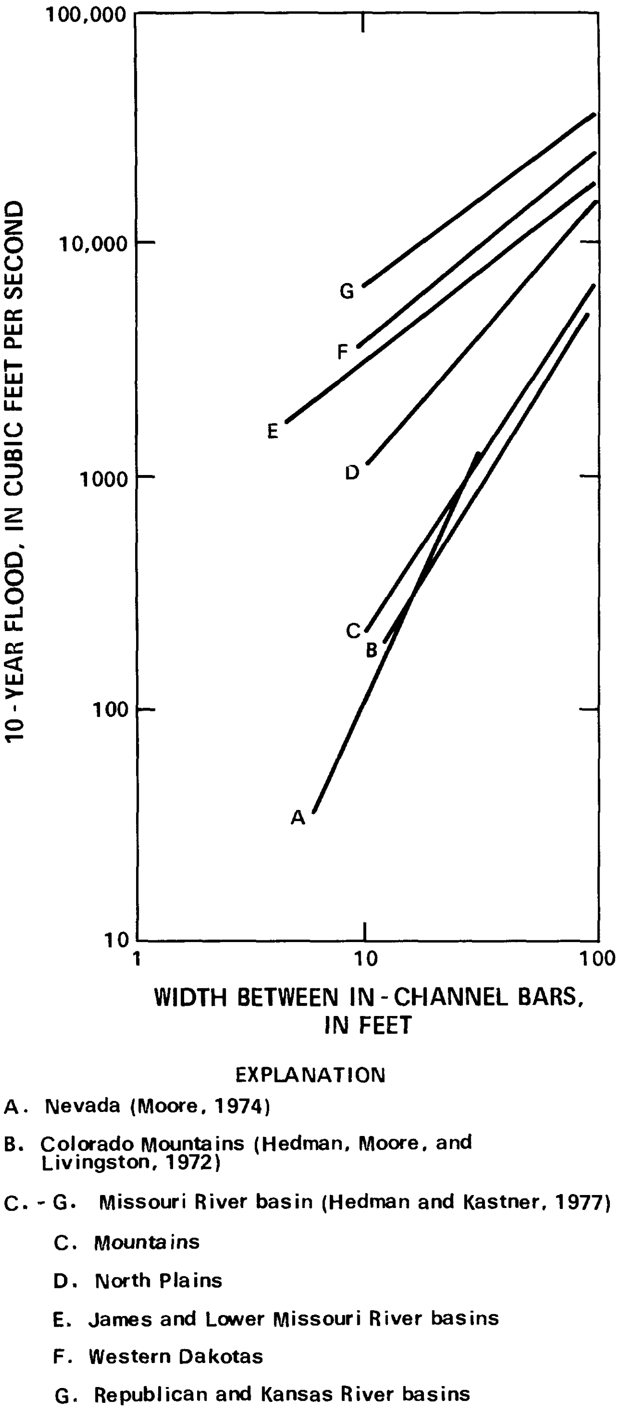


Figure 2. Relations between 10-year flood and width between in-channel bars.

greater than the mean annual flow were discarded." The results are of limited practical use as only 34 percent of the sample variance was explained by an equation using width; a relation using only precipitation explained 83 percent of the sample variance. In an earlier study of small drainages in the Sleeper's River basin of northern Vermont, Zimmerman and others (1967) found that stream width did not increase in the downstream direction for drainage area less than 0.8 square mi. They attributed this to the effect of vegetation, mostly tree roots, and to relatively small annual peak discharges. This may partly explain the poor results obtained by DeWalle and Rango (1972).

Moore (1974) extended his earlier study (Moore, 1968) for Nevada to include the 10-year flood characteristic. He developed separate relations for perennial and ephemeral streams. The 10-year flood was a function of both width and depth for ephemeral streams but was related to only the width for perennial streams.

Fields (1975) developed statewide relations for the mean annual discharge and the 25- and 50-year floods in Utah using the in-channel bar feature. The State was divided into three hydrologic areas for floods, and separate relations were developed for the individual areas; flood flows were related to only the width of the section.

In one of the first studies of a large geographical region, Hedman and Kastner (1977) related mean annual flow and flood flows for the Missouri River basin to the width of the in-channel bar section and the active channel. Relations also were defined between the flow characteristics and conventional basin characteristics. The basin was divided into six hydrologic areas for both mean annual flow and floods, but the regions for mean annual flow generally differed from those for floods. Standard errors of estimate were comparable for relations using width of the in-channel bar section and the width of the active-channel section; however, standard errors of relations based on drainage area and climatic characteristics generally were greater except for mean annual flow in southwestern Iowa and northern Missouri.

Active-Channel Section

While studying Kansas streams, E. R. Hedman (U.S. Geological Survey, written commun., 1972) recognized a channel feature somewhat higher than the in-channel bars that had been used previously. He first referred to this feature as the active flood plain but redefined it as the active channel (Hedman and others, 1974). Osterkamp and Hedman (1977, p. 256) described the active channel as ". . . a short-term geomorphic feature subject to change by prevailing discharges. The upper limit is defined by a break in the relatively steep bank slope of the active channel to a more gently sloping surface beyond the channel edge. The break in slope normally coincides with the lower limit of permanent vegetation so that the two features, individually or in combination, define the active channel reference level. The section beneath the reference level is that portion of the stream entrenchment in which the channel is actively, if not totally, sculptured by the normal process of water and sediment discharge."

Since then, the active-channel section has been used in numerous studies to define mean annual and flood flows in the Western States and in selected Eastern States. These investigations are summarized in table 2, and 10-year flood relations are compared for selected studies in figure 3.

The active-channel section was first used by Hedman, and others (1974) to define flood-frequency relations in

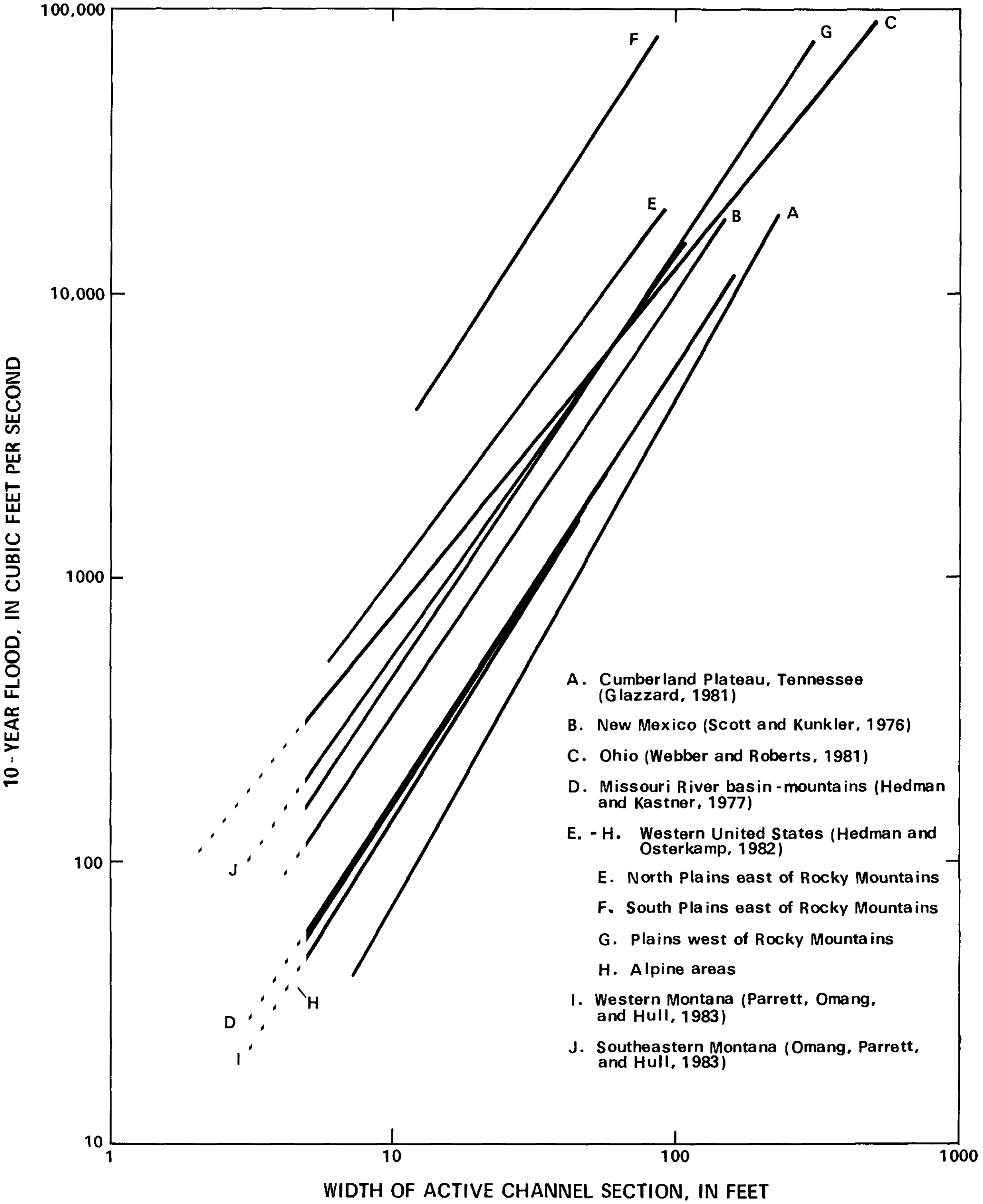


Figure 3. Relations between 10-year flood and active-channel width.

Kansas. They proposed that, because the active-channel feature was formed by infrequent flows, the active-channel section was a better descriptor of floods than was the in-channel bar section.

Scott and Kunkler (1976) related the width of the active channel to characteristics of the 2- through 50-year floods in New Mexico. One set of relations was used for the State; however, an area in the southeastern part of the State was excluded because the channels were actively entrenching. The relations using channel width gave significantly smaller standard errors of estimate than similar relations that used basin and climatic characteristics.

A similar study for Ohio (Webber and Roberts, 1981) defined one set of equations that could be used statewide to estimate the 2- through 100-year floods; the average standard errors of estimate ranged from 42 to 55 percent.

Glazzard (1981) defined relations for the mean annual flow and 2- through 100-year floods in the Cumberland Plateau, Tennessee, using the active-channel width. The average standard errors of estimate were about 60 percent for floods. He also used variables representing stream gradient and percentage of silt, clay, and coal in stream-bank material. Although the additional variables produced some decrease in standard error for mean annual flow, there was no improvement in the flood relations.

Hedman and Osterkamp (1982) used the active channel section in an analysis of mean annual and flood characteristics (2- through 100-year floods) for the western one-half of the conterminous United States. Their final equations expressed the flow characteristics as functions of only the active-channel width. For floods, the area was subdivided into four areas based on similarity of climatic conditions. The four areas were (1) alpine and pine-forested, (2) Northern Plains east of the Rocky Mountains, (3) Southern Plains east of the Rocky Mountains, and (4) plains and intermontane areas west of the Rocky Mountains. Their results are shown in table 3.

Osterkamp and Hedman (1982) expanded on the earlier Missouri River basin study by Hedman and Kastner (1977) by considering the effect of channel-sediment properties, channel gradient, and discharge variability. They concluded (p. 1), "Results show that channel width is best related to variables of discharge, but that significant improvement, or reduction of the standard errors of estimate, can be achieved by considering channel-sediment properties, channel gradient, and discharge variability." They did not include terms in the regression relations to represent the additional factors; instead, the data were stratified based on those factors, and each group of data were analyzed separately.

Main-Channel Section

The third and highest reference level used is the main-channel section (also referred to as the whole-channel section). This section was described by Riggs (1974, p. 53) as ". . .variously defined by breaks in bank slope, by the edges of the flood plain, or by lower limits of permanent vegetation." He also notes, "In selecting the channel width, one should avoid a high reference level that does not reflect the present flow regime. This is most often a possibility on ephemeral streams."

Comparing the above descriptions with the various descriptions of bankfull stage, it is evident that the main-channel section and the bankfull section are the same for perennial streams. The relationship is less obvious for ephemeral streams where distinct flood plains may not be formed; however, there is no evidence to indicate that the sections are not the same when determined properly.

The study by Riggs (1974) presented reconnaissance level relations between 10-year flood and main-channel width for ephemeral streams in Utah and Wyoming and perennial streams in Alaska. Relations also were compared for the 50-year flood in the western mountains, Kansas, and Kentucky.

Riggs and Harenberg (1976) demonstrated for Owyhee County, Idaho, how channel-geometry measurements could be used to provide estimates of flood characteristics without visiting the site. The relationship between the 10-year flood and main-channel width was developed and used to estimate the 10-year flood at 79 sites in and adjacent to Owyhee County. The resulting estimates and those for 33 gaging stations were plotted on a map of the county; the map can be used for interpolation to make estimates at intermediate sites.

Lowham (1976) used the main-channel section to define relations for mean annual flow and 2- through 100-year flood flows for Wyoming. For floods, the State was divided into four hydrologic areas, and separate relations were defined for each area. Average standard errors of estimate for all frequencies ranged from about 34 to 75 percent and were smaller than standard errors for comparable relations that used drainage basin and climatic variables. More recently, Lowham (1982) developed a relation between the geometric mean of peak discharges (approximately the 2-year flood) and main-channel width for Wyoming that had an average standard error of estimate of 47 percent. The relation applies ". . .to all types of streams, including perennial, intermittent, and ephemeral types of either the mountains or plains, provided the channel is stable and has been formed by the hydraulic forces of floodflows" (Lowham, 1982, p. 37).

Harenberg (1980) used the bankfull width to define relations for the 1.5- through 100-year floods for Idaho.

Table 3. Equations for determining flood-frequency discharge for streams in Western United States
[Modified from Hedman and Osterkamp (1982)]

Areas of similar climatic characteristics	Equation[1]	Standard error of estimate (percent)
Alpine and pine-forested	$Q_2 = 1.3W_{AC}^{1.65}$	44
	$Q_{10} = 4.4W_{AC}^{1.55}$	38
	$Q_{25} = 7.0W_{AC}^{1.50}$	42
	$Q_{50} = 9.6W_{AC}^{1.45}$	45
	$Q_{100} = 13W_{AC}^{1.40}$	50
Northern plains east of Rocky Mountains	$Q_2 = 4.8W_{AC}^{1.60}$	62
	$Q_{10} = 46W_{AC}^{1.35}$	40
	$Q_{25} = 61W_{AC}^{1.30}$	44
	$Q_{50} = 130W_{AC}^{1.30}$	50
	$Q_{100} = 160W_{AC}^{1.25}$	58
Southern plains east of Rocky Mountains (subject to intensive precipitation events)	$Q_2 = 7.8W_{AC}^{1.70}$	66
	$Q_{10} = 84W_{AC}^{1.55}$	56
	$Q_{25} = 180W_{AC}^{1.50}$	57
	$Q_{50} = 270W_{AC}^{1.50}$	59
	$Q_{100} = 370W_{AC}^{1.50}$	62
Plains and intermontane areas west of Rocky Mountains	$Q_2 = 1.8W_{AC}^{1.70}$	120
	$Q_{10} = 14W_{AC}^{1.50}$	60
	$Q_{25} = 22W_{AC}^{1.50}$	62
	$Q_{50} = 44W_{AC}^{1.40}$	71
	$Q_{100} = 59W_{AC}^{1.40}$	83

[1] Active-channel width, W_{AC}, in feet; discharge, Q_n, in cubic feet per second, where n is the recurrence interval, in years.

This bankfull width is equivalent to the whole-channel width used in the Owyhee County report (W. C. Harenberg, U.S. Geological Survey, oral commun., 1982). The equations were applicable statewide and had average standard errors of about 70 percent.

The relations between 10-year flood and main-channel width for these studies are shown in figure 4.

USE OF CHANNEL-GEOMETRY RELATIONS

Channel-geometry measurements are proven indices for use in estimating flood-frequency characteristics at ungaged locations. The technique can be used where relations between flow characteristics and traditional basin and climatic characteristics are poor, or channel measurements may be used to provide virtually independent estimates for comparison with the traditional approaches. However, the method may not provide reliable results for areas where bedrock prevents the channel from adjusting to accommodate the normal regimen of flow. Similarly, the approach is not applicable on braided, sand-channel streams where channels have not stabilized. Where possible, sections should be located in straight reaches where flows are approximately uniform. In meandering streams, Lowham (1976) suggested locating sections in the cross-over area, midway between bends. Channel dimensions need to be measured at two or three cross sections separated by at least one channel width, and average values should be used in computations.

Regardless of which of the three sections is used, experience is needed to identify the proper reference level. Before making channel measurements, a few days of field instruction should be obtained from a person experienced in the technique. Training needs to be done in a hydrologic environment that is similar to that where the relations will be used; the various sections generally are much easier to identify on perennial streams than on ephemeral streams. In using an existing relation, only those variables contained in the relation need to be measured. If a new relation is being developed, however, other factors such as channel slope and bed and bank material should be obtained in addition to the width and average depth of the section.

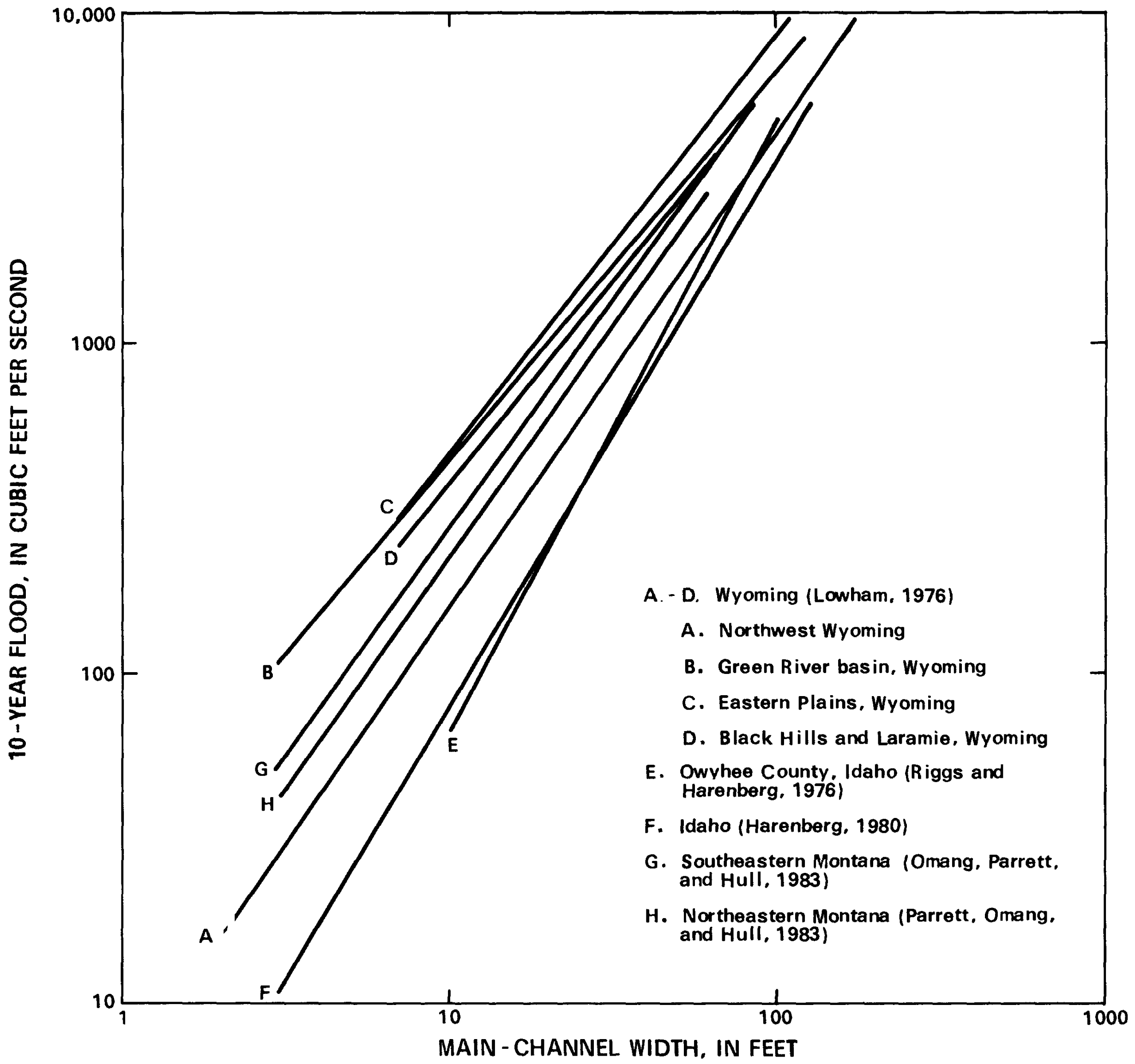


Figure 4. Relations between 10-year flood and main-channel width.

RELIABILITY

The reliability of flow estimates from channel characteristics depends on both the applicability of the regional relation (calibration and model errors) and on the ability of different individuals to recognize and measure the channel dimensions used as independent variables (application error).

The calibration and model errors include those in estimating the discharge characteristics used to develop the relations and are reflected in the standard errors of estimate reported for individual studies. However, at this time, the components cannot be separated; that is, the contributions attributed to errors in the calibration discharge estimates, to the use of the power, and to measurement errors by the individuals developing the relations cannot be identified separately. Most investigations using channel geometry have found that standard errors of estimate are equal to or less than the standard errors for conventional methods.

The principal difference between the conventional regression relations and those using channel geometry is in the degree of subjectivity involved in defining the independent variables. For example, numerous maps of an area may give mean annual precipitation, but, if a particular map is specified, all users could derive about the same estimated value for a particular basin. With relations based on channel geometry, however, the user needs to be able to recognize the feature and to measure it consistently.

Table 4. Summary of cross correlations between measurements by individuals
[From Wahl, 1976]

Section	Statistics of correlation coefficients		
	Mean	Standard deviation	Range
Low Bar:			
Width	0.95	0.055	0.74–0.99
Depth	.74	.128	.51– .93
Active Channel:			
Width	.97	.028	.91– .99
Depth	.59	.164	.27– .83
Main Channel:			
Width	.92	.067	.79– .99
Depth	.59	.193	.16– .89

Variation Between Individuals

Wahl (1976) conducted a test designed to define the possible variability of channel measurements by individuals. An added objective of the test was to gain insight into potential advantages and disadvantages of the three reference levels. The test was conducted in northern Wyoming. Seven individuals, all experienced in using channel-geometry techniques, independently visited 22 sites and measured channel dimensions in sections of their choosing. Only general reaches of each stream were identified so the cross sections at which individuals measured channel dimensions were of their own choosing; thus, the variability of measurements between individuals reflected the combined effects of differences in cross-section location within the test reach and differences in identification of the reference levels. This should reflect the variability resulting from trained individuals measuring channel size in an ungaged reach.

A summary of the statistics of cross-correlation coefficients between measurements for width and average depth of the three reference levels is given in table 4. The data in table 4 show a high correlation among width measurements for all three reference levels. However, the correlation among depth measurements is low. This can be rationalized by considering that depths are relatively shallow and that slight differences in locating the top of a reference level will have little effect on the overall measurement of width but a significant effect on the average depth. Wahl (1976) also used analysis of variance to test for differences among individuals in the average values of a given channel-size dimension. The hypothesis of no difference among means for individuals was accepted at the 95-percent level for widths of all three reference levels.

Relations between a discharge characteristic, Q, and channel width, W, usually take the form

$$Q = aW^b, \qquad (5)$$

where a and b are numerical constants. This is a linear relation when expressed in logarithms:

$$\log Q = \log a + b \log W. \qquad (6)$$

For the Wyoming test, the average standard deviation of log W (base 10 logarithms) for the seven individuals' estimates was 0.089. Given a relation of the form of equation 6, the standard error in log Q produced by variation in estimates of W is b times the standard error of log W. Wahl (1976) assumed that b averaged about 1.5 and arrived at an estimate of the standard error in log Q of 0.13 log unit due to variation in width measurements alone. This converts to an error of about 30 percent in estimated discharge. In addition, Wahl (1976) noted an average bias (with respect to the mean) in log W of 0.06 log unit or about 14 percent.

The effect of the variation in channel-width measurements by individuals is to increase the error of applying a relation to more than that indicated by the standard error of estimate, which shows the calibration and model error. Assuming the three errors are independent, the true error would be the square root of the sums of the squares of the individual components. For example, the 25-year flood for the alpine area from table 3 shows an average standard error of estimate of 42 percent or 0.178 log unit. The true error in log units of using this relation, accounting for both variation and possible bias in width measurements, would be

$$((0.178)^2 + (0.13)^2 + (0.06)^2)0.5 = 0.228. \qquad (7)$$

This yields an average error of 55 percent compared with the calibration error of 24 percent. The relationship between standard error of estimate and application error

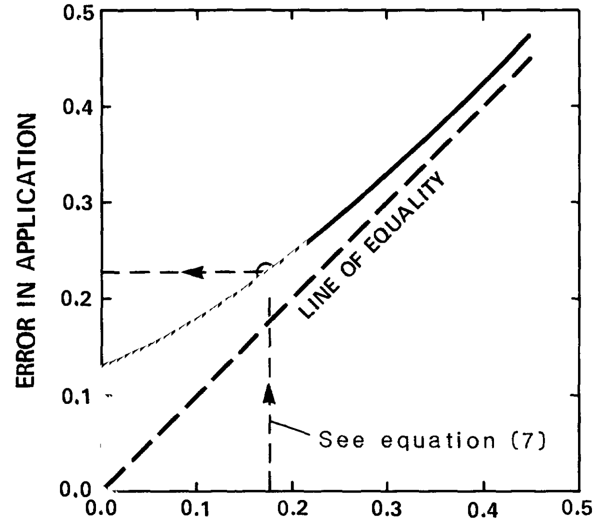


Figure 5. The effect of differences in width measurements on the standard error of estimate. All values are base 10 logarithms.

is shown in figure 5; this relationship assumes that the exponent of width is 1.5 and that the errors are independent.

It should be noted, however, that the sites in the Wyoming test were chosen for their diversity. The sites ranged from ephemeral streams in a nearly desert environment to perennial streams in a high mountain environment. The variability of measurements in this test probably is greater than normally would be encountered in applying channel-geometry measurements in a particular hydrologic area.

Some Comparisons

Comparing published results for different physiographic areas is difficult because the areas have morphological and hydrological differences. In addition, three different reference levels have been used, and some relations include independent variables not used in other studies. However, general comparisons are possible for studies that have overlapped or covered similar physiographic regions. For example, agreement shown in figure 2 between the 10-year flood results for the mountains of Colorado (Hedman and others, 1972) and the mountains of the Missouri River basin (Hedman and Kastner, 1977) is good. Results for the mountains of Nevada (Moore, 1974) also compare well with the above results.

Similar comparisons in figure 3 show that for the 10-year flood and the active-channel width, the relations for the alpine areas of the Western United States (Hedman and Osterkamp, 1982) and for the mountains in the Missouri River basin (Hedman and Kastner, 1977) are almost identical. The relation for New Mexico (Scott and Kunkler, 1976) has about the same exponent but has a different intercept.

Selected relations for the 10-year flood and the main-channel section are shown in figure 4. Only the results for Owyhee County, Idaho (Riggs and Harenberg, 1976) and the statewide study for Idaho (Harenberg, 1980) are directly comparable and are quite similar.

NEED FOR ADDITIONAL STUDY

Studies to date (1984) have clearly shown that stable channel dimensions are viable indices of the flow characteristics of rivers. Much needs to be done, however, to realize fully the potential of this approach. A number of features including the in-channel bar section, active-channel section, and the main-channel or whole-channel section presently are being used to define flow characteristics. Consequently, it is difficult to make comparisons between studies, and the applicability of individual results are dependent on the ability of a user to identify the feature used in developing the relation.

Relations need to be defined between the dimensions of the various reference levels and the areas over which the relations apply. Riggs (1978) developed the following relation between main-channel width and active-channel width:

$$MC = 1.75\ AC^{0.96}, \qquad (8)$$

where MC is the main-channel width, and AC is the active-channel width; all units are in feet. He suggested that this relation could be used in semiarid regions to estimate one width from another. However, a similar relation developed by the author for the Wyoming test data given by Wahl (1976) produced unusable results. This probably was because of the extreme variation in stream types in the Wyoming test.

Additional work is needed to determine the role of other variables. Several investigators (Schumm, 1960; Glazzard, 1981; Osterkamp and Hedman, 1982) have examined the relation between sediments in the bed and banks and channel size. Results to date (1984) have varied from region to region. Andrews (1984) examined data for gravel-bed streams in Colorado and separated the data into two groups depending on whether bank vegetation along the study reach was light or thick. He made width, depth, and velocity dimensionless by dividing each by the median particle diameter in the riverbed surface. Regression relations for hydrologic-geometry exponents showed no significant difference between data for light and thick bank vegetation; however, the regression coefficients a, c, and k were significantly different. This implies that exponents for gravel-bed rivers are the same regardless of region.

Examination of the hydraulic-geometry exponents in table 1 suggests that for a given channel type, a fixed relation may exist between some formative discharge and channel width. If so, there would be justification for imposing a slope for width-discharge relations and allowing the constant (intercept) to be determined by the data. This would minimize the variability among relations that is now produced by fitting curves to a limited range of data. Based on the theoretically derived relations for the regime equations, such a formative discharge, if it exists, should relate to width raised to the 1.8 to 2.0 power. However, this would only be true for the formative discharge of a river, which is unknown; using the same exponent for other discharges would imply that the variability of flows of large streams is as large as that of small streams. Osterkamp and Hedman (1977) have attempted this approach, but additional work is needed.

Much of the work to date (1984) has dealt with efforts to define regional relations (calibration). Ways should be sought to make the calibration results more useful. Additional work also is needed to refine estimates of the application errors. The application errors estimated by Wahl (1976) probably are anomalously large because of the extreme variability designed in the experiment.

REFERENCES CITED

Ackers, Peter, 1964, Experiments on small streams in alluvium: Proceedings, American Society of Civil Engineers, v. 90, no. HY4, p. 1-38.

Andrews, E.D., 1984, Bed-material entrainment and hydraulic geometry of gravel-bed rivers in Colorado: Bulletin of the Geological Society of America, v. 95, no. 3, p. 371-378.

Blench, Thomas, 1969, Mobile-bed fluviology: Edmonton, The University of Alberta, 168 p.

Brush, L. M., Jr., 1961, Drainage basins, channels, and flow characteristics of selected streams in central Pennsylvania: U.S. Geological Survey Professional Paper 282-F, p. F145-F181.

DeWalle, D. R., and Rango, Albert, 1972, Water resources applications of stream channel characteristics on small forested basins: Water Resources Bulletin, v. 8, no. 4, p. 697-703.

Emmett, W. W., 1972, The hydraulic geometry of some Alaskan streams south of the Yukon River: U.S. Geological Survey open-file report, 44 p.

______1975, The channels and waters of the upper Salmon River area, Idaho: U.S. Geological Survey Professional Paper 870-A, 116 p.

Engelund, Frank, and Hansen, Eggert, 1967, A monograph on sediment transport in alluvial streams: Copenhagen, Teknisk Forlag, 62 p.

Fields, F. K., 1975, Estimating streamflow characteristics for streams in Utah using selected channel-geometry parameters: U.S. Geological Survey Water-Resources Investigations 34-74, 19 p.

Glazzard, C. F., 1981, Streamflow characteristics related to channel geometry of selected streams on the Cumberland Plateau, Tennessee: University of Tennessee, unpublished Master's Thesis, 132 p.

Harenberg, W. C., 1980, Using channel-geometry measurements to estimate flood flows in Idaho: U.S. Geological Survey Water-Resources Investigations 80-32, 39 p.

Hedman, E. R., 1970, Mean annual runoff as related to channel geometry in selected streams in California: U.S. Geological Survey Water-Supply Paper 1999-E, 17 p.

Hedman, E. R., and Kastner, W. M., 1972, Mean annual runoff as related to channel geometry of selected streams in Kansas: Kansas Water Resources Board Technical Report 9, 25 p.

______1977, Streamflow charactistics related to channel geometry in the Missouri River basin: U.S. Geological Survey Journal of Research, v. 5, no. 3, p. 285-300.

Hedman, E. R., Kastner, W. M., and Hejl, H. R., Jr., 1974, Selected streamflow characteristics as related to active-channel geometry of streams in Kansas: Kansas Water Resources Board Technical Report 10, 21 p.

Hedman, E. R., Moore, D. O, and Livingston, R. K., 1972, Selected streamflow characteristics as related to channel geometry of perennial streams in Colorado: U.S. Geological Survey open-file report, 14 p.

Hedman, E. R., and Osterkamp, W. R., 1982, Streamflow characteristics related to channel geometry of streams in western United States: U.S. Geological Survey Water-Supply Paper 2193, 17 p.

Joering, E. A., and Preul, H. C., 1973, A set of regime equations for indirectly estimating streamflow characteristics: International Water Resources Association, September 24-28, 1973, Proceedings, p. 411-426.

Kellerhals, Rolf, 1967, Stable channels with gravel-paved beds: American Society of Civil Engineers, Proceedings, v. 93, no. WW1, p. 63-84.

Kennedy, R. G., 1895, Prevention of silting in irrigation canals: Institute Civil Engineers Proceedings, v. 119, p. 281-290.

Kondrat'ev, N. E., and others, 1962, River flow and river channel formation: Ruslouoiprotsess, Translated by Israel Project for Scientific Translations, Ltd., 172 p.

Kopaliani, F. D., and Romashin, V. V., 1970, Channel dynamics of mountain rivers in Soviet Hydrology—Selected Papers: American Geophysical Union, v. 5., p. 441-452.

Langbein, W. B., 1964, Geometry of river channels: American Society of Civil Engineers, Proceedings, v. 90, no. HY2, p. 301-312.

______1965, Closure of "Geometry of river channels": American Society of Civil Engineers, Proceedings, v. 91, no. HY3, p. 297-313.

Leliavsky, Serge, 1955, An introduction to fluvial hydraulics: New York, Dover Publications, 257 p.

Leopold, L. B., and Langbein, W. B., 1962, The concept of entropy in landscape evolution: U.S. Geological Survey Professional Paper 500-A, 20 p.

Leopold, L. B., and Maddock, Thomas, Jr., 1953, The hydraulic geometry of stream channels and some physiographic implications: U.S. Geological Survey Professional Paper 252, 56 p.

Leopold, L. B., and Miller, J. P., 1956, Ephemeral streams—Hydraulic factors and their relation to the drainage net: U.S. Geological Survey Professional Paper 282-A, 36 p.

Li, Ruh-Ming, Simons, D. B., and Stevens, M. A., 1976, Morphology of cobble streams in small watersheds: American Society of Civil Engineers, Proceedings, no. HY8, p. 1101-1117.

Lindley, E. S., 1919, Regime channels: Punjab Engineering Congress Proceedings, v. 7.

Lowham, H. W., 1976, Techniques for estimating flow characteristics of Wyoming streams: U.S. Geological Survey Water-Resources Investigations 76-112, 83 p.

______1982, Streamflows and channels of the Green River basin, Wyoming: U.S. Geological Survey Water-Resources Investigations 81-71, 73 p.

Mahmood, Khalid, and Shen, H. W., 1971, The regime concept of sediment-transporting canals and rivers, Chapter 30 *in* Shen, H. W., ed. River Mechanics: Fort Collins, Colorado State University, 39 p.

Moore, D. O., 1968, Estimating mean runoff in ungaged semiarid areas: International Association of Scientific Hydrology Bulletin 13, v. 1, p. 29-39.

______1974, Estimating flood discharges in Nevada using channel-geometry measurements: Nevada Department of Highways Hydrologic Report 1, 43 p.

Nash, J. E., 1959, Discussion of "A study of bankfull discharge of rivers in England and Wales" by M. Nixon: London, Institute of Civil Engineers Proceedings, v. 14, p. 395-425.

Nixon, M., 1959, A study of the bankfull discharges of rivers in England and Wales: London, Institute of Civil Engineers Proceedings, v. 12, p. 157-174.

Omang, R. J., Parrett, Charles, and Hull, J. A., 1983, Mean annual runoff and peak flow estimates based on channel geometry of streams in southeastern Montana: U.S. Geological Survey Water-Resources Investigations 82-4092, 33 p.

Osterkamp, W. R., and Hedman, E. R., 1977, Variation of width and discharge for natural high-gradient stream channels: Water Resources Research, v. 13, no. 2, p. 256-258.

______1981, Channel geometry of regulated streams in Kansas as related to mean discharge, 1970-80: Kansas Water Office Technical Report 15, 32 p., 3 appendices.

______1982, Perennial-streamflow characteristics related to channel geometry and sediment in the Missouri River basin: U.S. Geological Survey Professional Paper 1242, 37 p.

Parrett, Charles, Omang, R. J., and Hull, J. A., 1983, Mean annual runoff and peak flow estimates based on channel geometry of streams in northeastern and western Montana: U.S. Geological Survey Water-Resources Investigations 83-4046, 53 p.

Pettis, C. R., 1937, Discussion of "Stable channels in erodible material" by E. W. Lane: Transactions of the American Society of Civil Engineers, v. 102, p. 149-152.

Riggs, H. C., 1974, Flash flood potential from channel measurements: International Association of Scientific Hydrology Publication 112, Proceedings of Paris Symposium, p. 52-56.

______1978, Streamflow characteristics from channel size: American Society of Civil Engineers, Proceedings, v. 104, no. HY1, p. 87-96.

Riggs, H. C., and Harenberg, W. A., 1976, Flood characteristics of streams in Owyhee County, Idaho: U.S. Geological Survey Water-Resources Investigations 76-88, 14 p.

Schumm, S. A., 1960, The shape of alluvial channels in relation to sediment type: U.S. Geological Survey Professional Paper 352-B, 30 p.

Scott, A. G., and Kunkler, J. L., 1976, Flood discharges of streams in New Mexico as related to channel geometry: U.S. Geological Survey Open-File Report 76-414, 29 p.

Smith, T. R., 1974, A derivation of the hydraulic geometry of steady state channels from conservation principles and sediment transport laws: Journal of Geology, v. 82, p. 98-104.

Stall, J. B., and Fok, Yu-si, 1968, Hydraulic geometry of Illinois streams: Illinois State Water Survey Research Report 15, 47 p.

Wahl, K. L., 1976, Accuracy of channel measurements and the implications in estimating streamflow characteristics *in* Modern Developments in Hydrometry: Padua, Italy, World Meteorological Organization, v. 2, p. 311-319.

Webber, E. E., and Roberts, J. W., 1981, Floodflow characteristics related to channel geometry in Ohio: U.S. Geological Survey Open-File Report 81-1105, 28 p.

Williams, G. P., 1978, Bankfull discharge of rivers: Water Resources Research, v. 14, no. 6, p. 1141-1154.

Wolman, M. G., 1955, The natural channel of Brandywine Creek, Pennsylvania: U.S. Geological Survey Professional Paper 271, 56 p.

Zimmerman, R. C., Goodlett, J. C., and Comer, G. H., 1967, The influence of vegetation on channel form of small streams: International Association of Scientific Hydrology Symposium of Berne, River Morphology, no. 75, p. 255-274.