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Workshop Proceedings

EVALUATING APPROACHES AND TECHNOLOGIES FOR MONITORING ORGANIC CONTAMINANTS IN THE AQUATIC ENVIRONMENT

Ann Arbor, MI
June 21-23, 2006

Funded by NOAA's Coastal Services Center through the Alliance for Coastal Technologies (ACT)

An ACT 2006 Workshop Report

A Workshop of Developers, Deliverers, and Users of Technologies for

Monitoring Coastal Environments:

Evaluating Approaches and Technologies for Monitoring Organic Contaminants in the Aquatic Environment

Ann Arbor, MI
June 21-23, 2006

Sponsored by the Alliance for Coastal Technologies (ACT) and NOAA's Center for Coastal Ocean Research in the National Ocean Service.

Hosted by ACT Partner, University of Michigan.

ACT is committed to develop an active partnership of technology developers, deliverers, and users within regional, state, and federal environmental management communities to establish a testbed for demonstrating, evaluating, and verifying innovative technologies in monitoring sensors, platforms, and software for use in coastal habitats.

TABLE OF CONTENTS

Executive Summary

An ACT 2006 Workshop Report

The Alliance for Coastal Technologies (ACT) convened a workshop on Evaluating Approaches and Technologies for Monitoring Organic Contaminants in the Aquatic Environment in Ann Arbor, MI on July 21-23, 2006. The primary objectives of this workshop were to: 1) identify the priority management information needs relative to organic contaminant loading; 2) explore the most appropriate approaches to estimating mass loading; and 3) evaluate the current status of the sensor technology. To meet these objectives, a mixture of leading research scientists, resource managers, and industry representatives were brought together for a focused two-day workshop. The workshop featured four plenary talks followed by breakout sessions in which arranged groups of participants where charged to respond to a series of focused discussion questions.

At present, there are major concerns about the inadequacies in approaches and technologies for quantifying mass emissions and detection of organic contaminants for protecting municipal water supplies and receiving waters. Managers use estimates of land-based contaminant loadings to rivers, lakes, and oceans to assess relative risk among various contaminant sources, determine compliance with regulatory standards, and define progress in source reduction. However, accurately quantifying contaminant loading remains a major challenge. Loading occurs over a range of hydrologic conditions, requiring measurement technologies that can accommodate a broad range of ambient conditions. In addition, in situ chemical sensors that provide a means for acquiring continuous concentration measurements are still under development, particularly for organic contaminants that typically occur at low concentrations. Better approaches and strategies for estimating contaminant loading, including evaluations of both sampling design and sensor technologies, need to be identified. The following general recommendations were made in an effort to advance future organic contaminant monitoring:

1. Improve the understanding of material balance in aquatic systems and the relationship between potential surrogate measures (e.g., DOC, chlorophyll, particle size distribution) and target constituents.

2. Develop continuous real-time sensors to be used by managers as screening measures and triggers for more intensive monitoring.

3. Pursue surrogate measures and indicators of organic pollutant contamination, such as CDOM, turbidity, or non-equilibrium partitioning.

4. Develop continuous field-deployable sensors for PCBs, PAHs, pyrethroids, and emerging contaminants of concern and develop strategies that couple sampling approaches with tools that incorporate sensor synergy (i.e., measure appropriate surrogates along with the dissolved organics to allow full mass emission estimation).

5. Fund market/needs assessment for new technologies based on ACT and the Cooperative Institute for Coastal and Estuarine Environmental Technology (CICEET) workshops.

6. Promote standardization of output among sensors and open protocols in sensor technology development and improve data management/visualization components when new technology reaches the commercialization point.

Alliance for Coastal Technologies

The Alliance for Coastal Technologies is a NOAA-funded partnership of research institutions, resource managers, and private sector companies dedicated to fostering the development and adoption of effective and reliable sensors and platforms. ACT is committed to providing the information required to select the most appropriate tools for studying and monitoring coastal environments. Program priorities include transitioning emerging technologies to operational use rapidly and effectively; maintaining a dialogue among technology users, developers, and providers; identifying technology needs and novel technologies; documenting technology performance and potential; and providing the Integrated Ocean Observing System (IOOS) with information required for the deployment of reliable and cost-effective networks.

> ACT is organized to ensure geographic and sector involvement:
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> - Headquarters is located at the UMCES Chesapeake Biological Laboratory, Solomons, MD.
>
> - Board of Directors includes Partner Institutions, a Stakeholders Council, and NOAA/CSC representatives to establish ACT foci and program vision.
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> - There are currently eight ACT Partner Institutions around the country with coastal technology expertise that represent a broad range of environmental conditions for testing.
>
> - The ACT Stakeholder Council is comprised of resource managers and industry representatives who ensure that ACT focuses on service-oriented activities.

To accomplish these goals, ACT provides these services to the community:

- Third-party testbed for quantitatively evaluating the performance of new and existing coastal technologies in the laboratory and under diverse environmental conditions.

- Capacity building through technology-specific workshops that review the current state of instrumentation, build consensus on future directions, and enhance communications between users and developers.

- Information clearinghouse through a searchable online database of environmental technologies and community discussion boards.

The ACT workshops are designed to aid resource managers, coastal scientists, and private sector companies by identifying and discussing the current status, standardization, potential advancements, and obstacles in the development and use of new sensors and sensor platforms for monitoring, studying, and predicting the state of coastal waters. The workshop's goal is to help build consensus on the steps needed to develop and adopt useful tools, while facilitating critical communication among the various groups of technology developers, manufacturers, and users.

ACT Workshop Reports are summaries of the discussions that take place between participants during the workshops. The reports also emphasize advantages and limitations of current technologies while making recommendations for both ACT and the broader community on the steps needed for technology advancement in the particular topic area. Workshop organizers draft the individual reports with input from workshop participants.

ACT is committed to exploring the application of new technologies for monitoring coastal ecosystem and studying environmental stressors that are increasingly prevalent worldwide. For more information, please visit www.act-us.info.

Goal for the Organic Contamination Workshop

The ACT workshop on organic contaminants monitoring was convened on July 21-23, 2006, in Ann Arbor, MI, to examine the state of current approaches and technologies in monitoring aquatic organic contaminants. The overall goal of the workshop was to foster the awareness and communication among leaders from industry, resource management, and academia as to the needs and limitations for bringing new technologies into practice and to foster better monitoring approaches.

Participants were given the following specific charges to address:

- Identify the priority management information needs relative to organic contaminant loading:
  - What resource is being managed (e.g., receiving water, influent, waste stream, non-point source runoff)?
  - What constituents of concern, including emerging contaminants, need to be monitored to meet your program goals?
  - What temporal scale is most important to assess in order to meet program needs (e.g., continuous vs. discrete sampling)?
  - How is monitoring information used to guide management actions?
  - How are monitoring programs limited by current sampling and analytical capabilities?
- Explore the most appropriate approaches to estimating mass loading:
  - What is the optimal sampling strategy to capture desired concentration or load relationships (e.g., surrogate or ancillary measurements)?
  - How does seasonal variation effect loading estimation (e.g., dry weather, wet weather, annual loading?
  - How important is compound specificity or differentiation of phases (e.g., dissolved vs. particulate)?

  - What temporal scale is most important to assess (e.g., continuous vs. discrete sampling)?
  - What type of detection is required (e.g., passive samplers vs. active sensors, required detection limits)?
- Recognize the current status of the sensor technology:
  - What are the priority needs for new technology development?
  - What are the limitations of existing technologies?
  - What barriers exist to the development of new technologies?

Organization of the Organic Contamination Workshop

The workshop was sponsored by NOAA's Alliance for Coastal Technologies and hosted by the University of Michigan. The workshop was organized by Tom Johengen and facilitated by Eric Stein of the Southern California Coastal Water Research Project, Dwight Trueblood of the Cooperative Institute for Coastal & Estuarine Environmental Technology, and Marc Burrows of the International Joint Commission. The workshop was held over the course of two days at the University of Michigan and followed a prescribed format that ACT has developed for these technology workshops. The event opened with an evening dinner reception during which participants were introduced and two presentations given. The first presentation was delivered by Tom Johengen and described the structure and goals of the ACT program, and the second presentation, given by Eric Stein of the Southern California Coastal Water Research Project, was designed to set the stage for the following two days of deliberations. On the morning of the second day, participants were briefed on the format and objectives of the workshop by Tom Johengen and then listened to a plenary talk given by Eric Barnowski of the Ira Township Water Plant. Following the presentation, the first breakout session was convened to stimulate discussion and address the charges of the workshop. For each breakout session, three groups of eight to nine participants each were formed and asked to respond to a set of specific questions. For each session, the groups were mixed to contain an equal number of members from the three sectors. After each breakout session, all groups reconvened in plenary sessions to present the responses from each group and to allow for additional discussion. The second plenary presentation was given by Nate Bosch of the University of Michigan. The second breakout session convened after this presentation with a new set of discussion questions and new groups. The third and final plenary presentation of the day began after lunch and featured Debra Deininger of Synkera Technologies. Breakout Session III began after this presentation. On the final day, the facilitators led a discussion among all participants to synthesize the main conclusions from prior discussions and to develop a set of specific tasks. Lastly, participants tried to identify some specific action items or functions that ACT should aim to accomplish to promote these technology advancements.

Monitoring Organic Contaminants: A Statement of the Problem

There exists at present two major concerns for quantifying mass emissions and detection of organic contaminants for protecting receiving waters and municipal water supplies. Managers use estimates of land-based contaminant loadings to rivers, lakes, and oceans to assess relative risk among various contaminant sources, determine compliance with regulatory standards, and define progress in source reduction. However, accurately quantifying contaminant loading remains a major challenge. Loading occurs over a range of hydrologic conditions, requiring measurement technologies that can accommodate a broad range of ambient conditions. In addition, in situ chemical sensors that provide a means for acquiring continuous concentration measurements are still under development, particularly for organic contaminants which typically occur at low concentrations. Better approaches and strategies for estimating contaminant loading, including evaluations of both sampling design and sensor technologies, need to be identified. Discussions are needed that examine trade-offs among the use of available sensor-based contaminant measurement techniques, monitoring for more easily measured surrogates parameters, recommended frequency/timing for collecting discrete samples for direct chemical analysis, and the use of smart sensors to make concentration measurements at the most appropriate time points. Secondly, sampling and detection strategies used by managers to detect organic contaminants in water supplies used for municipal activities and human consumption need to be addressed. The current range of technologies available to measure contaminants and the requirements for real-time field-based measurements to provide appropriate response time for protective actions are subjects that need to be explored.

Plenary Presentations

Four keynote presentations were delivered during the workshop to help set the stage for the discussion breakout sessions. On the first evening of the workshop, Eric Stein presented the introductory talk, *Evaluating Approaches and Technologies for Monitoring Organic Contaminant Loading – Workshop Introduction and Goals,* during which he discussed challenges of the accurate assessment mass loading of constituents, including varying ambient condition and broad ranges of expected constituent concentrations. The presentation then outlined the workshop goals and the three primary discussion areas: what are the priority management information needs relative to organic contaminant loading, what is the most appropriate approach to estimating mass loading, and what is the current status of the sensor technology? Next, the presentation outlined current challenges of measuring organics across various temporal scales (i.e., instantaneous measures vs. annual composites) and under different conditions (i.e., storm water, effluent, municipal water supply). Finally, three alternate strategies for estimating mass loading of organics were proposed for further discussion; passive samplers, active sensors, and surrogate measures. The presentation concluded with an overview of the workshop organization to set the stage for the following day's breakout sessions.

On the second day of the workshop, Eric Barnowski gave a stimulating presentation entitled, *The St. Clair River/Lake St. Clair Drinking Water Monitoring and Notification System*. This presentation described the St. Clair River and Lake St. Clair monitoring program. The goals of the program include; protection of drinking water, development of surrogate detection technology, development of a water quality database, utilization of existing resources, development of an environmental training and education platform, and the determent of future spills. The monitoring program was developed in response to the repeated discharge of toxic pollutants into the river and lake system. This program is a coordinated effort by Federal, state, county, and local governments to protect the St. Clair River and Lake St. Clair, as both provide drinking water to many U.S., Canadian, and First Nation residents. The monitoring program seeks to place continuous monitoring equipment at water plants and other strategic locations to detect changes in water quality. Detection of measurable contaminants will then trigger an automated alert system notifying all stakeholders and authorities of a potential contamination event.

The second plenary talk of the day was entitled, *Tributary Loading Estimation Protocols*, and was presented by Nate Bosch. This presentation outlined sampling considerations for estimating annual tributary loads and introduced two different load estimation protocols. Several aspects must be considered when considering a sampling program that aims at estimating loads. Daily water discharge measurements (or some other measurement to which the parameter of interest is correlated) are needed for the time period of interest. The frequency of sampling (i.e., monthly) also needs to be considered. Nate advised a sampling program that included stratification based on flow and season; systematic sampling rather than random, and point (or instantaneous) sampling as opposed to integrated sampling approaches. The two load estimation protocols introduced were the USGS Estimator and the Beale Ratio Estimator. The USGS Estimator program develops a regression based on flow, time, and season in order to estimate missing concentrations. With this complete set of concentrations and daily stream-flow measurements, daily loads are summed to give estimates for annual loads. The Beale Ratio Estimator program calculates a ratio between measured loads and total flow. This ratio is then used to adjust the average measured daily loads to allow estimation of annual loads. Strengths and weaknesses of each estimation protocol were then discussed.

The final plenary talk of the day entitled, *Acoustic Sensors for Detection of Persistent Organic Contaminants in Water*, was presented by Debra Deininger of Synkera Inc. This presentation gave workshop attendees an overview of Synkera's recent work with acoustic sensors for detecting organic contaminants in water. Deininger highlighted current limitations of persistent organic analyses where a sample is collected in the field and then brought back to the lab for analysis. These limitations include expense, inefficiency, delayed results, and potential for contamination. There is a need for a rugged low-cost, and directly submersible field method. Novel approaches utilizing nanotechnologies and nanofabrication may offer attractive solutions to these limitations. Deininger described Synkera's research and development efforts to design a new acoustic wave sensor for the detection of persistent organic contaminants in water. Acoustic wave devices operate by propagating an acoustic wave through or on the surface of a piezoelectric resonator. Sensors utilizing this concept can be configured to measure a wide range of parameters, including torque, pressure, humidity, temperature, mass, and chemical species. They are particularly attractive as chemical sensors due to their small size and low cost, inherent durability, reliability, and capability of passive and/or remote operation. An array of these micro-machined sensors will allow for sensitive and relatively specific response to persistent organic contaminants. Potential commercial applications of these sensors are extremely promising. These sensors have likely applications in marine environmental research, environmental monitoring, and municipal drinking water assessment. Not only could these sensors replace existing analysis methods, but this technology would also likely allow for improvements in the scope and detail in future measurement of chemical contaminants in gases and liquids.

Synthesis of Discussion Questions

1) Priority management information needs relative to organic contaminant loading

Workshop attendees identified several different resources that required management oversight and monitoring, including storm water, coastal margin habitats, tributaries, streams that provide drinking water, and estuaries. Based on these resources, both high and moderate priority constituents of concern were listed. Constituents, which were highest priority, included legacy chemicals (DDT, PCBs), organics, sediments, biological constituents (bacteria, harmful algal blooms), heavy metals (lead, mercury, copper, zinc), dissolved oxygen, and augmented water discharge (e.g., hydromodification). Moderate priority constituents of concern were listed as pharmaceuticals (Tylenol, estrogen), personal care products (antibacterial soap), fire retardants, PBDE, and pyrethroids.

Management of these aquatic resources requires not only the identification of constituents of concern but also the temporal scale of assessment that is of greatest management importance (e.g., annual loading vs. instantaneous concentrations). Attendees quickly made clear that the question of temporal scale was system-dependant. Different resources and concerns would dictate importance of either acute or chronic considerations or both. For example, drinking source water operations would likely require continuous sampling, while tributary loading estimates require only weekly or event-based measurements. Workshop participants were very excited about the possibilities of “smart” sampling where a continuous surrogate measure allowed for warning to indicate more intense sampling was needed.

The monitoring information gathered can guide management actions in three ways – quick response, information feedback, and longer-term planning. Examples of quick responses would be shutting down drinking water intakes, rerouting storm water, or posting a citizen advisory. Monitoring also allows information feedback pertaining to early detection of new contaminants, local land management decisions, or direction of future research. Long-term planning may also be aided in various ways, such as using compliance monitoring data to drive models, making coastal environment management decisions based on regional monitoring, and evaluation of impacts from certain dischargers into an aquatic environment.

Despite the promise of these monitoring efforts, there are many limitations related to both sampling and analysis. The high cost of monitoring equipment impedes the quality and quantity of sensors one can afford. Environments that are hard to access require sensors that are remotely operated and can relay data back to users and are rugged and have low maintenance requirements.

For constituents of concern that require lab analysis, the analysis often takes too long to make rapid-response decisions. Because many sensor technologies are constrained by detection limits and limited ability to discern specific chemical species, the specifications of the sensor should match the management need (e.g., higher detection limits may be acceptable for early warning of contamination of drinking water supply). A "one size fits all" is likely not the most efficient strategy to pursue. The final limitations relate to the user or operator themselves. There must be a high level of competence in using a sensor technology or completing a lab analysis. Likewise, there needs to be a comfort and trust with new methods or technologies before they will be acceptable.

2) Appropriate approaches to estimating mass loading

When optimal sampling strategies were discussed, workshop participants quickly concluded that the strategy would be dependant on constituents of concern and management priorities. Two more concepts of interest were determination of the spatial scale of interest and exploration of the possibilities of using surrogate measures. Determining the spatial scale may be dependant on the extent of patchiness and microstructure in the system; e.g., lake depth contour for lake sampling, tributary network in river systems for source identification, or the level of detail one wishes to estimate mass loading at a watershed mouth. Many helpful surrogates were discussed, as well as the possibility of using these measures to trigger changes in sampling frequency. Some examples include use of total suspended matter for legacy organics, caffeine for sewage, and various bio-indicators. Coordinating multiple surrogate indicators seems especially promising. Limits to uses of surrogates do exist and need to be recognized. In scientific studies, specificity is important, so surrogates may have limited usefulness.

Seasonal variation will also significantly effect loading estimation, and the importance of knowing one's own system was highly stressed. This variation also depends on dominant seasonal meteorological patterns. These drivers would include wave events, precipitation events, in-stream processing, ephemeral streams, stagnant flow, and low flow conditions.

Just as spatial resolution needs to be defined, so to does the temporal resolution of chemical measurements. As determined before, multiple time scales are required depending on management priorities or constituents of interest. Continuous sampling is often useful for the short term but not needed for long-term. Time-integrated sampling is necessary for many low-level organics due to detection limit capabilities. Discrete sampling is most useful for event-based or annual loading estimates. Adaptive, or "smart," sampling is ideal; the frequency and even types of measurements can be changed as needed based on real-time information.

Another consideration is compound specificity or differentiation of phases. There is a clear goal of being specific, but this goal needs to be balanced with other goals of spatial and temporal resolution as discussed above. The level of specificity is also driven by chemical behavior. Organic compounds may change over time to more or less harmful chemicals for example. Specificity is critical for source tracking. For proper risk assessment and toxicity concerns, the specific compound needs to be identified. Nutrients, for example, have different species with widely different sources and different effects.

The type of detection and detection limits are other considerations for determining the best approach for mass loading estimates. Passive samplers work well on week or month time scales or for integrative measures, but the time necessary to achieve equilibration limit their use for event-scale monitoring. Active samplers, on the other hand, have the advantages of being real-time, continuous, reversible, and interactive. Detection limits are an important concern because some regulatory limits are below current detection limits. Estimating loads is also severely limited by non-detects, so there is a need to improve detection capabilities at low levels. Appropriate detection limits should be based on meaningful biological endpoints and specific management needs.

3) Current status of the sensor technology for organic contaminants

Workshop participants started their discussion about the current status of sensor technology with an identification of priority needs for new technology development. They identified general, parameter-specific, application-specific, and technology-specific needs. General needs identified included chemical selectivity, assessment versus ability to determine effectiveness of treatment, ability to do monitoring in real-time, sensitivity to low levels, reliability and stability, accuracy, cost, low energy consumption, ability for adjustment to specific sites or conditions, and possibility of using "smart" technology. More specific needs in relation to specific parameters were also identified. Despite the workshop's focus on organic contaminants, participants recommended better sensors for a variety of constituents, including total organic carbon, biological, total phosphorus and total nitrogen, particle size/concentration, particle density, and dissolved organic matter. Application-specific needs were also discussed. For drinking water protection, the goals are to understand when contamination will be present near water intakes, where it is coming from, how much is there, and how effective treatment measures were for mitigating the contamination. These goals translate into needs for lower detection limits, real-time detection, and sensing of broad spectrum of parameters. For understanding receiving waters and to allow for ecosystem forecasting, the needs include continuous observations during episodic events, post event mapping, quantification ability, better auto-sampling (in-field sample prep), and field serviceability. The final category discussed by workshop attendees was technology-specific needs. Two specific needs identified were liquid chromatography/mass spectrometry in the field and acoustic sensors, which can tell not only what compounds are present but also the concentrations for those compounds identified.

After laying out a list of general parameter-specific and technology-specific needs, the limitations of existing technology became readily apparent. General limitations that were discussed included turbidity interfering with analyses, lack of chemical selectivity, poor power management, data management inefficiencies, biofouling, and lack of a rugged design. Limitations associated with specific parameters were also identified. For dissolved oxygen, limitations of slow response speed, biofouling, a limited duty cycle, and low sensitivity were recognized. Organic sensors have identified limitations of being very expensive and highly technical. For biological sensors, existing limitations include: complexity, not readily available off-the-shelf, and cost. Particle/turbidity sensors have limitations of being expensive, not allowing for concentration measurements, and biofouling. Cost is the major limitation for hydrodynamic sensors. In addition to general limitations and limitations associated with certain parameters, there are also limitations that pertain to specific technologies. In situ mass spectrometers are limited due to high power consumption, extremely high cost, an inadequate chemical size limit, and analysis of dissolved phase only. Surface enhanced Raman spectroscopy is similarly limited in its usefulness because of its high cost, use of dissolved phase only, and low sensitivity. Limitations associated with lab-based analyses often include high cost, low capacity to run large numbers of samples, and a long turn-around time.

Passive sampler technologies have their own limitations, such as long equilibration times, course temporal resolution, lack of a proven track record, and poor flow estimation.

In addition to identifying the needs and current limitations in existing technology, workshop participants also composed a list of barriers which thwart the development of new technologies. The first barrier identified was the time required for implementing any new technology. A lack of good technology in the "pipeline" increases implementation time. Time is also lost due to poor coordination of new sensor research and development. Certification of new technologies adds more time to development. There also needs to be a better pairing of research and development with test implementations in order to reduce development time. The second major barrier identified was lack of funding for research and development. New technology is nurtured with funding that supports costs associated with this development. The third and final barrier identified was the lack of a market for some technologies. There is often a disconnect between the technology needs of the research community and the broader market community to which the industry responsible for developing new technologies needs to respond. Industry needs to weigh the risk associated with technology development against the potential strength of a new market. The market is hard to predict because it is fragmented with different types of technology requirements that are continuously changing according to the users' needs.

Specific Workshop Recommendations

- Improve the understanding of materials balance in aquatic systems and their relationship between potential surrogate measures (such as DOC, chlorophyll, particle size distribution) and target constituents.
- Develop continuous real-time sensors to be used by managers as screening measures and triggers for more intensive monitoring.
- Pursue surrogate measures and indicators of organic pollutant contamination, such as CDOM, turbidity, or non-equilibrium partitioning.
- Develop continuous field deployable sensors for PCBs, PAHs, pyrethroids, and emerging contaminants of concern, and develop strategies that couple sampling approaches with tools that incorporate sensor synergy (i.e., measure appropriate surrogates along with the dissolved organics to allow full mass emission estimation).
- Fund market/needs assessment for new technologies based on ACT and the Cooperative Institute for Coastal and Estuarine Environmental Technology (CICEET) workshops.
- Promote standardization of output among sensors and open protocols in sensor technology development and improve the data management/visualization component when new technology reaches commercialization point.

Specific Recommendations for ACT

- ACT/CICEET should have a follow-up workshop that focuses specifically on a given application and better defined set of sensor technologies.
- ACT can work with industry to promote exposure and acceptance of new technologies through Performance Demonstrations and/or Training Workshops.
- ACT needs to leverage other initiatives, such as NSF CLEANER and Integrated Ocean Observing System test-bed activities and workshops to have a broader impact and promote new technologies coming to market.

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