

N61414.SF.001881
NAB LITTLE CREEK
5090.3c

METHODS FOR THE DETERMINATION OF CHEMICAL SUBSTANCES IN MARINE AND
ENVIRONMENTAL SAMPLES NAB LITTLE CREEK VA
11/1/1992
U S EPA REGION III

#6

EPA/600/R-92/121
November 1992

**Methods for the Determination of Chemical Substances in
Marine and Estuarine Environmental Samples**

Environmental Monitoring Systems Laboratory
Office of Research and Development
U.S. Environmental Protection Agency
Cincinnati, OH 45268



Printed on Recycled Paper

Foreword

Environmental measurements are required to determine the quality of ambient waters and the character of waste effluents. The Environmental Monitoring Systems Laboratory - Cincinnati (EMSL-Cincinnati) conducts research to:

- Develop and evaluate analytical methods to identify and measure the concentration of chemical pollutants in marine and estuarine waters, drinking waters, surface waters, ground waters, wastewaters, sediments, sludges, and solid wastes.
- Investigate methods for the identification and measurement of viruses, bacteria, and other microbiological organisms in aqueous samples and to determine the responses of aquatic organisms to water quality.
- Develop and operate a quality assurance program to support the achievement of data quality objectives in measurements of pollutants in marine and estuarine waters, drinking waters, surface waters, ground waters, wastewaters, sediments, and solid wastes.
- Develop methods and models to detect and quantify responses in aquatic and terrestrial organisms exposed to environmental stressors and to correlate the exposure with effects on chemical and biological indicators.

This EMSL-Cincinnati publication, "Methods for the Determination of Chemical Substances in Marine and Estuarine Environmental Samples" was prepared as the continuation of an initiative to gather together under a single cover a compendium of standardized laboratory analytical methods for the determination of nutrients, metals and organics in marine matrices. It is the goal of this initiative that the methods that appear in this manual will be multilaboratory validated. We are pleased to provide this manual and believe that it will be of considerable value to many public and private laboratories involved in marine studies for regulatory or other reasons.

Thomas A. Clark, Director
Environmental Monitoring Systems
Laboratory - Cincinnati

Abstract

This manual contains seven methods for determination of nutrients, metals, and chlorophyll. Methods 353.4, revision 1.2, and 365.5, revision 1.3, for the measurement of nitrite + nitrate and orthophosphate, respectively, appeared in the 1991 interim manual. Since then they have undergone multilaboratory validation studies. Method 365.5 performed well in the study and multilaboratory data are presented in the revision of the method that appears here. The performance of Method 353.4 in the study indicated that the cadmium reduction column chemistry and maintenance require further investigation. The method has been retained in this manual so that further testing can continue using a standardized method description.

Method 440.0 for measurement of total particulate carbon and nitrogen is based upon a well established combustion technique. Procedures for partitioning the organic and inorganic fractions of carbon are also presented. A multilaboratory study is in progress, and the results will be included in a subsequent revision of the method.

The three metals methods represent current state-of-the-science in metals measurements. Two of the methods are graphite furnace atomic absorption techniques and the third uses inductively coupled plasma mass spectrometry. Single laboratory performance data are included in the methods. Although few laboratories currently have the instrumentation capabilities to perform all of these methods, it is extremely important to present them in order to stimulate the development of laboratory capability before multilaboratory studies can be conducted.

Method 445.0 is for the determination of chlorophyll *a* and the pheopigments using fluorescence detection. This method has been used for many years for low level measurement of chlorophyll. The method was evaluated using two natural water samples of primarily green and blue-green algae.

The numbering of methods was correlated with previous EMSL-Cincinnati methods whenever possible. The metals methods are 200 series, the nutrients nitrite + nitrate and orthophosphate are 300 series, and the particulate carbon and nitrogen, and chlorophyll methods are 400 series.

Contents

	Page
Disclaimer	ii
Foreword	iii
Abstract	iv
Acknowledgments	vi
Introduction	1

Method Number	Title	Revision
200.10	Determination of Trace Elements in Marine Waters by On-Line Chelation Preconcentration and Inductively Coupled Plasma - Mass Spectrometry	1.6
200.12	Determination of Trace Elements in Marine Waters by Stabilized Temperature Graphite Furnace Atomic Absorption	1.0
200.13	Determination of Trace Elements in Marine Water by Off-Line Chelation Preconcentration with Graphite Furnace Atomic Absorption	1.0
353.4	Determination of Nitrite + Nitrate in Estuarine and Coastal Waters by Automated Colorimetric Analysis	1.3
365.5	Determination of Orthophosphate in Estuarine and Coastal Waters by Automated Colorimetric Analysis	1.4
440.0	Determination of Carbon and Nitrogen in Sediments and Particulates of Estuarine/ Coastal Waters Using Elemental Analysis	1.4
445.0	<i>In Vitro</i> Determination of Chlorophyll <i>a</i> and Pheophytin <i>a</i> in Marine and Freshwater Phytoplankton by Fluorescence	1.1

Evolution of an Urban Estuarine Harbor: Norfolk, Virginia

Maynard M. Nichols and Mary M. Howard-Strobel
804-642-7269

Virginia Institute of Marine
Science
School of Marine Science
College of William and Mary
Gloucester Point, VA, 23062,
USA

Marine Science Institute
University of Connecticut
Groton, CT, 06340, USA

ABSTRACT

NICHOLS, M. N., and HOWARD-STROBEL, M. M., 1991. Evolution of an Urban Estuarine Harbor: Norfolk, Virginia. *Journal of Coastal Research*, 7 (3), 745-757. Fort Lauderdale (Florida). ISSN 0749-0208.



The history of dredging and disposal has been compiled from historical charts and records to determine the course of harbor evolution at Norfolk, Virginia. Dredging activities between 1872 and 1982 have produced large geometric changes with important hydrographic and sedimentological consequences. The harbor once had a shallow irregular channel floor bordered by broad shoals, marshland and tributary creeks. Today after 100 years, dredging has deepened the channel 1.8 fold, smoothed the natural profile and increased sedimentation rates more than 90 times expected rates. Disposal as land fill has buried many creeks and marshes, moved the shore channelward and reduced the estuary area 26%. As a consequence these changes have reduced the tidal prism and entrance exchange. The dredge-fill-sedimentation cycle follows three stages of harbor evolution: (1) dredging entrance bars and the estuary head, (2) channel enlargement seaward with bordering landfill and open water disposal, and (3) contained disposal seaward of the early port, or ocean disposal. This case study shows that a series of small dredge and disposal projects in a small estuarine harbor can produce large cumulative effects that are the same order as natural geologic processes. Several other harbors follow similar stages of harbor evolution.

ADDITIONAL INDEX WORDS: *Estuarine sediments, harbor, dredging and disposal, estuary hydrodynamics.*

INTRODUCTION

In most estuarine harbors of the U.S. Atlantic coast, drastic changes have taken place in the shore configuration, bathymetry, hydraulic regime and sedimentation rates. Not all changes are of recent origin. They began on a large scale with the advent of steam power, enlargement of iron ship hulls and increased ship drafts in the late-1800s. Concurrently, steam power also made it possible to accelerate channel dredging, and thus provide greater water depth for larger ships. This set off a sequence of dredging, dumping and landfill activity. At first the changes were relatively small, producing only local variations in the immediate harbor environs. Later, however, the changes were large-scale and proceeded over many decades. The regularly dredged channels today therefore, are a cumulative

effect of numerous small changes, mainly in the last 100 years.

This paper addresses the historical changes produced by dredging and filling in the Elizabeth River estuary, Norfolk Harbor, Virginia. It focuses on large-scale and long-term effects of dredging and disposal, which are expressed by changes in bathymetry and shore configuration. These changes are analyzed to extract temporal trends showing the course of harbor evolution.

DATA SOURCES AND METHODS

The amount and location of material dredged comes from extensive files, charts and annual reports of the U.S. Army Engineer District, Norfolk (U.S. ARMY ENGINEER DISTRICT, NORFOLK, 1872-1982). These data consist of: (1) project records of federally controlled, U.S. Army Corps of Engineers projects, including the main shipping channel and adjacent anchorages; and (2) permit records of non-Corps projects, mainly

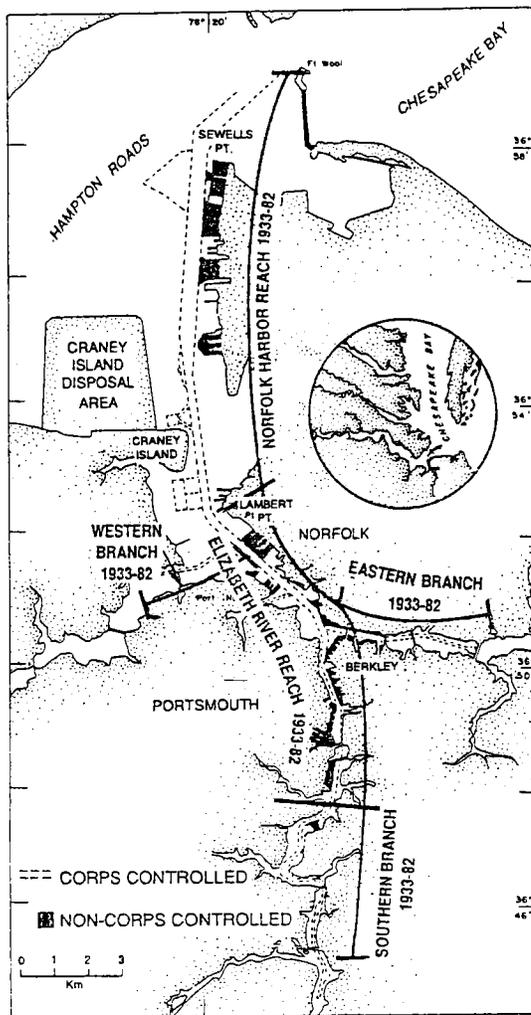


Figure 1. Location of Elizabeth River estuary, Norfolk Harbor (inset), designation of dredged channels with Corps non-Corps (private) zones of maintenance dredging responsibility.

private projects, including channels off the main shipping channel, anchorages and berths (Figure 1). The amount and location of dredged material removed from the channels is defined by comparing Corps bathymetric survey charts prepared before and after dredging.

The locations of historic disposal areas, shoreline changes and landfill history are taken from both Corps charts and records as well as charts of the U.S. COAST AND GEODETIC SURVEY (NATIONAL OCEAN SURVEY) dated 1853, 1872-

73, 1911 and 1982. Changes are revealed by comparing shorelines and bathymetry, after adjustment to a common vertical datum, coordinate system and common scale by reduction or enlargement in a Map-O-Graph unit.

SITE DESCRIPTION

The Elizabeth River system which includes Norfolk Harbor, is a drowned tributary estuary of Chesapeake Bay incised in coastal plain deposits (Figure 1). Prior to the advent of large-scale dredging and disposal the shoreline was indented with small creeks bordered by marshes, which formed a dendritic pattern of waterways (Figure 2A). The longitudinal channel profile was interrupted by deep holes and shoals of muddy sediment (Figure 3).

Present-day channel sediments are predominantly soft mud with water content ranging 35 to 70% and total organic carbon 0.8 to 3.5%. A sediment budget (NICHOLS and HOWARD-STROBEL, 1987) revealed that the estuary receives 55,000 tons of fine sediment on the average each year, of which 93% is introduced from seaward zones in Hampton Roads, 3% from upland runoff and 4% from combined industrial and waste water discharge in addition to plankton production.

Although the estuary was initially shaped by geologic processes, man's concentrated urban activities, which accelerated about 1880, have greatly modified the bathymetry and reshaped the shoreline. Shores and beaches have been bulkheaded to prevent erosion and provide transportation facilities like piers, docks, boat slips and shipping terminals. Creeks and marshlands have been buried for airfields, industry and residential areas. Channels have been dredged for a length of 36 km to accommodate shipping. Today, after 100 years of accelerated development little is left of the natural system along the main estuary.

HISTORICAL BACKGROUND

The trends of dredging and filling have proceeded with growth of the cities of Norfolk and Portsmouth, their environs, and the changing patterns of maritime trade, industry and military activities. Port development and related dredging activities evolved in three stages:

ge are revealed by
dymetry, after
vertical datum, coor-
n scale by reduction
Graph unit.

DIPTION

stem which includes
ed tributary estuary
ed in coastal plain
o the advent of large-
al the shoreline was
reeks bordered by
dendritic pattern of
e longitudinal chan-
d by deep holes and
(Figure 3).

liments are predomi-
r content ranging 35
arbon 0.8 to 3.5%. A
s and HOWARD-STRO-
the estuary receives
t on the average each
duced from seaward
3% from upland run-
industrial and waste
ion to plankton pro-

as initially shaped by
concentrated urban
ed about 1880, have
ymetry and reshaped
l beaches have been
erosion and provide
ke piers, docks, boat
ninals. Creeks and
uried for airfields,
reas. Channels have
of 36 km to accom-
r 100 years of accel-
is left of the natural
uary.

CKGROUND

and filling have pro-
cities of Norfolk and
is, and the changing
e, industry and mili-
pment and related
d in three stages:

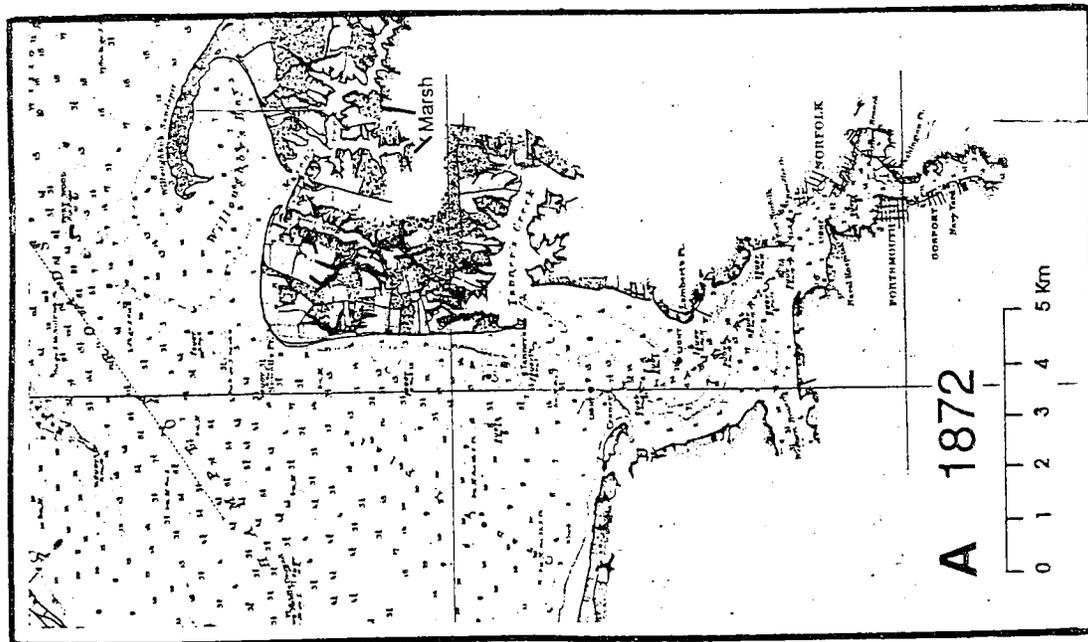
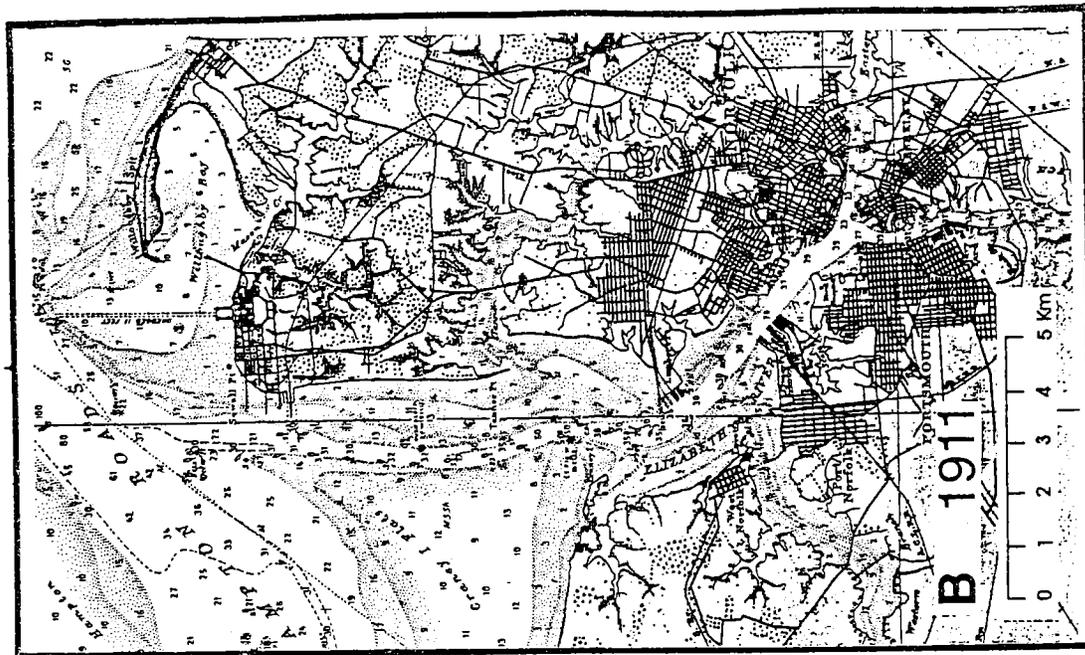


Figure 2. Historic charts of the U.S. Coast and Geodetic Survey showing shore morphology and bathymetry of the Elizabeth River; (A) 1872, prior to extensive dredging activity, (B) 1911, after early development and construction of coal piers.

LITERATURE CITED

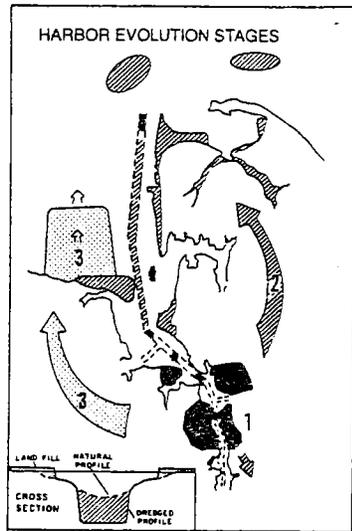


Figure 10. Schematic diagram showing stages in the evolution of dredging and disposal in Norfolk Harbor. For explanation of stages see text. Inset lower left in schematic cross section comparing typical natural and dredged profiles.

activity can reverse the natural geologic evolution of estuarine filling by sedimentation while associated land filling can reverse the natural marine transgression.

- (4) An estuarine harbor like Norfolk may be expected to evolve through three stages: (1) dredging entrance bars and the estuary head, (2) channel lengthening and seaward enlargement with land fill on bordering shores or in open water outside the harbor, and (3) contained disposal within the harbor seaward of the initial port site, or alternately, ocean disposal.

ACKNOWLEDGEMENTS

This study was supported by grant R806002-02 of the U.S. Environmental Protection Agency, Chesapeake Bay Program. Thanks are due to Mr. Gene Whitehurst of the U.S. Army Engineer District, Norfolk, for assistance with Corps' historical dredging records. Kay Stubblefield of VIMS drafted the figures. This is Virginia Institute of Marine Science contribution number 1639.

- BERGER, R.C.; HELTZEL, S.B.; ATHROW, R.F.; RICHARDS, D.R., and TRAWLE, M.J., 1985. Norfolk Harbor and channels deepening study. U.S. Army Engineer Waterways Experiment Station, Vicksburg, Mississippi. *Technical Report HL-83-3*, 53p.
- BRUSH, G.; DAVIS, F.W., and STENGER, C.A., 1980. Sediment accumulation and the history of submerged aquatic vegetation and eutrophication in the Patuxent and Ware Rivers: A stratigraphic study. *Contract Report 806-680-01* to the U.S. E.P.A. Chesapeake Bay Program, Annapolis, Maryland, 60p.
- COCH, C.A.; TAVOLARO, J.F.; KRAUSER, R.G., and TISCHBEIN, P., 1983. Alternatives to open water disposal of contaminated dredged material. In: Patin, T.R., (ed.), *Management of Bottom Sediments Containing Toxic Substances, Proceedings, 9th U.S./Japan Experts Meeting*. (Jacksonville, Florida), pp. 176-197.
- FEHRING, W.K., 1985. History of the Port of Tampa. In: Treat, S.; Simon, J.L., and Lewis, R.R., (eds.), *Proceedings, Tampa Bay Area Scientific Information Symposium*. Tampa, Florida: Bellwether Press, pp. 512-524.
- HARD, C.G. and PALMER, H.D., 1976. Sedimentation and ocean engineering ocean dumping. In: Stanley, D. J. and Swift, D. J. P., (eds.), *Marine Sediment Transport and Environmental Management*. New York: Wiley, pp. 557-577.
- LEWIS, R.R., III, 1976. Impact of dredging in the Tampa Bay estuary, 1876-1976. *The Coastal Society, Proceedings of the Second Annual Conference* (New Orleans), pp. 31-55.
- MCDOWELL, D.M. and O'CONNOR, B.A., 1977. *Hydraulic Behavior of Estuaries*. New York: Wiley 292p.
- NICHOLS, M., 1979. The problem of misplaced sediment. In: Palmer, H. and Gross, M.G., (eds.), *Ocean Dumping and Marine Pollution*. Stroudsburg, Pennsylvania: Dowden, Hutchinson and Ross, pp. 147-161.
- NICHOLS, M. and HOWARD-STROEBEL, M.M., 1987. Man's physical effects on the Elizabeth River. In: Kuo, C. and Younos, T., (eds.), *Effects of Upland and Shoreline Land Use on the Chesapeake Bay. Proceedings of the Chesapeake Bay Research Conference*. (Williamsburg, Virginia), pp. 166-177.
- RICHARDS, D. and MORTON, R., 1983. Norfolk Harbor and channels deepening study. U.S. Army Engineer Waterways Experiment Station, Vicksburg, Mississippi, *Report 1*. Physical Model Results; Chesapeake Bay Hydraulic Model Investigation, *Technical Report HL-83-13*, 75p.
- SCHUBEL, J. and WILLIAMS, A., 1976. Dredging and its impact on upper Chesapeake Bay: Some observations. *The Coastal Society, Proceedings of the Second Annual Conference* (New Orleans) pp. 70-115.
- SUSZKOWSKI, D.J., 1978. Sedimentology of Newark Bay, New Jersey: An urban estuarine bay. Ph.D. Dissertation, University of Delaware, Newark, Delaware, 222p.
- U.S. ARMY ENGINEER DISTRICT, NORFOLK, 1872-1982.