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CONCEPTS IN MARINE POLLUTION MEASUREMENTS

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Meaningful Chemical Measurements in the Marine Environment—Transition Metals

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The following comments present a critical, but not negative, point of view that seeks identification of improved approaches to "marine pollution effects" studies. The current literature has many examples of the disquiet that the authors experience in reviewing or participating in recent studies. As pointed out by Dayton (1982), in reviewing the proceedings of a symposium: The Shore Environment, "Environmental protection programs are increasingly criticized by ecologists, regulatory and management agencies, and private business as being of questionable quality and value. Because regulatory agencies and many ecologists are uncomfortable with the highly probabilistic nature of ecology, there is a tendency, often a legal necessity, for impact studies to be very detailed and specific and to collect reams of data that have no underlying logic and defy generalization or test. This prevents the growth of coastal ecology as a science." It seems interesting and paradoxical that the collection of a large amount of data prevents the growth of a particular science, but it seems to be true.

Further on in Dayton's review, he expresses what may be the cause of the paradox: "Though the editors have been successful in presenting integrated holistic studies and many of the papers are current and innovative, explicit recognition of the importance of attempting to falsify hypotheses as a scientific method is generally lacking. Assuredly, emphasis on rigorous testing can be overdone when the hypotheses are trivial. Nevertheless, I would have hoped to see more evidence of the use of the experimental methods and an explicit recognition of the scientific futility of testing general hypotheses with computer analyses of data collected without concern for mechanistic questions. . . . It is to be hoped that increasing sophistication of regulatory agencies and decreasing funds will soon result in a merger of mechanistic science and environmental monitoring." This example illustrates the point that data collection without clear hypothesis formulation is really the cause of the "prevention of the growth of coastal ecology as a science."

A feeling of dissatisfaction is expressed also by Gross (1981) in a review of Industrialized Embayments and Their Environmental Problems: A Case Study at Swansea Bay. He remarks that, "the volume will be a useful reference to researchers interested in coastal ocean areas and their alteration by human activities. Its weaknesses are the familiar failure to demonstrate the relevance of the science presented and the failure to explain the science to nonscientists. It is worth noting that none of the papers in the volume refers to comparable U.S. environmental studies such as the Corps of Engineers' Dredged Material Research Program, or NOAA's New York Bight Project. So far as I know, the neglect is mutual: Environmental studies of the 1970's were apparently done in nearly scientific isolation. Perhaps this accounts for the slight progress made in environmental studies during the past ten years." It seems a reasonable guess that the lack of "relevance of science presented" can be ascribed to the absence of clearly stated hypotheses to guide the work.

We cite one more example of unavoidable critical appraisals. The NAS-NRC committee to evaluate outer continental shelf (OCS) environmental studies came to this conclusion: "The program does not now effectively contribute to leasing decisions or to the accrual of sound scientific information adequate for OCS management, both offshore and onshore. While the Bureau of Land Management (BLM), which administers the program, does not define it as a research program as such, a scientifically sound activity is nevertheless required. Our concern for the scientific content of the program, as distinguished from its utility to BLM, is that we could find very little evidence of explicit hypotheses or statements of scientific purpose for which the data were intended. Thus gathering of the data prescribed through formal bid instructions often leads to descriptive data for unknown purpose but does not necessarily lead to invalid scientific information. We do not wish to imply that we judge all work of this BLM program unscientific. However, the general lack of a scientific construct and specific hypotheses combined with uncertain relevance for departmental decisions, greatly erode the potential value of the program. Therefore, we urge BLM to execute a problem analysis to identify the information required to develop a program design suitable to obtain this information. Without a second scientific design focused on the relevant issues, the present program will continue to produce inconclusive descriptions."

Current examples of distress in "marine pollution effects" studies could also be found in the drafts of "synthesis reports" for the NOAA New York Bight program and the EPA Chesapeake Bay Toxic Substances Program. The point is that chemical measurements have formed a substantial part of the data collection, and identification of improved "meaningful" measurements can be based only on recognition of current deficiencies. Our perception is that the dissatisfaction with many recent marine pollution effects studies results from failure to apply the scientific method to these problems. Table 1 is a simplistic outline of application of the scientific method to the study of estuarine and coastal processes. Perhaps the perplexity concerning the quality of the current literature comes from a failure to recognize that most work does not progress very far along the sequence in Table 1.

To illustrate this point, Boehm (1982) has given permission for quotation of a figure from a manuscript that describes measurements of some organic compounds in the New York Bight region. The data suggested to Dr. Boehm that several processes (resuspension and transport) need to be considered in the system that was sampled (Figure 1). The point that we would like to make is that Boehm's excellent work went only as far as Step 3 in Table 1. A limited amount of new data permitted him to formulate some speculative conclusions. The reader is frustrated in that there is no indication that the work is to be carried forward in terms of testing the significance of these hypothesized processes to produce a scientifically "meaningful" study.

Table 1. Scientific method for studying estuarine and coastal processes.

1. Exploratory Data Collection
2. Summary Description - Qualitative or Semiquantitative
3. Formulation of Process Hypotheses (Modelling Equations)
4. Data Collection for Hypotheses Evaluations (Model Quantitative Evaluation)
5. Scientific, Quantitative Tentative Conclusions
6. Use and Testing of Conclusions
    - A. Evaluation of Forecasts
    - B. Verification of Management Decisions

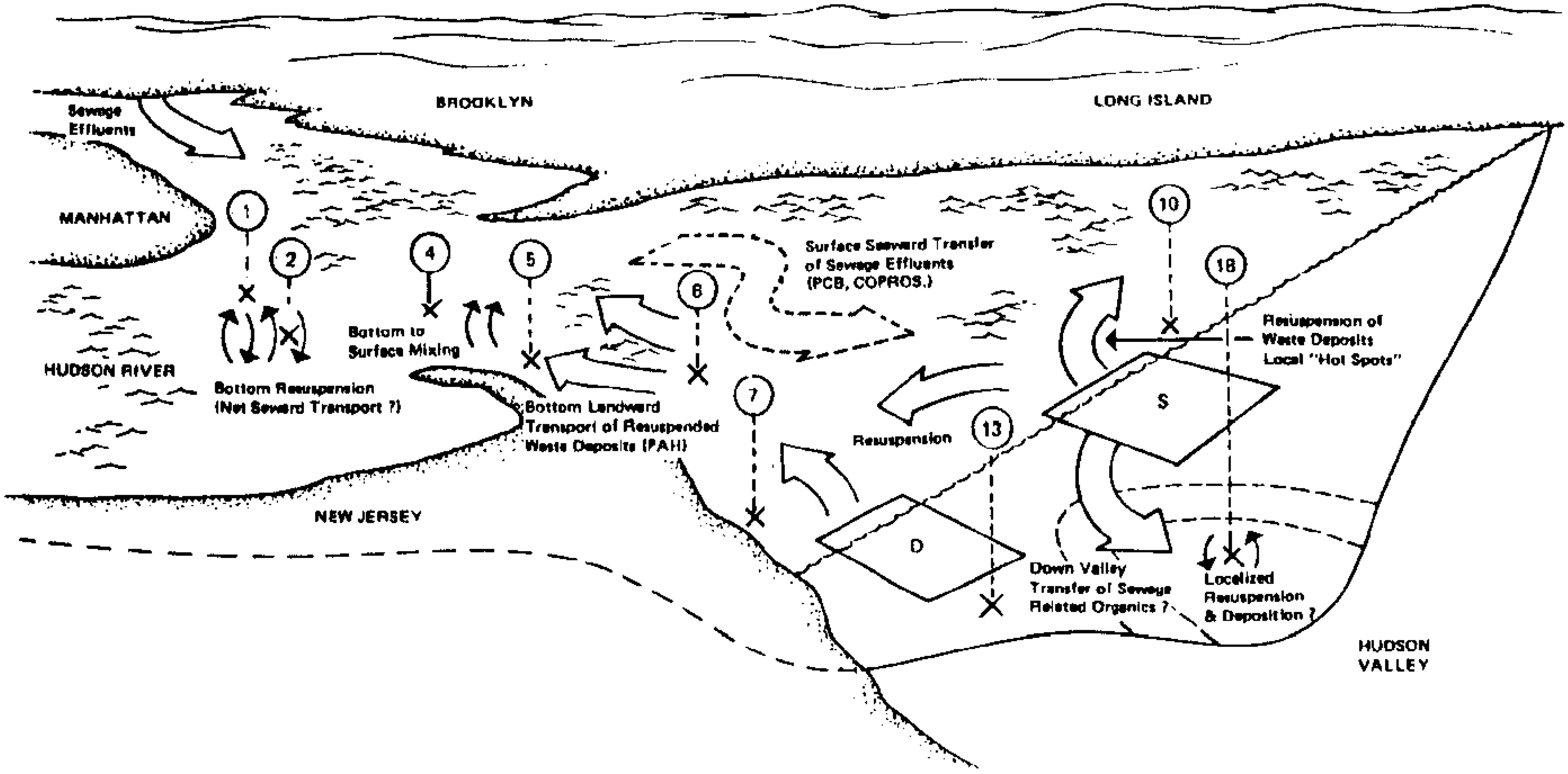

Figure 1. Organic pollutant resuspension and transport systems as suggested by data. Numbers refer to stations; arrows represent surface transport; arrows represent bottom or middle water transport (Boehm 1982).

We think that Dayton's hopes for increasing sophistication of regulatory agencies may lie primarily in the direction of recognition that many "research" programs have been stopped short of the scientific phases in Table 1 or have been continued for many years as monitoring or "baseline" data collection efforts without recognition that the scientific method has not been invoked.

The final inference that we would like to draw from the above briefly described examples is that the scientific method can be cost effective. Mindless monitoring will never produce understanding of environmental processes that will be useful in formulating public policy and regulations. Assessment of probable environment effects (impacts) should become realistic and meaningful as understanding, rather than larger data files, becomes the specified goal of environmental studies.

LIMITATIONS OF CURRENT TRACE METAL DATA

For inorganic materials, marine "pollution effects" often imply a focus on toxic substances such as some of the transition metals (Cu, Zn, Cd, Hg, Pb, Ni, Cr, etc.). In contrast to the synthetic organic materials that are entirely anthropogenic these metals are naturally present and "pollution effects" need to be discerned against the natural background occurrences.

Unanticipated Temporal and Spatial Viability

Many of the data for the transition metals cannot be interpreted in terms of the processes that control metal abundance in estuarine and coastal waters because the designs of the sampling programs did not adequately anticipate the temporal and spatial variability that is present. Variability can be considered as composed of two parts.

1. Components considered in the equations that are the quantitative hypotheses (models). These may have annual, seasonal, daily, tidal and diurnal time scales and spatial scales of meters to kilometers. The sampling design should be derivative from the hypotheses and, in absence of clear statements of hypotheses, the data interpretation is frequently based on an ad hoc scheme developed posteriorly.

2. Random variability (noise) that comes from the lack of homogeneity in the system being sampled. While it is trivially obvious that the sampling must be carried out with sufficient replication to provide "representative" data, much of the current information is woefully deficient in this regard, as will be illustrated in the following examples. However, particular note should be taken that regular variability not considered in the sampling design then contributes to the noise; for example, processes that are operative on daily,

> tidal or diurnal time scales would contribute variability if monthly sampling is used to look at seasonal cycles and samples are collected at different times of the day or stages of the tide.

Some data from the recent literature illustrate these features. For the toxic metals, anthropogenic damage (pollution) may occur primarily in the estuarine and coastal environments. The processes that cause variability in metal concentrations are diagramed in Figure 2. Attention should be directed to the obvious feature (which is neglected to a remarkable extent in much current work) that the estuarine and coastal environments are places where upland drainage mixes with water from the open oceans. A major cause of temporal and spatial variations in metal concentrations for these environments may be the processes that take place outside the study area; that is, the drainage basin chemical dynamics may be reflected in the estuarine or coastal area. The major variations in the source water can be ascribed frequently to seasonal variations in discharge rates, particularly with respect to suspended solids and associated metals, as shown in Figure 3, for samples from the mouth of the Susquehanna River as it enters the Chesapeake Bay.

Further perspective on the challenge to understanding the dynamics of anthropogenic metal damage is displayed in Figure 4. It is important to remember that these temporal variations at the head of Chesapeake Bay will be expressed as spatial variations in the estuary as these waters continue to move seaward. Downstream "pollution" would need to be discerned against this substantial variability. Zinc is predominantly associated with settleable solids, but does not correlate very well with the variations in iron concentrations. Week-to-week variations of twofold or more were found, with a pulse of soluble zinc in January. Copper and nickel were roughly equally distributed between the solid phase and filter-passing or "soluble" phase. The winter pulse of nickel might be a vegetative input, but the possibility of inputs from the burning of fossil fuels needs to be studied using rainwater samples from the watershed. However, the lack of large metropolitan areas on the Susquehanna watershed may rule out fossil fuels as a quantitatively important source. The lack of an increase in the copper and nickel concentrations during February, March and May, comparable with the increase shown by iron, manganese, and zinc suggests that the solids carrying the copper and nickel have a different source and character.

The challenge to understanding is reflected further by the data plotted in Figure 5, which are the same values as those shown in Figure 4 except that the observed metal contents of the samples are expressed as weight concentrations in either the settleable or filterable solids. The most striking feature is the seasonal varia-

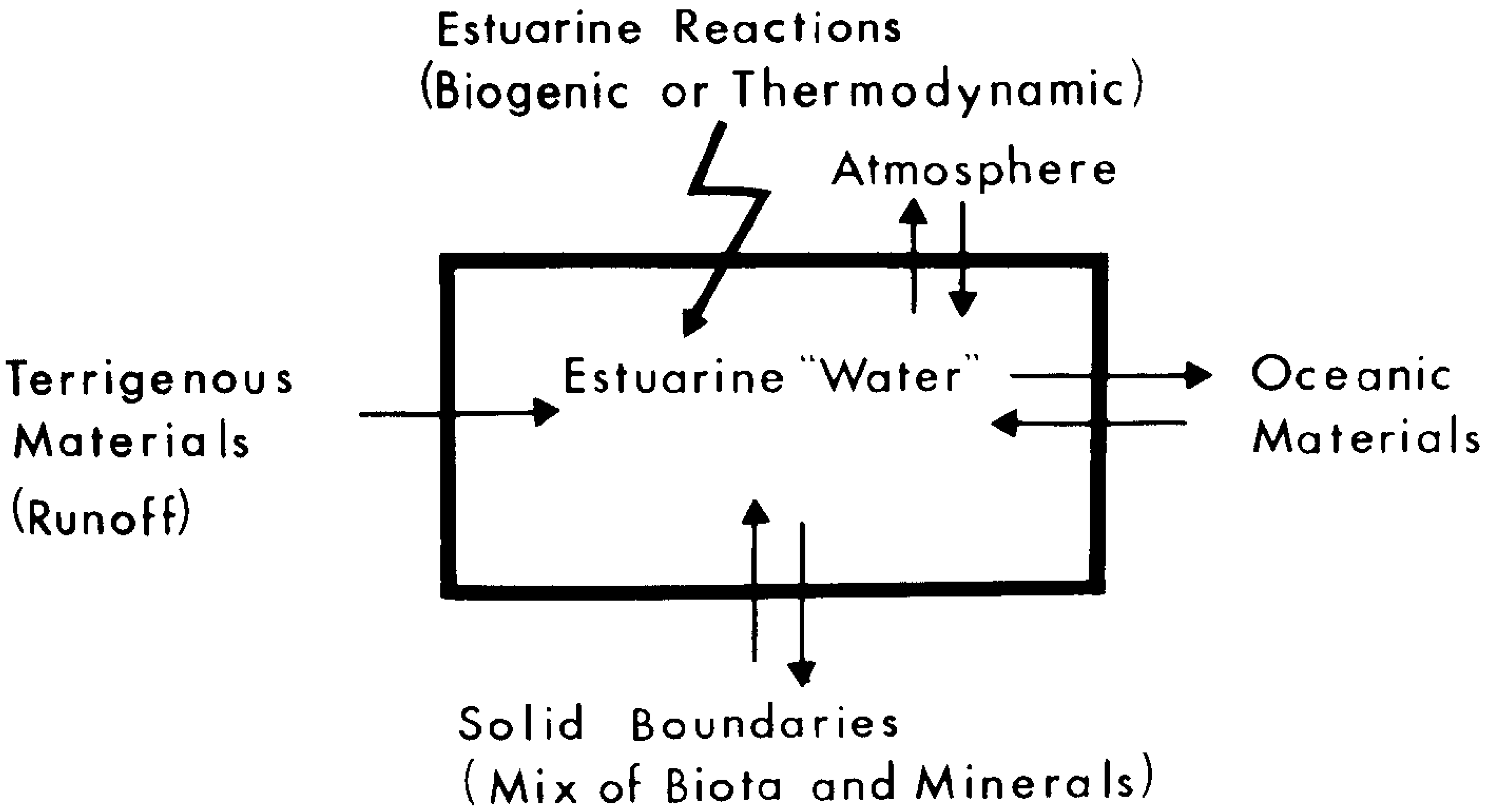

Figure 2. Schematic representation of the processes that affect the composition of estuaries (Carpenter et al. 1975).

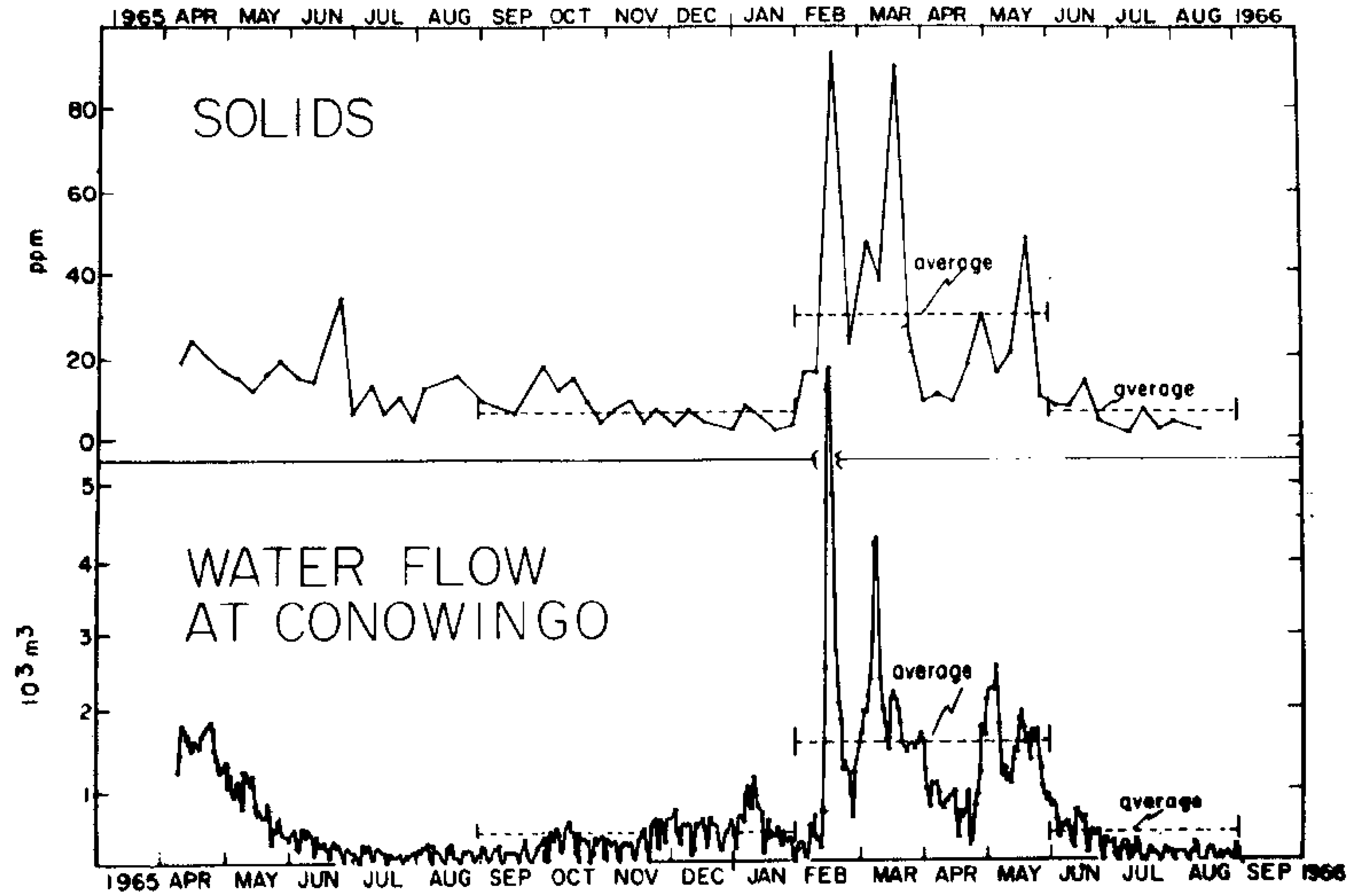

Figure 3. Flow rates of the Susquehanna River and the concentrations of suspended solids in the samples (Carpenter et al. 1975).

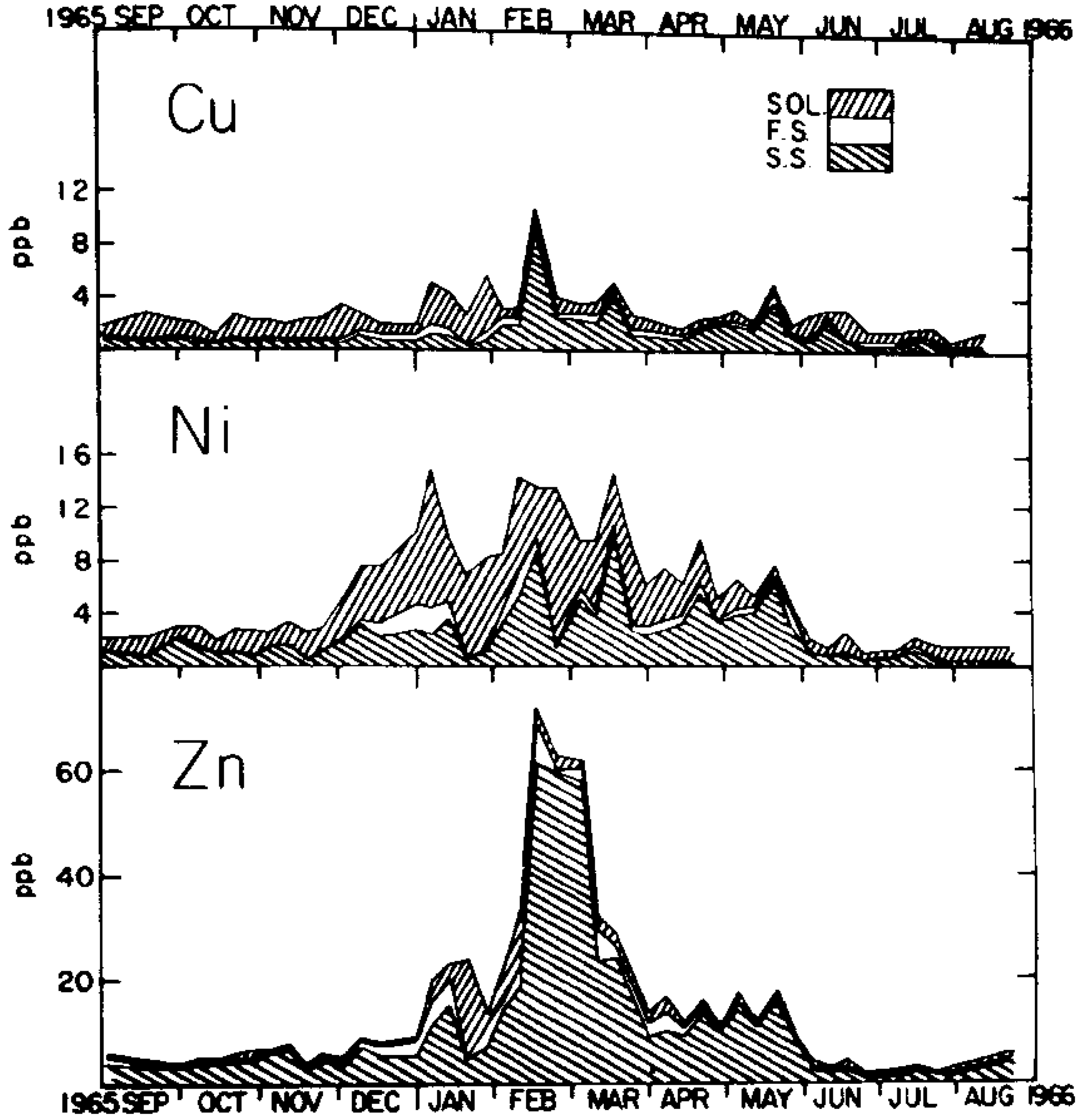

Figure 4. Copper, nickel and zinc concentrations in the soluble, filtered-solids and settled-solids fractions of the samples (Carpenter et al. 1975).

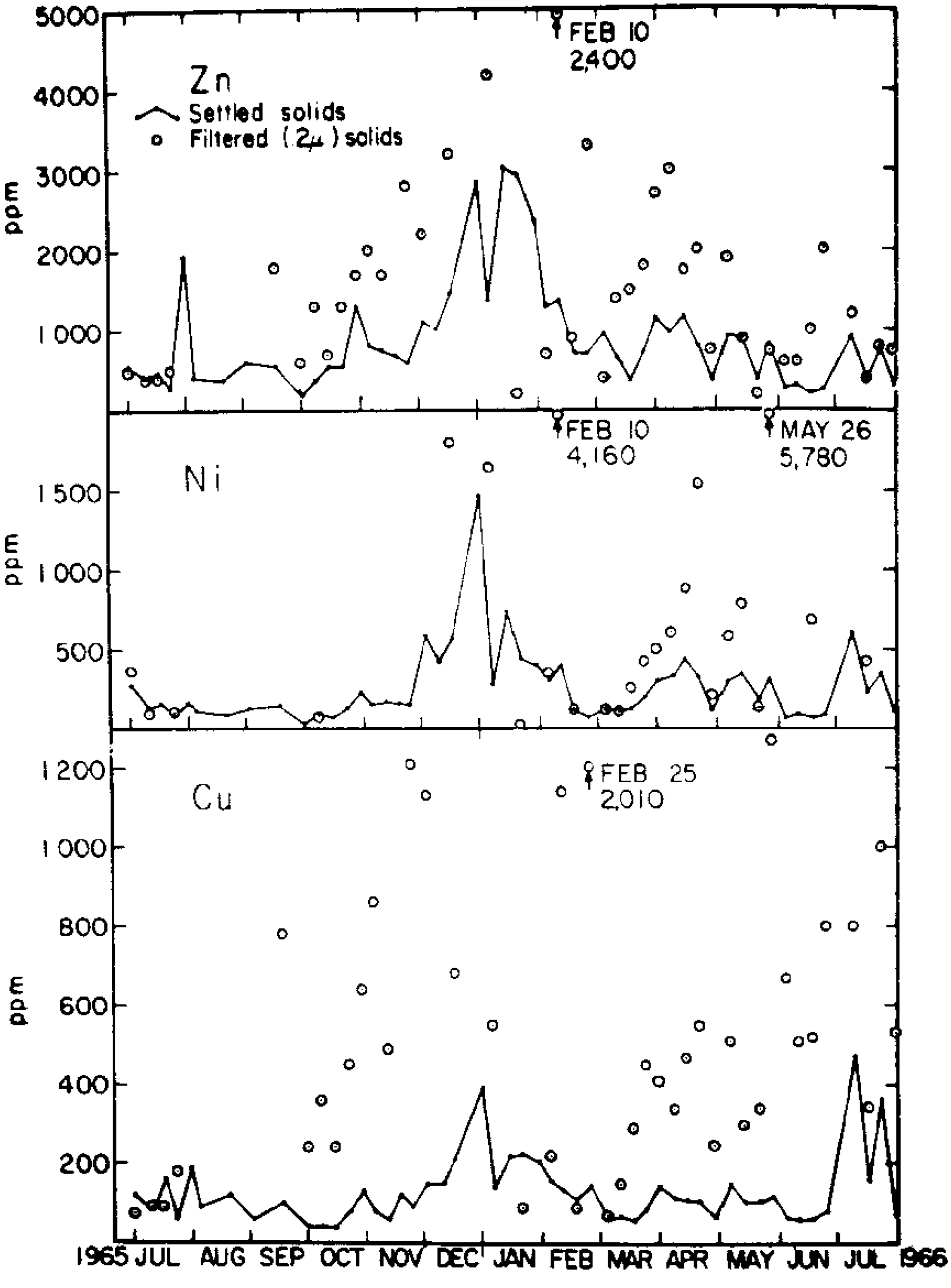

Figure 5. Zinc, nickel and copper concentrations in the separated solids (Carpenter et al. 1975).

tion in the composition of the solids, metal-rich materials being more abundant during December and January. The non-settleable or filterable materials (either small size or low density) probably were high in organic and aluminosilicate content; they frequently had much higher concentrations of metals, but were extremely variable.

The variable metal content of the solids as a function of particle size or density is present also in estuarine sediments. Huggett (1981) reported the data shown in Figure 6 that displays an intimidating large variation in the copper content of Chesapeake Bay sediments. Detection or realistic perception of estuarine damage due to anthropogenic copper in the face of this observed variability requires greater skill and thoughtfulness than has been present in much recent work.

That the metal content of suspended material in estuaries like Chesapeake Bay is highly variable has been documented recently by Nichols et al. (1982). Many observations (5576) were made and Table 2 summarizes the data. The expectable variability due to the processes diagramed in Figure 1 is clearly present but the absence of process hypotheses in the program design impairs interpretation of this large data set in terms of the relative significance of the various processes and resolution of anthropogenic contributions to this system.

One source of variability that was unusually well documented by Nichols et al. (1982) was the temporal variation in suspended solids and associated metals. As shown in Figure 7, variations greater than twofold were found over a tidal cycle. This source of variability was mitigated by scheduling observations close to slack water (± 1 hour) and does not contribute to the data summarized in Table 2. However, from the point of view of aquatic toxicology and evaluation of possible anthropogenic damages, these time variations in the concentrations of suspended solids and associated metals need to be considered in terms of possible responses by organisms. Bioassay data in the literature have been focused on time invariant exposure to various toxicants and one cannot help but wonder whether, in the "real-world" environments such as Chesapeake Bay, the organisms respond to the mean metal concentrations or to the complex temporal variations.

Seasonal variability in both natural and anthropogenic metal concentrations derives largely from variations in the values of upland runoff. Consider an anthropogenic input to the river or near the head of an estuary and the resulting concentration distribution as shown in Figure 8, which might be a plot of a single survey. Measurement of chlorinity or salinity makes it possible to compute the effects of dilution with sea water, and such plots have been used to estimate the effects of processes other than dilution. However, simple interpretation is not possible; for example, the difference labeled with a question mark in Figure 8 might be due to

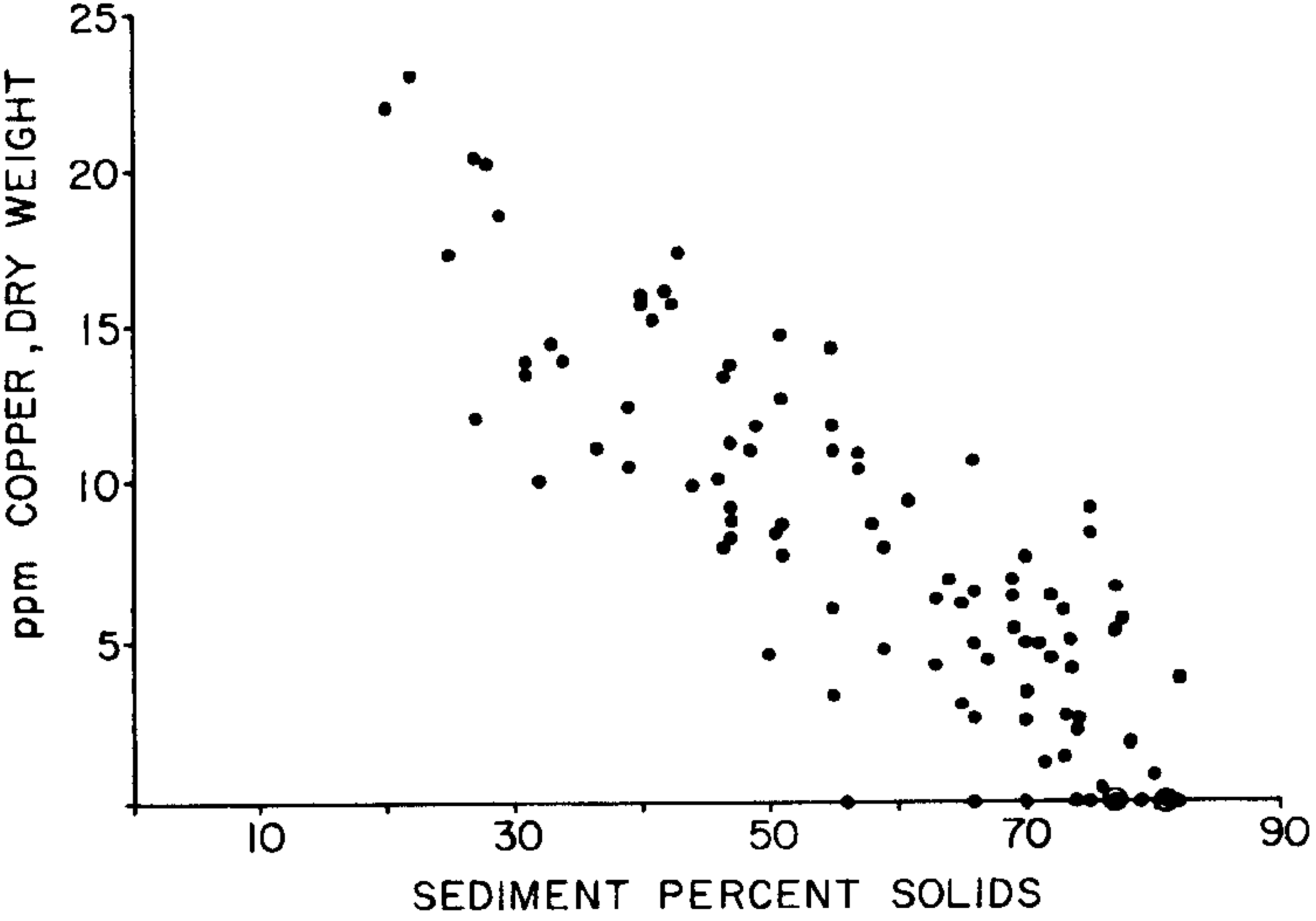

Figure 6. Copper concentrations in the top 2 cm of bottom sediments from Chesapeake Bay plotted with the respective percent solids (Huggett 1981).

Table 2. Summary of mean metal concentrations and range of Bay-wide values in suspended material, expressed as weight per weight and weight per volume*.

$\mu g\ g^{-1}$			$\mu g\ L^{-1}$		
Metal	Mean	Range	Metal	Mean	Range
As	13.00	0.55-100.00	As	0.32	0.006-5.00
Cd	14.16	0.12-790.00	Cd	0.14	0.003-3.80
Cu	127.96	9.90-570.00	Cu	1.84	0.068-17.00
Fe(%)	3.11	0.29-17.00	Fe	0.88	0.01-12.00
Pb	160.30	21.00-730.00	Pb	2.27	0.10-15.00
Mn	2.88	0.08-46.00	Mn	65.13	0.48-1000.00
Hg	3.89	0.05-59.00	Hg	0.035	0.01-0.47
Ni	95.80	4.80-770.00	Ni	2.00	0.03-34.00
Sn	17.97	0.25-290.00	Sn	0.20	0.01-4.80
Zn	0.75	0.10-7.10	Zn	11.02	0.55-94.00

* Nichols et al. (1982)

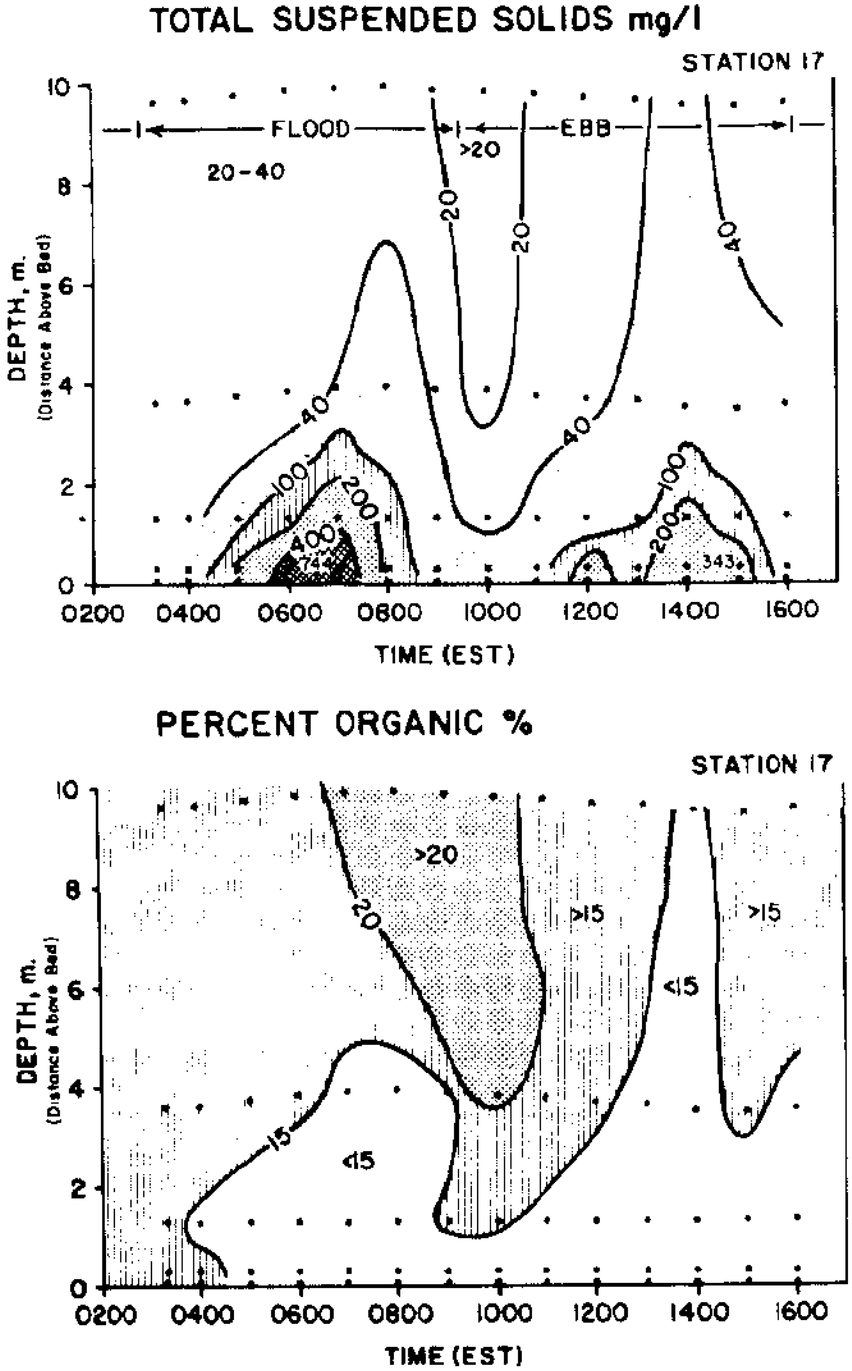

Figure 7. Temporal variations of total suspended solids and percent organic content with depth (Nichols et al. 1982).

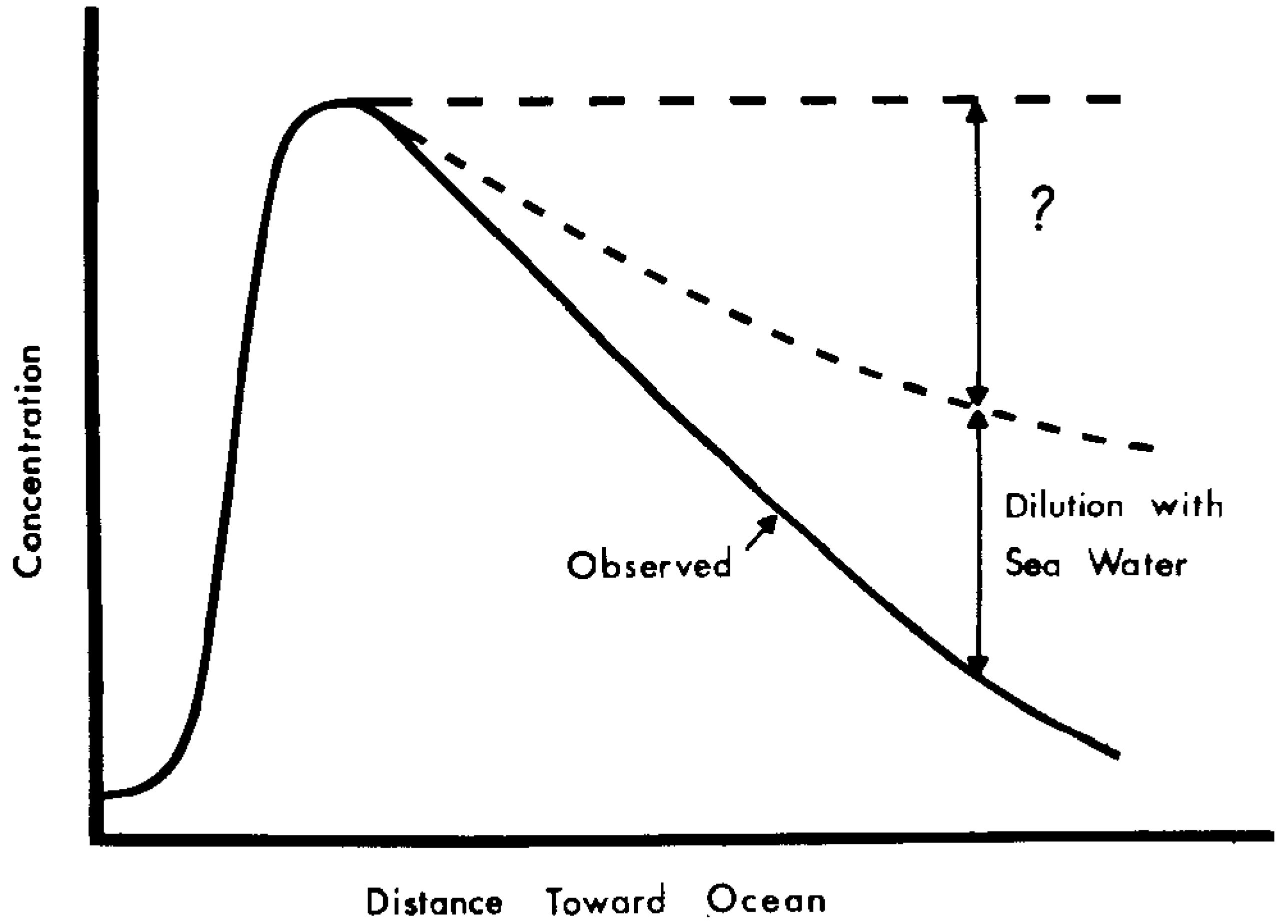

Figure 8. Example of the longitudinal concentration variation from a point source input (contamination), solid line. Small-dash curve represents estimate of concentration that would have been found if no dilution had been present. Difference between small-dash curve and large-dash curve requires identification of additional process from several possibilities.

(a) transformation of the constituent into a form not determined in the analytical procedure, (b) loss to the sediments, (c) input of the constituent having varied with time, or (d) the flow rate of the river having varied with time. The last possibility always exists, and the curve in Figure 8 may simply indicate that the water in the more seaward part of the estuary passed the point of contaminant input at a high rate of flow and never had the concentration that was being produced at the source point at the time of the survey. Evaluation of this effect requires adequate time-varying "models" (equations) for estuarine flow and mixing and a comprehensive set of data for variations as a function of both position and time. Because of these features, our understanding of the fate of contaminants has not progressed very far, and progress awaits simultaneous developments in theory and observation.

Natural variabilities in trace metals are present in marine and estuarine organisms as well as in bottom and suspended sediments. An example of this phenomenon in organisms which supposedly integrate varying inputs of substances over time and thus smooth out temporal variations is presented utilizing copper and zinc in oysters, Crassostrea virginica (Huggett et al. 1973). In this study replicate oganisms were collected from the same bed at the same time and were analyzed. The resulting data showed that the metal concentrations in individuals, which were presumed to be the same age, often differed as much as 100% and occasionally 300%. In addition, it was shown in this and further studies that even in the absence of pollution sources, oysters in fresher waters of estuarine systems contain more metals than those from more saline waters (Huggett et al. 1975).

Obviously if natural variations such as these are not incorporated into the sampling design, then valid conclusions relative to the impact of human activity will be difficult if not impossible.

Total Metal Content as Subject of Data

Most data are for total metal content. Although the total concentrations of various metals in suspended solids and sediments are of interest in simple geochemical studies, such data are of limited use in assessing anthropogenic damage. The recent, extensive study of Chesapeake Bay sediments by Helz et al. (1981) provides a good example of geochemical studies of estuarine sediments. This group carried out 8000 individual analyses of 12 metals and came to the conclusion that "a number of processes may influence the observed vertical profiles (of sediment metal concentrations). No single process, such as anthropogenic contamination, provides an adequate explanation for all the data." This work provides a good example of the labor required to provide a description of the metal distributions in Chesapeake Bay sediments and indicates that in the absence of hypothesis formulations, resolution of the magnitudes of the various processes awaits further scientific studies based on this work.

However, knowledge of the abundance of the metals in the sediments does not provide a basis for evaluating anthropogenic damage. Helz et al. used refluxing in a 90-10 mixture of nitric and hydrochloric acids to solubilize the metals from the sediment samples. This harsh technique had the virtue of giving reproducible results but probably solubilized much metal that would not be available to benthic organisms. Data obtained by such means do not appear to be applicable to understanding the toxicity or lack of toxicity of metals in estuarine sediments.

This point is demonstrated very clearly in the recent work of Rubinstein et al. (1982) of the EPA Gulf Breeze laboratory. Sandworms, hard clams and grass shrimps were exposed for 100 days to sediments from New York harbor that had been contaminated with PCBs, mercury and cadmium. Some transfer of PCBs to the animals was found but no transfer of mercury or cadmium was observed. As they state, "Results from this study support the contention that sediment concentration alone does not reflect bioavailability and that bioassays and field monitoring remain the most direct method for estimating bioaccumulation potential of sediment bound contaminants at this time." It seems clear that new, appropriate chemical techniques for characterization of the metal content of sediment solids are needed for "meaningful measurements of marine pollution".

Another example of the importance of bioavailability in assessing impacts from anthropogenic inputs was demonstrated in a study by Haven and Morales-Alamos (1979). In this work Kepone-contaminated sediments were collected from the James River in Virginia and presented to oysters as a suspension under controlled laboratory conditions. Analysis of the oyster feces and pseudofeces showed that the Kepone levels averaged 3.5 times higher in the feces than in the pseudofeces. The explanation is that oysters selectively differentiate the particles that they filter. Those that they pass through their gut are voided as feces and the remainder exit as pseudofeces. Since Kepone is associated with the organic fraction of the sediments (Huggett et al. 1980) and since the oysters obtain their energy requirement from it and hence "eat" this fraction, the feces are relatively enriched with the pesticide. Obviously, in the case of Kepone and oysters, more relevant information would be obtained if the organic fraction of sediment were analyzed rather than the total. Even though this example concerns an organic compound, it appears likely that such differentiations are important for metals as well.

Dependence of Toxicity on Undetermined Chemical Speciation

The attitude of administrators and regulators that inexpensive, simple testing techniques for "marine pollution" are what is needed is not surprising. However, the truth stands squarely in the way of simplistic "quick-fixes" and biogeochemical quackery. Even for the simple "dissolved" toxic metal content of estuarine and coastal waters, the toxicity depends on the chemical form of the metal. Regulatory strategy that seeks reasonable protection of marine life and public health by shying away from both overprotection and underprotection will have to be based on the translation of scientific knowledge into policy, rather than vice versa. The intricacy that must be faced may be illustrated by drawing on the recent literature concerning the aquatic toxicity of copper. The purpose is not to review the literature on copper, but rather to cite some work that shows the nature of the "tiger that we have by the tail".

At the present time, many states have adopted water quality standards for copper; for example, the State of Florida 1979 standard was promulgated at 0.015 mg L^{-1} (15 ppb) for marine waters from the older general value of 0.5 mg L^{-1} (500 ppb). The guidance provided by the NAS/NAE (ESB 1972) states "on the basis of data available at this time, it is suggested that concentrations of copper equal to or exceeding 0.05 mg L^{-1} (50 ppb) constitute a hazard in the marine environment and levels less than 0.01 mg L^{-1} (10 ppb) present minimal risk of deleterious effects." Presumably that guidance was considered in setting the revised Florida water quality standard for copper.

The NAS/NAE report drew primarily on bioassay work with larger marine animals. Subsequent research (Sunda and Gillespie 1979; Sunda and Ferguson 1982) has shown that smaller organisms, particularly bacteria and phytoplankton, are remarkably sensitive to ionic copper, responding (with growth reduction) at levels of approximately 0.0005 ppb free cupric ion. In seawater, inorganic complexes (with hydroxide and carbonate anions) form with a ratio of inorganically complexed copper to free copper of roughly 60 to 1. If this inorganic complexing were the only detoxification present, the water quality criterion would need to be roughly 0.03 ppb to protect bacteria and phytoplankton. Since the natural copper concentrations in estuarine and coastal waters range from 1 to 0.1 ppb, copper toxicity would be widespread were it not for detoxification by complexing with organic materials. As Sunda and coworkers (ESB 1972; Sunda and Gillespie 1979) have shown, the organic complexing of copper is extensive and nearly all the copper (96-99%) in their samples was organically bound.

It seems obvious that site-specific knowledge is necessary to establish water quality standards for copper. Bioassay techniques would be useful except that they are extremely tedious and require great skill and care by the observer. Chemical techniques may be an attractive alternative but, in view of the extremely low concentration of copper that causes biological responses, the chemical techniques will not be as simple or inexpensive as regulatory personnel might hope. However, such costs may be minuscule compared with the economic burdens of overprotecting or underprotecting our aquatic environments.

One candidate technique for observing the capacity of natural waters to bind or detoxify copper is anodic stripping voltametry (ASV). Discussions in the recent literature have raised questions as to whether there are undiagnosed artifacts in the use of ASV. Some recent unpublished work by M. J. Spencer in her doctoral research at the University of Miami will be briefly outlined to show that the ASV technique, in which the copper complexing capacity of samples is determined by titration with copper, provides data that, if properly interpreted, are a good measurement of copper complexing capacity (Figure 9).

The first point brought out by Spencer's research is that the copper-binding compounds can be isolated from seawater by ultrafiltration (500 daltons nominal pore size). Having found a way to concentrate the compounds, she could determine the complexing capacity by an independent method based on an equilibrium binding gel filtration technique, obtaining results such as those shown in Figure 10. The integral quantity of copper shown in this chromatogram corresponds to 38 nM (2.4 ppb) complexing capacity in the original sample, and the titrimetric value for this sample was 35 nM. This agreement between the two measurements that involve entirely different techniques seems to be strong evidence that her ASV procedure and data interpretation are sound.

A second point in Spencer's work is that pseudopolarograms (like those shown in Figure 11), constructed from stripping peak versus plating potential data, showed that the copper-organic complex was electroactive--albeit to a lesser extent than would be possible for the inorganic copper complexes or no-titration. This previously unidentified property of the compounds has led to erroneous interpretations of the ASV titration data by a number of authors. Spencer derived equations for the calculation of the conditional stability constant based on an electroactive copper-organic complex mode. To test the soundness of this methodology, she titrated irradiated seawater samples containing known additions of EDTA with a standardized copper solution. The average conditional stability constant determined from these titration data was 2.3×10^{8}, which agrees quite well with the value of 1.9×10^{8} calculated from the literature for the various competing reactions with the calcium, magnesium, carbonate and hydroxide in seawater.

Using this new knowledge, Spencer determined an average conditional stability constant of 1.0×10^{9} for a number of samples from southeastern Florida coastal waters. This value is an order of magnitude higher than that calculated using the methodology of previous investigators in which the complexes were assumed to be nonelectroactive. When this average value is used together with typical values for the total copper and complexing capacity in southeastern Florida waters, 98.6% of the copper is predicted to be in the organic form and only 0.02% in the free copper ion or toxic form.

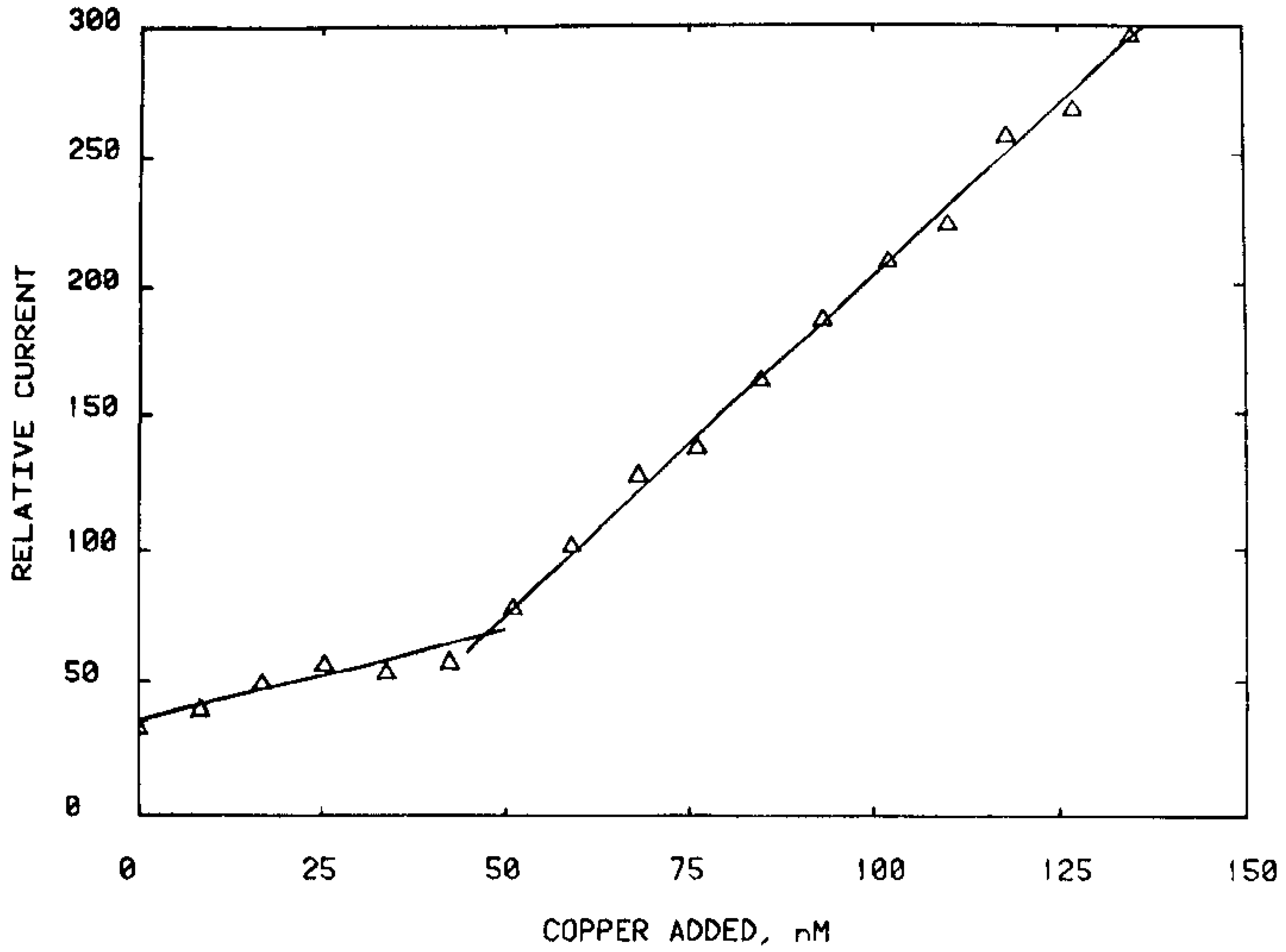

Figure 9. Titration of a Biscayne Bay sample with a copper solution. ASV was used to follow the course of the titration.

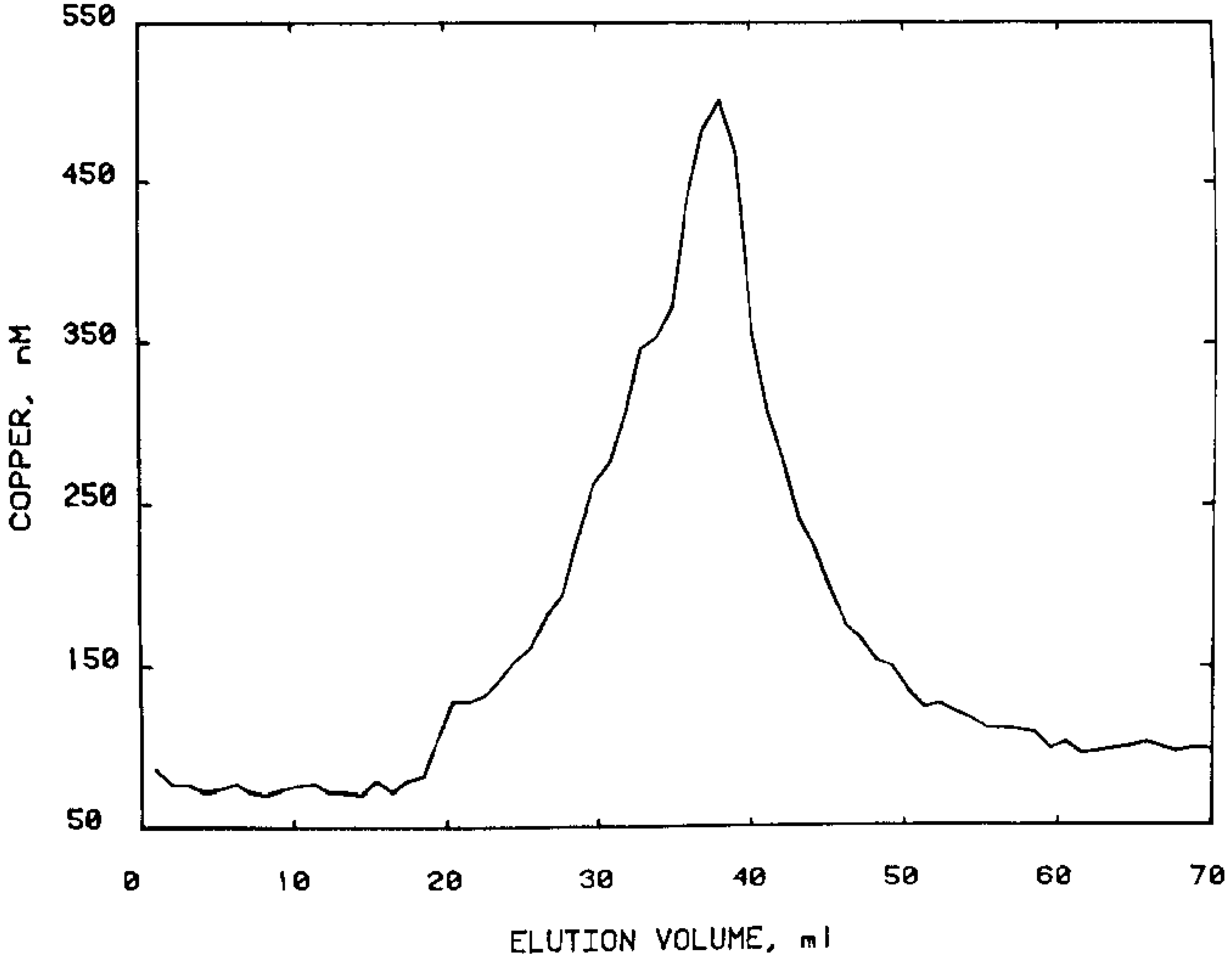

Figure 10. Chromatogram using equilibrium binding gel filtration of isolated copper complexing compounds to confirm titrimetric measurement of complexing capacity.

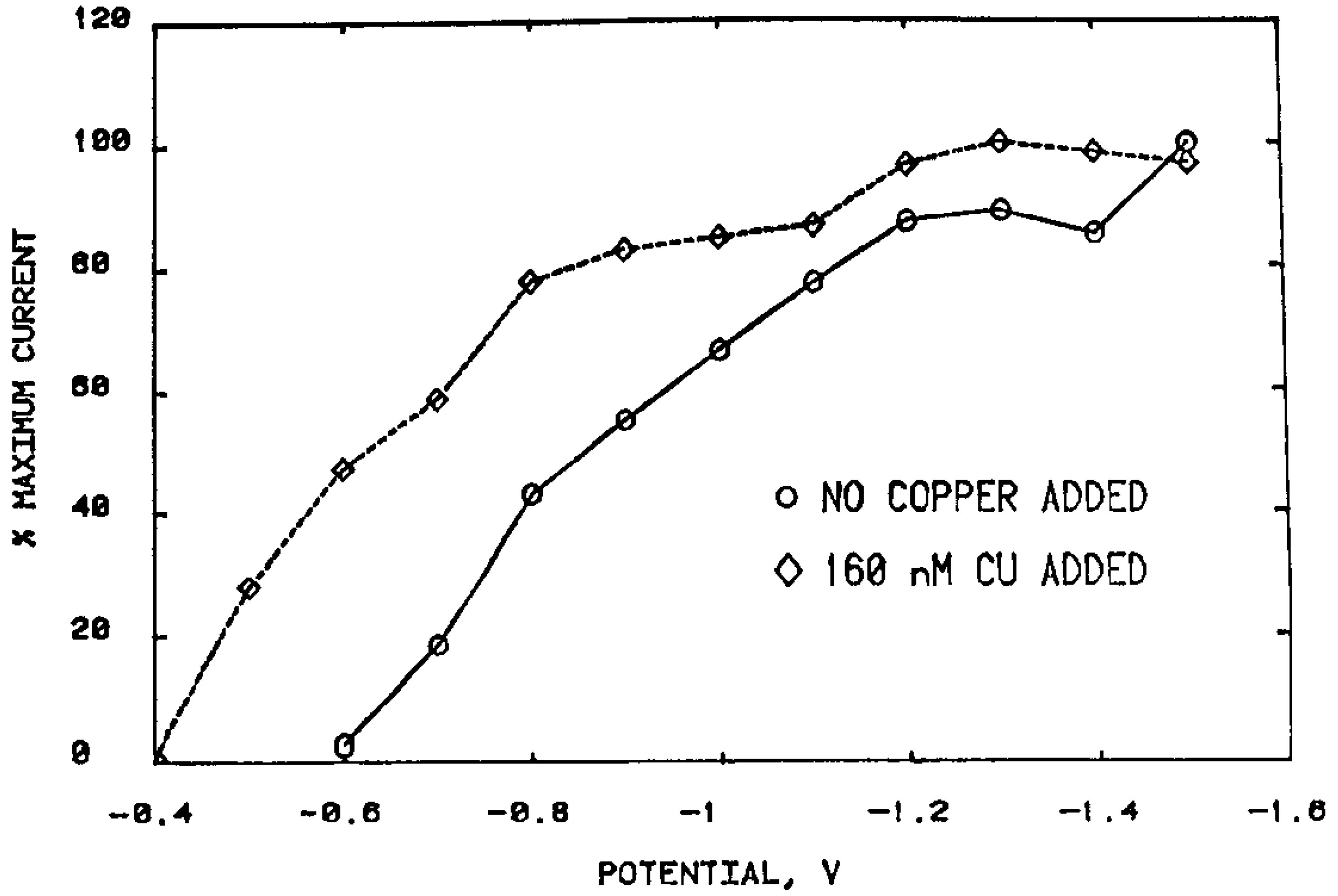

Figure 11. Pseudopolarograms of original sample showing one wave corresponding to reduction of organically complexed copper, and of copper spiked sample showing overlapping waves from inorganic and organic reductions.

It seems probable that the ASV titration technique with copper can yield observations having the same information content as that obtained with the tedious and tricky bioassay techniques.

Recent research clearly shows that aquatic organisms do not respond to the "total" toxic metal concentration but that the metal speciation controls the observed responses. "Meaningful" chemical measurements must reveal the speciation. The penalty of cost and complexity with the appropriate techniques should be more than offset in the utility of the resulting data.

CONCLUSION

This brief survey has been intended to support the following views. Many of the data (measurements) that might have some bearing on "marine pollution effects" from transition metals do not appear to be meaningful. This deficiency exists because the scientific method has been inadequately applied and the nature of the problems have not been well understood. In the positive sense it appears that, currently, sufficient descriptive data exist and new techniques are being developed for chemical measurements that will permit work with increased "meaning" or understanding in the future. "More of the same" doesn't look useful, but the groundwork for improvement has been laid. Research that seeks quantitative understanding of estuarine and coastal biogeochemical processes, including anthropogenic damage, must be carried out before straightforward monitoring or proctoring will be useful.

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