COMMENTS ON CALIFORNIA STATE WATER RESOURCES CONTROL BOARD'S

PROPOSED ADOPTING RESOLUTION REGARDING THE TOTAL MAXIMUM DAILY LOAD FOR TOXIC POLLUTANTS IN DOMINGUEZ CHANNEL AND GREATER LOS ANGELES AND LONG BEACH HARBOR WATERS

JANUARY 25, 2012

Submitted by: Date: February 3, 2012

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California Building Industry Association
California Business Properties Association
California Chamber of Commerce
Construction Industry Coalition on Water Quality
Pacific Legal Foundation

The above listed entities appreciate the opportunity to submit public comments to the California State Water Resources Control Board ("State Board"), in response to the issuance of a proposed adopting resolution for the Los Angeles Regional Water Quality Control Board's ("Regional Board") amendment to its water quality control plan to incorporate a total maximum daily load ("TMDL") for toxic pollutants in Dominguez Channel and Greater Los Angeles and Long Beach Harbor Waters ("the TMDL") dated January 25, 2012.[1] These comments are also being submitted to the United States Environmental Protection Agency ("U.S. EPA"), as the TMDL was originally noticed as a joint Regional Board-U.S. EPA undertaking.

While we appreciate the State Board's attempt to address certain issues with the TMDL through the proposed resolution, we are forced to conclude that the resolution does not address our concerns. In particular, the resolution requires near compliance with the grossly and unnecessarily low standards of the TMDL before stakeholders would have any chance of relief from them, rendering such relief illusory. The State Board should also not give weight to the Regional Board staff's memo to it dated January 27, 2012 as it contains errors, misrepresenting (surely unintentionally, but nevertheless deeply troubling) each TMDL target for organics as being 1,000 times higher than it actually is in the TMDL. (See table in footnote one, where the targets for organics are misstated in "mg/kg," rather than what they actually are, "ug/kg," a factor of 1,000 less.) The fact that the Regional Board is urging adoption, but still plainly is creating confusion over the gross and unnecessary conservatism of the TMDL underscores the need for remand.

Since the December 6, 2011 State Board meeting, we have followed the State Board's direction and met with Regional Board staff to discuss the "key questions" and "fundamental issues" with the TMDL. Unfortunately, material progress was not made in addressing the numerous problems and questions regarding the technical underpinnings of the TMDL, mainly because more time is needed to accomplish that task – a fact reinforced by the errors in the Regional Board's January 27 memo.

Because fundamental technical and policy problems with the TMDL remain, we respectfully request that the State Board remand the TMDL to the Regional Board, providing the Regional Board the necessary time to work through the TMDL's issues. We believe remand would be productive, for example allowing the Regional Board to incorporate carry through into the loading capacities, calibrating and validating the models, removing reliance on sediment quality benchmarks that the State Board in other proceedings has heavily criticized, and making the TMDL consistent with the State Board's SQO policies. In fact, we believe that changes such as these are required, or the TMDL will remain invalid, and legally vulnerable.

To this end, we have provided an alternative resolution with this comment letter that provides a potential framework for remand. While we understand that U.S. EPA still may proceed with adoption to meet its March 24, 2012 deadline, we would anticipate that U.S. EPA

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[1] These comments are based on the State Board's proposed resolution identified as the attachment to item 7 of its agenda for its February 7, 2012 meeting. We respectfully request that these public comments, appendices, and attachments submitted herewith be given appropriate consideration, be placed in the administrative record for the TMDL and be maintained in the agency's records.

would consider any such adoption procedural, and that the agency would provide the Water Boards sufficient time to revise the TMDL. We prefer to work with the Regional Board on remand, and with U.S. EPA on restraint, rather than face the prospects of a state-adopted TMDL, with such far-reaching legal and technical problems.

I. THE PROPOSED ADOPTING RESOLUTION DOES NOT CURE OUR CONCERNS WITH THE TMDL

We have consistently maintained that adoption of the TMDL would be premature because the significant issues with the TMDL should be addressed and remedied before the TMDL is adopted, rather than the possible relief of re-opener proceedings six years down the road that provide no meaningful assurance of the needed TMDL reforms. The proposed adopting resolution does not address the serious implementation and technical concerns with the TMDL or provide a proper technical and legal foundation for the TMDL.

A. Implementation Issues

1. The TMDL May Still Be Used For Improper Purposes

The proposed adopting resolution does not provide any clarity that might allow stakeholders and responsible parties to determine what the TMDL is, and how it may be properly implemented. While Paragraph 6 of the Preamble contains some intent to limit the use of the sediment targets contained in the TMDL, the proposed adopting resolution by omission may be read to imply that the sediment targets are intended for use in setting cleanup standards in remedial dredging and capping. The following revision would cure this particular problem: "sediment targets included in the Basin Plan amendment are not ~~intended~~ to be used as 'clean-up standards' for navigational, capital, maintenance, or remedial dredging or capping activities." Without these clarifications, the sediment targets contained in the TMDL may be utilized in an improper and unlawful way, and there might be ambiguity as to how these targets will be used.

2. The Proposed Adopting Resolution Does Not Address Implementation Problems That Arise From A Lack Of Proper Technical Conditions

By law, TMDLs are required to be developed only where the TMDLs for the pollutants at issue are "suitable for calculation." 33 U.S.C. § 1313(d). U.S. EPA has interpreted "suitable for calculation" to mean that the "proper technical conditions" are present.[2] U.S. EPA has explained:

> "Proper technical conditions" refers to the availability of the analytical methods, modeling techniques and data base necessary to develop a technically defensible TMDL. These elements will

[2] Total Maximum Daily Loads Under Clean Water Act, 43 Fed. Reg. 60,662 (Dec. 28, 1978).

> vary in their level of sophistication depending on the nature of the pollutant and characteristics of the segment in question.[3]

Thus, EPA interprets pollutants to be suitable for calculation of a TMDL only where "proper technical conditions" are met, i.e., where there exists (1) analytical methods; (2) modeling techniques; and (3) data necessary to develop a "technically defensible" TMDL.

The proposed adopting resolution implicitly acknowledges that the "proper technical conditions" are not present for the TMDL, and does not address the significant implementation issues that arise from this lack of "proper technical conditions." Paragraphs 8, 9, and 10 of the Preamble discuss "special studies" and other data gathering work necessary to provide the "proper technical conditions" for the TMDL. However, these paragraphs envision this work coming after adoption of the TMDL, not before a TMDL is developed as required by law. Because the "proper technical conditions" are not present for the TMDL, adoption of the TMDL, and management decisions based on the TMDL, would be arbitrary and capricious.

Failure to support the TMDL with the "proper technical conditions" will result in implementation problems that have not been acknowledged or addressed in the proposed adopting resolution. Because the State Board has proposed postponing the work to establish the "proper technical conditions" until after the TMDL is adopted, parties subject to the TMDL will be forced to comply with requirements that are not well grounded in science. This makes the prospects of relief during the oft-mentioned "re-opener" during the sixth year of implementation illusory; not only is there no guarantee that the TMDL will be reformed in six years, but the TMDL, and its unsupported requirements, will already have been in place and implemented for that period.

Furthermore, the proposed adopting resolution states that even in the event of re-opener, reconsideration of allocations will not be made "prior to making significant progress toward achieving the final allocations." Preamble at Paragraph 9. This language suggests that it is even more unlikely that the TMDL will be reformed because, as our prior comments have indicated, progress towards achieving final allocations that lack "proper technical conditions" will be extremely difficult, if not impossible, to achieve.

B. Technical Issues

Both the Regional and State Boards have received numerous comments documenting technical aspects of the TMDL that must be reconsidered to render the TMDL technically defensible, both from stakeholders and the Regional Board's own peer reviewers. The proposed adopting resolution does not cure these deficiencies.

Our prior comments demonstrate that scientific experts with countless years of experience in relevant fields have identified multiple technical issues with the TMDL, including, but not limited to: (i) improper determination of the assimilative (or loading) capacity of the water bodies; (ii) lack of model calibration and validation; (iii) selective use of portions of the modeling that ignore the significant mass that "carries through" the system; (iv) assigning loads

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[3] *Id*. at 60,662.

to clean or relatively clean sediments; (v) uncertain aerial deposition rates that are assumed to overwhelm the TMDL's allocations; (vi) inappropriate use of the Fish Contaminant Goals without risk assessment; (vii) and use of screening values as sediment targets. As described in the attached memorandum prepared by Dr. Charles Menzie in response to questions asked of him at the State Board's December 6, 2011 meeting, there also are concerns that the TMDL diverges from precedent used for TMDLs elsewhere in California and the country.[4] An inventory of important technical flaws of the TMDL can be found in the "Framework for Addressing Technical Issues Associated with the TMDL" which Dr. Menzie also prepared and submitted to the Regional and State Boards.[5]

Of particular concern, and not addressed in the proposed adopting resolution, is the determination of the assimilative, or "loading," capacity of the waterbodies at issue. By definition, a TMDL is dependent on a proper determination of this capacity. "TMDL" is defined to correspond to the loading or assimilative capacity of the water body, which then is available to be allocated to point source wasteloads and nonpoint source loads, with appropriate reservations. 40 C.F.R. §§ 130.2(i), 130.2(g), and 130.2(h). "Loading capacity" is the "greatest amount of loading that a water can receive without violating water quality standards." 40 C.F.R. § 130.2(f). As the Regional Board staff have acknowledged, the TMDL modeling predicts that significant amounts of mass are naturally flushed through the harbor system. Because these significant masses "carry through" the harbor system and therefore do not put the water body in non-compliance with water quality standards, these masses must be considered as a component of the loading capacity. However, this was not recognized in the TMDL, as the Regional Board staff has stated that the loading capacity and allocations are based only on "what deposits." Dr. E. John List discussed this concept and the implications of it in a letter submitted in advance of the technical meeting with the Regional Board staff on January 25, 2012.[6]

Dr. Menzie's memoranda and Dr. List's letter demonstrate part of our attempt to engage Regional Board staff constructively on these technical issues, as directed by the State Board at the December 6, 2011 hearing. However, as explained below, Regional Board staff wanted to discuss only steps that might be taken to fix the TMDL <u>after</u> it is adopted, instead of ways to address these technical problems now.

It must be reiterated that these issues are inextricably intertwined with the implementation of the TMDL and the management decisions that will necessarily be made on the

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4 Dr. Charles Menzie, "Why TMDLs for Dominguez Channel are Low in Comparison to Newport Bay." January 6, 2012. Submitted to the Regional Board staff and State Board members previously on January 6, 2012. We incorporate Dr. Menzie's memorandum into these comments here by reference.

5 Dr. Charles Menzie, "Framework for Addressing Technical Issues Associated with the TMDL." Submitted to the Regional Board staff and State Board members previously on January 8, 2012. We incorporate Dr. Menzie's memorandum into these comments here by reference.

6 Dr. E. John List, "TMDL and Sediment 'Carry Through.'" January 23, 2012. Submitted to the Regional Board staff and State Board members previously on January 24, 2012. We incorporate Dr. List's letter into these comments here by reference.

basis of the TMDL. Because these fundamental technical issues have gone unaddressed, the TMDL is not supported by proper technical conditions and the standards and targets established by the TMDL are unreliable. Use of these unreliable targets and standards in subsequent management decisions necessarily will lead to implementation problems. Considering the staggering cost of implementation of the TMDL (estimated by some to be up to $9 billion, and by the Regional Board itself at approximately $900 million), it becomes apparent that the technical issues with the TMDL are very real concerns that must be addressed now.

The State and Regional Boards' frequent suggestions (as set forth in Paragraph 8 of the Preamble to the proposed adopting resolution) that these technical issues can be addressed through post-hoc "special studies" indicates that no TMDL should be adopted at this time, when data on which to base the TMDL are scarce or nonexistent. The fact that "special studies", including those referenced in Paragraph 8 of the Preamble, have become a central point of discussion for this TMDL distracts from the real issue – the current scientific understanding and data are so weak that there ought not to be a TMDL at this time. As just one example, Dr. List has provided a short discussion of how the TMDL for DDT is not based on actual data, resulting in a lack of "proper technical conditions."[7]

II. PROCEEDINGS SINCE DEC. 6 HAVE NOT RESULTED IN PROGRESS

At the December 6, 2011 State Board meeting, the State Board directed the Regional Board staff to further engage with stakeholders to address "fundamental" questions regarding the TMDL. During January 2012, stakeholders twice met with the Regional Board staff, but, as described below, progress was not made during these discussions.

A. January 9, 2012 Meeting Regarding Implementation Issues

On December 22, 2011, the Regional Board staff noticed a public meeting to be held on January 9, 2012 "to provide [the] State Board with additional information and details on the TMDL and to work with stakeholders to provide more clarity on TMDL implementation options and schedule". The Regional Board staff's agenda for the meeting focused solely on issues relating to the implementation of the TMDL.

At this meeting, Regional Board staff reiterated that significant amounts of sediment "carry through" the Harbor Waters. However, staff also confirmed that the TMDL ignores the significant volumes that "carry through." As discussed above, this assumption results in improper calculation of the loading capacity of the waterbodies, which in turn results in grossly under inclusive and technically unsupported TMDLs and allocations.

Because the only topic that the Regional Board staff were willing to discuss at this meeting was TMDL implementation, Regional Board staff were willing to hold a second meeting to discuss technical issues. That meeting occurred on January 25, 2012.

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[7] Dr. E. John List, "TMDL for DDT'" February 3, 2012. We incorporate Dr. List's letter into these comments here by reference.

B. January 25, 2012 Meeting Regarding Technical Issues

It became clear at the January 25, 2012 meeting that Regional Board staff was not willing to engage in constructive and substantive discussions on technical issues. Regional Board staff and U.S. EPA were focused on offering to work with stakeholders to fix and revise this allegedly "technically defensible" TMDL once adopted. Suggestions by stakeholders that technical issues with the TMDL must be addressed before it is adopted were met with renewed offers to address technical issues after adoption.

At the January 25 meeting, Regional Board staff stated that stakeholders had not offered any constructive ideas on what could have been done differently with the TMDL. Several members of the stakeholder group that participated in the meeting offered numerous, concrete examples of constructive suggestions that had been offered; Regional Board staff did not substantively respond to these comments.

At the end of the meeting, Regional Board staff reemphasized that it intended to work with stakeholders to revise and fix the TMDL once it is adopted, and members of the stakeholder group reemphasized the desire to get the technical issues in the TMDL right in the first instance, before adoption. Because the issue of the proper time to address technical issues became the central issue of the meeting, only a very limited discussion of the underlying key technical issues and fundamental questions occurred.

III. THE REGIONAL BOARD'S MEMORANDUM TO THE STATE BOARD DEMONSTRATES FURTHER INCONSISTENCIES BETWEEN THE TMDL AND THE LAW

On January 27, 2012, Regional Board staff submitted a memorandum on certain aspects of the TMDL to the State Board. This memorandum was prepared pursuant to the State Board's request of Regional Board staff at the December 6, 2011 meeting. Generally, this memorandum repeats the same issues that we have addressed in our previously submitted comments, and as such, we disagree with the statements of the Regional Board staff for the reasons outlined in those previously submitted comments.

That said, we would like to highlight one gross mischaracterization in the Regional Board staff's memorandum regarding the interplay of the OEHHA's Fish Contaminant Goals ("FCGs"), the goals that were selected as the fish tissue targets in the TMDL, and the State Board's Water Quality Control Plan for Enclosed Bays and Estuaries – Part 1 Sediment Quality (the "SQOs"). On page 5 of the Regional Board's memorandum, the Regional Board staff state:

> The targeted fish tissue levels to protect human health are based on OEHHA's [FCGs]. This is consistent with the direction in the [SQOs] to consider OEHHA policies for fish consumption and risk assessment and U.S. EPA human health risk assessment policies.

While the SQOs do suggest that the Regional Boards look to OEHHA policies for fish consumption and risk assessment, the Regional Board staff memorandum misinterprets the SQOs direction. The SQOs plainly indicate how the Regional Boards are to include OEHHA fish consumption polices, like the FCGs, when conducting their own human health risk assessments,

and not in any other context (such as setting a TMDL target). In its entirety, Section VI, Human Health, of the SQOs state:

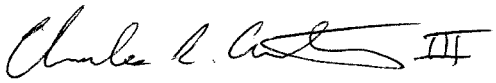
> The narrative human health objective in Section IV. B. of this Part 1 shall be implemented on a case-by-case basis, based upon a human health risk assessment. In conducting a risk assessment, the Water Boards shall consider any applicable and relevant information, including California Environmental Protection Agency's (Cal/EPA) Office of Environmental Health Hazard Assessment (OEHHA) policies for fish consumption and risk assessment, Cal/EPA's Department of Toxic Substances Control (DTSC) Risk Assessment, and U.S. EPA Human Health Risk Assessment policies.

Based on this directive, the SQO framework does not authorize the use of the FCGs as stand-alone values in a TMDL in isolation from a risk assessment (as was done here). The use of the FCGs without risk assessment is yet another inconsistency between the TMDL and the State Board policy reflected in the SQOs, is arbitrary and capricious, and violates the SQOs and the Porter Cologne Act. We would urge that as part of a remand, that the State Board direct the Regional Board to conduct a human health risk assessment so that the Regional Board may exercise its discretion appropriately to consider the FCGs in that assessment. The current use of the FCGs is an abuse of discretion.

IV. CONCLUSION

We urge the State Board to remand the TMDL to the Regional Board with directions to complete the necessary steps to ensure a reasonable and technically defensible TMDL, and one based on sound policy. Remand would provide the time necessary to address the TMDL's issues – time plainly necessary in light of the lack of progress made in the short window since the December 6 hearing. We have included with this letter a draft remand resolution to illustrate direction the State Board might give to the Regional Board.

Kind regards,



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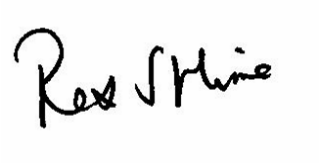
On behalf of Montrose Chemical Corporation of California

Paul Meyer
American Council of Engineering Companies California

Richard Lyon
California Building Industry Association



Rex S. Hime
California Business Properties Association

Valerie Nera
California Chamber of Commerce

Mark Grey
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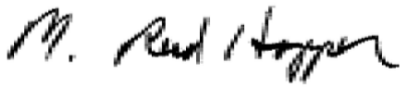

Reed Hopper
Pacific Legal Foundation

Attachments

STATE WATER RESOURCES CONTROL BOARD'S

CONSIDERATION OF A PROPOSED RESOLUTION APPROVING AN AMENDMENT TO THE WATER QUALITY CONTROL PLAN FOR THE LOS ANGELES REGION TO INCORPORATE A TOTAL MAXIMUM DAILY LOAD FOR TOXIC POLLUTANTS IN DOMINGUEZ CHANNEL AND GREATER LOS ANGELES AND LONG BEACH HARBOR WATERS

February 7, 2012 Board Meeting, Item 7

EXHIBITS TO FEBRUARY 3, 2012 COMMENTS SUBMITTED BY LATHAM & WATKINS LLP ON BEHALF OF MONTROSE

Exhibit	Description
A.	Proposed Draft Resolution Remanding the TMDL to the Regional Board.
B.	January 6, 2012 Memorandum from Charles Menzie, Ph.D., Exponent to Sam Unger, Executive Officer, California Regional Water Quality Control Board, Los Angeles Region Regarding "Why TMDLs for Dominguez Channel are Low in Comparison to Newport Bay."
C.	Hardy, J.T. (1982), The Sea Surface Microlayer: Biology, Chemistry and Anthropogenic Enrichment. *Progress in Oceanography*, 11 (4), pp. 307-328.
D.	"Framework for Addressing Technical Issues Associated with the TMDL," prepared by Charles Menzie, Ph.D.
E.	January 23, 2012 Memorandum from E. John List, Ph.D., P.E., Environmental Defense Sciences to Sam Unger, Executive Officer, California Regional Water Quality Control Board, Los Angeles Region Regarding "TMDL and Sediment 'Carry Through'"
F.	Hickey, Barbara M. "River discharge plumes in the Santa Barbara Channel", p. 65, 5th California Islands Symposium (Physical Oceanography) 1999
G.	Ahn *et al.*, "Coastal Water Quality Impact of Stormwater Runoff from an Urban Watershed in Southern California", *Environ. Sci. Technol.*, 2005, 39 (16), pp 5940–5953
H.	Warrick *et al.,* "River plume patterns and dynamics within the Southern California Bight", USC Sea Grant Publication AR07 USC, pages 215-236
I.	February 3, 2012 Letter from E. John List, Ph.D., P.E., Environmental Defense Sciences to the Clerk of the Board and State Board Members Regarding "TMDL for DDT."
J.	"TMDLs for legacy chemicals (PCBs and DDT) are not based on reliable technical information." Presentation of Charles Menzie, Ph.D., for the State Board at its February 7, 2012 Meeting.

Exhibit A

STATE WATER RESOURCES CONTROL BOARD
RESOLUTION NO. 2012 – xxxx

REMANDING AN AMENDMENT TO THE WATER QUALITY CONTROL PLAN FOR THE LOS ANGELES REGION TO INCORPORATE A TOTAL MAXIMUM DAILY LOAD FOR TOXIC POLLUTANTS IN DOMINGUEZ CHANNEL AND GREATER LOS ANGELES AND LONG BEACH HARBOR WATERS[1]

WHEREAS:

1. The Los Angeles Regional Water Quality Control Board (Regional Board) adopted a revised Basin Plan for the Los Angeles Region on June 13, 1994 which was approved by the State Water Resources Control Board (SWRCB) on November 17, 1994 and by the Office of Administrative Law (OAL) on February 23, 1995.

2. On May 5, 2011 the Regional Board adopted Resolution No. R11-008 amending the Basin Plan to incorporate a Total Maximum Daily Load (TMDL) for toxic pollutants in the Dominguez Channel and Greater Los Angeles and Long Beach Harbor Waters.

3. SWRCB finds that the Basin Plan amendment as adopted by the Regional Board should be revised and clarified before adoption by SWRCB.

4. A Basin Plan amendment does not become effective until approved by SWRCB and until the regulatory provisions are approved by OAL.

THEREFORE BE IT RESOLVED THAT:

1. Pursuant to Water Code Section 13245, the SWRCB hereby remands the Basin Plan amendment to incorporate a TMDL for toxic pollutants in the Dominguez Channel and Greater Los Angeles and Long Beach Harbor Waters as adopted under Regional Board Resolution R11-008 for further deliberations consistent with the SWRCB's directives contained herein and all applicable laws, regulations and SWRCB policies.

2. The SWRCB hereby directs the Regional Board to:

    a. Revise the Basin Plan amendment to be consistent with the following understanding: This Basin Plan Amendment is not intended to, and is not to be interpreted as, setting any cleanup levels for sediments or as mandating any removal or remediation action by any person or entity. The TMDL is not to be utilized in any form as a remediation, removal or dredging order, and is not to be interpreted as requiring specific actions at any sites or as establishing cleanup standards to be achieved at those sites.

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[1] This remand resolution is provided to illustrate some of the main points that the State Board might wish to address upon remand, and is not intended to capture each and every problem with the TMDL, as defects in this TMDL continue to be discovered as these proceedings have progressed.

b. Revise the TMDL and the Basin Plan Amendment so as to provide more clarity and to remove ambiguity of the anticipated obligations and responsibilities of the various identified parties under the TMDL.

c. Revise the TMDL as needed to ensure compliance with SWRCB's Water Quality Control Plan for Enclosed Bays and Estuaries – Part 1 Sediment Quality (the SQOs). Compliance with the SQOs requires consideration of multiple lines of evidence to determine whether sediment is impacted, and does not involve reliance on the "Effects Range Low" chemical concentration values. SQO compliance requires completion of the step-wise approach to establish a numeric target to properly calculate loading capacity, load allocations, and waste load allocations appropriate for inclusion in a TMDL. This step-wise approach includes stressor identification, studies on chemical linkage to impairment, identification of pollutant chemicals or classes of chemicals and identifying sources.

d. Revise the TMDL to remove the reliance on Fish Contaminant Goals (FCGs) as an endpoint in the form of a TMDL target. The Office of Environmental Health Hazard Assessment (OEHHA), which publishes the FCGs, states that FCGs "provide a starting point for OEHHA to assist other agencies that wish to develop fish tissue-based criteria with a goal toward pollution mitigation or elimination," and supports the use of FCGs in risk assessments by other agencies. The FCGs were developed "without regard to economic considerations, technical feasibility, or the counterbalancing benefits of fish consumption." (OEHHA, Development of Fish Contaminant Goals and Advisory Tissue Levels For Common Contaminants In California Sport Fish: Chlordane, DDTs, Dieldrin, Methylmercury, PCBs, Selenium, and Toxaphene at iii (June 2008).) The Regional Board's assessment of risk should consider OEHHA's Advisory Tissue Levels (ATLs), as well as FCGs. ATLs correspond to a level of no health risk to individuals that consume sport fish and reflect the "unique health benefits associated with fish consumption." (Id.) The Regional Board shall adopt regionally appropriate fish tissue targets in accordance with risk assessment principles, SWRCB policy, and accounting for fish that swim to surrounding areas, such as the nearby Palos Verdes Shelf, where fish tissue targets already exist.

e. Reconsider and revise the modeling upon which the TMDL is based to ensure that proper calibration, validation, and mass balance computations are included. The Clean Water Act requires that a TMDL be a balance between the loading or assimilative capacity of a water body (i.e., the mass of a pollutant the water body can assimilate without violating water quality standards), on the one hand, and various categories into which that capacity is distributed (e.g., how much mass of the pollutant will be allowed to enter the water body from point and nonpoint sources, considering natural background). There must be equivalency between loading capacity and the sum of the distribution categories. This equivalency, required by law, is a mass balance, and the current conceptual model and mathematical modeling approach of the TMDL does not support this equivalency.

f. Revise the Substitute Environmental Document (SED) to ensure compliance with CEQA. The SED shall include an analysis of all environmental impacts associated with the proposed project and all reasonably foreseeable methods of compliance with the TMDL. The SED shall also include an analysis of sufficient project alternatives that offer potentially substantial environmental advantages over the described project. An analysis of a reasonable range of environmentally advantageous project alternatives is necessary under CEQA to enable the decision maker to make an informed decision to select the environmentally superior project alternative.

g. Have further direct collaboration with all interested stakeholders, followed by additional peer review of the revised TMDL, to facilitate the above directives and promote the use of sound science, modeling techniques and proper data sets, including necessary calibrations and validations. This further direct collaboration shall include periodic meetings with the stakeholders as appropriate to achieve these goals.

CERTIFICATION

The undersigned, Clerk to the Board, does hereby certify that the foregoing is a full, true, and correct copy of a resolution duly and regularly adopted at a meeting of the State Water Resources Control Board held on February 7, 2012.

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Jeanine Townsend
Clerk to the Board

Exhibit B

Exponent®

MEMORANDUM

TO: Sam Unger, Executive Officer, California Regional Water Quality Control Board, Los Angeles Region

CC: Charles Hoppin, Chair, State Water Resources Control Board

Frances Spivy-Weber, Vice Chair, State Water Resources Control Board

Tam Doduc, Member, State Water Resources Control Board

Thomas Howard, Executive Director, State Water Resources Control Board

Dr. Peter Kozleka, United States Environmental Protection Agency, Region 9

FROM: Charles Menzie, Ph.D.

DATE: January 6, 2012

SUBJECT: Why TMDLs for Dominguez Channel are Low in Comparison to Newport Bay

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During my presentation on December 6, 2011 before the California State Water Resources Control Board (State Board), I pointed out that the total maximum daily load (TMDL) for DDT for locations in the Dominguez Channel and Los Angeles Harbor areas (Channel/Harbor) were much lower than for Upper Newport Bay. I indicated that these differences reflected a difference in methodology between the TMDLs for these two systems. During my presentation, State Board Member Tam Dudoc inquired whether these differences simply were due to the differing methodology of the TMDLs as I stated in my presentation, or whether there were other factors involved, such as the existing load in Upper Newport Bay and the fisheries existing there. In response, I indicated that the differences were purely methodological and explained the differing approaches. Herein I provide more detail that may be helpful to you, the staff, and the Board members.

I am submitting this to you pursuant to your notice dated December 22, 2011, setting a January 9, 2012 meeting to discuss the TMDL as directed by the State Board at the December 6, 2011 meeting. This memorandum specifically addresses fundamental questions which the State Board directed the Los Angeles Regional Water Quality Control Board (Regional Water Board) to engage stakeholders on through additional exchanges in order to provide needed clarity and certainty on the TMDL. I will be participating in the January 9, 2012 meeting by telephone, and will be available to present these findings at that time, and respond to any questions you and

your staff may have. I request that this memorandum be placed into the administrative record for the TMDL.

To begin, it should be noted that there is a distinction between a TMDL that has been developed for the **waterbody** and the **sediment-only** TMDLs that the Regional Water Board developed for the eleven discrete areas within the Channel/Harbor. The Regional Water Board did not provide TMDLs for the waterbody.

The sediment TMDLs set by the Regional Water Board are much smaller than those that would have been developed for the waterbody because they leave out all the other dispersive processes that occur when a chemical enters an aquatic or marine system. For example, the compounds entering the system are suspended or dissolved in the water column. Only a small fraction of the mass in the water column will settle on the bottom. The balance will bypass the sediments or will otherwise be eliminated from the waterbody[1]. This conceptual difference between a "waterbody TMDL" and a "sediment TMDL" is a large part of the problem with the proposed Channel/Harbor TMDL values and is contributing to the apparent confusion over what these values represent and how they should be used to derive allocations. Notably, outside of the Los Angeles Region, TMDLs are typically developed for waterbodies (e.g., those for San Francisco Bay, Delaware River and Newport Bay and Harbor).

The discrepancy between a waterbody TMDL and sediment-onlyTMDLs is apparent from the U.S. Environmental Protection Agency's (EPA) definition of a TMDL:

"A TMDL is a calculation of the maximum amount of a pollutant that a waterbody can receive and still meet water quality standards, and an allocation of that load among the various sources of that pollutant. Pollutant sources are characterized as either point sources that receive a wasteload allocation (WLA), or nonpoint sources that receive a load allocation (LA)." - U.S. Environmental Protection Agency, 2011[2]

This memorandum demonstrates that in its calculations of TMDLs for the Channel/Harbor areas, the Regional Water Board arbitrarily has substituted "sediment" for "waterbody" in this definition. This memorandum also describes implications of this departure by the Regional Water Board from the intent and definition of a TMDL. Finally, this memo illustrates how the Regional Board's calculation involves only two values, the selected "target concentration" and a calculated sediment deposition rate.

[1] Dr. Susan Paulsen of Flow Science submitted comments on February 22, 2011 to the Regional Water Board that addressed solids and contaminant bypass for the Channel/Harbor system. These comments were based on the ERDC modeling work performed for the Regional Water Board. Based on this work, Dr. Paulsen calculated that roughly 65% of inflowing sediment passes through the system without depositing to the sediment bed; Dr. Paulsen also estimated that a large fraction of the DDT loading to the watershed (72-97%) is simulated to pass through the system without depositing to the sediments.

[2] U.S. Environmental Protection Agency, 2011, What is a TMDL?: U.S. Environmental Protection Agency, access date June 3, 2011.

In the Regional Water Board approach, the sole modeled physical process that influences the TMDLs for the Channel/Harbor areas is the sediment deposition rate. The smaller the calculated deposition rate for an area, the smaller the TMDL. This sole dependency of the TMDLs for the Channel/Harbor areas on deposition rates explains both the small TMDL values that have been derived for some locations as well as the variations among TMDLs for the eleven Channel/Harbor areas. It also it not logical. If only a small fraction of the mass of a target compound in the water column settles to the bottom, and if one assumes as the Regional Water Board does that it is that fraction that presents an environmental and human health risk, then the TMDL should be relatively larger – not smaller. Stated another way, if a large fraction of the water column mass bypasses the sediments where, ostensibly, it may present risk, then the TMDL should be in proportion to that large fraction. An odd implication of the current approach adopted by the Regional Water Board is that the smaller the deposition rate in an area (the smaller the sediment-only TMDL), the larger the load can be to the water column that bypasses the sediment. It should be apparent that this is illogical.

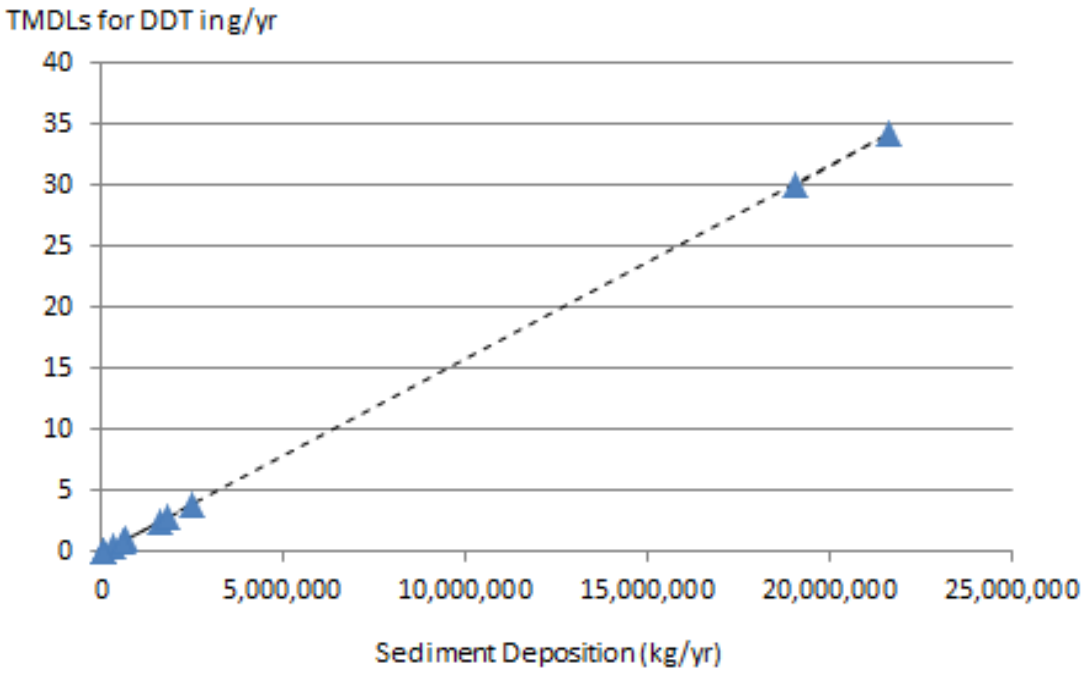
By relying solely on the sediment deposition rates, the TMDL improperly has assumed that it does not matter if the area is receiving primarily "clean" sediments or even if the sediments are primarily "dirty"; the TMDL derivation method used by the Regional Water Board for the Channel/Harbor areas will always yield a TMDL value that is proportional to a calculated sediment deposition rate. The consequence of this approach is that, when the TMDL is used for allocation purposes, it loses meaning for management of loads because it differs from a waterbody TMDL. In short, loads **to waterbodies,** as commonly understood by dischargers and others, are not equivalent to the derived TMDLs for **sediments**. The lack of equivalency contributes to the false conclusion that the sediments have to be removed.

We presented the following table in an earlier memorandum to show the variations in TMDLs for various Channel/Harbor areas. As the table shows, all the TMDLs rely on is a target sediment concentration (the ER-L value of 1.58 µg/kg) and are generated from modeled estimates of sediment deposition.

Table 1. DDT TMDLs for various areas of The System.

Waterbody	Area[1] (m^2)	Total Deposition[1] (kg/yr)	TMDL (Total DDT)[2] (g/yr)
Dominguez Channel Estuary	567,900	2,470,201	3.903
Consolidated Slip	147,103	355,560	0.562
Inner Harbor – POLA	6,228,431	1,580,809	2.498
Inner Harbor – POLB	5,926,130	674,604	1.066
Fish Harbor	368,524	30,593	0.048
Cabrillo Marina	310,259	38,859	0.061
Cabrillo Beach	331,799	27,089	0.043
Outer Harbor – POLA	5,885,626	572,349	0.904
Outer Harbor – POLB	10,472,741	1,828,407	2.889
Los Angeles River Estuary	837,873	21,610,283	34.144
San Pedro Bay	33,073,517	19,056,271	30.109

The linear relationship demonstrated in the following figure illustrates how the eleven TMDLs are solely a function of sediment deposition rates and sediment target level (e.g., the ER-L), and have no other relationship to loads into the system or to any other existing physical, biological, or health factor condition. Simply put, the TMDL is the deposition rate multiplied by the ER-L and each of the eleven TMDL values in the last column of the table fits on the slope of the straight line shown in the following figure. In other words, they simply reflect variations in modeled sediment deposition rates.



TMDLs for Dominguez Channel/Harbor Areas Vary Solely as a Function of Sediment Deposition Rate

The differences between a waterbody TMDL and the sediment-only TMDLs as derived by the Regional Water Board are central to the problems the sediment-only TMDLs have created. For example, if a discharger has an effluent entering a waterbody with little or no sediment deposition, that waterbody could have a calculated sediment-only TMDL that is extremely small because there are few sediments entering and/or depositing within the system, and therefore, a smaller number to multiply by the sediment target to calculate the TMDL.

When that sediment-only TMDL is presumed to be equivalent to a load to the waterbody, the TMDL process loses coherency, the allocations are incorrect, and the discharger is faced with a management problem that may not have any practical or meaningful resolution. The Channel/Harbor TMDL does not recognize that the sediment-only TMDLs are not the same as waterbody TMDLs. Instead, the Channel/Harbor TMDL treats the sediment-only TMDLs as if they were waterbody TMDLs. The result is that incorrect allocations are derived from inappropriate TMDLs. The load to the sediments does not readily translate to particular loads to waterbodies for point and nonpoint sources. Yet this fact is ignored in the Channel/Harbor TMDL. In fact, atmospheric inputs are treated as if they are loads to the sediments rather than to the waterbodies. There is no evidence that all mass entering the waterbodies from the atmosphere ends up accumulating on the bottom. In reality, this is highly unlikely to be the

case, and no reasonable scientist would make this assumption[3]. This presumed fate of chemicals entering from the atmosphere further contributes to the confusion over the TMDLs and the proposed allocation approach.

Another implication of having "sediment only" rather than "waterbody" TMDLs is that the sediment becomes the focus of management. The receiving water and the rest of the system have been left out of the analysis. Under the Regional Water Board's current conceptualization, the sediment drives the risks to benthic invertebrates (for which they use the ER-Ls) as well as the risks to human health via fish bioaccumulation (for which they use BSAFs combined with fish tissue target levels). The Regional Water Board does not rely upon the types of food-chain modeling that are commonly used for TMDL development but simply applies a sediment-based ratio to connect fish to the sediments. Thus, for the Regional Water Board, managing sediments becomes the main focus.

A further implication of the TMDL derivation method relied upon by the Regional Water Board is that it ignores the mass balance of sediments for the system. This includes ignoring inputs of clean sediments containing no DDT, and as DDT degrades naturally in the environment, subsequently deposited sediments will contain less and less DDT. Clean sediments can cover and/or dilute sediments that may contain measureable DDT levels within the Channel/Harbor areas, a process that further contributes to natural recovery. Despite the importance of knowing sediment loads for deriving TMDLs for waterbodies, there is no estimate of actual sediment loads in the Channel/Harbor TMDL. The Regional Water Board also has no estimate of the mass of DDT that is present in the sediments and therefore does not have any reliable estimate of what mass must be either removed or otherwise reduced.

During my presentation to the State Board, I contrasted the higher DDT TMDL developed for the Upper Newport Bay waterbody with the much lower sediment-only TMDLs for the Channel/Harbor areas. I explained that it is this difference - waterbody vs sediment TMDL - that

[3] Atmospheric deposition must enter the system through the surface layer. In order for these loadings to be sediment loads, all this material would need to sink through the water column and deposit in the sediments. The ERDC modeling work performed for the Regional Water Board and commented upon by Dr. Susan Paulsen of Flow Science in her comments to the Regional Water Board dated February 22, 2011 shows that this is not the case and that there is a substantial by-pass through the system for solids and contaminants that are washed into the system. Even greater by-pass would be expected for chemicals that enter the system from the atmosphere. As these chemicals land upon the sea surface, they can be captured within the thin film known as the sea-surface microlayer. Here they are trapped to some extent and can be dispersed out of the system by winds. The presence of these sea-surface microlayers and their importance as a reservoir for contaminants has been recognized for a long time. *See* Hardy, J. T. 1982. The sea-surface microlayer: biology, chemistry, and anthropogenic enrichment. *Prog. Oceanogr*. 11:307-328. (A copy of this study is attached to this memorandum for your convenience.) The assumption that atmospheric deposition is equivalent to sediment deposition for the channel/harbor system is not supported by the science or by the modeling performed for the Regional Water Board.

results in the illogical, incorrect[4], and confusing TMDLs that have been derived for the channel/harbor areas.

Other physical or biological differences between Upper Newport Bay and the Channel/Harbor locations do not explain why the TMDLs for the latter are much smaller. In fact, the sediment TMDLs developed for the Channel/Harbor areas do not consider the degree of impairment, nature of the biological environment, potential for human exposure, incoming sediment loads, or exchanges with the atmosphere or ocean. The Channel/Harbor TMDLs only reflect the two parameters mentioned above (sediment deposition rate and ER-L) and any variation among TMDLs is controlled only by one of these, the sediment deposition rate.

In summary, the sediment-only TMDLs derived by the Regional Water Board do not consider any ecological or human health conditions or degree of impairment. These sediment TMDLs are nothing more than the product of multiplying sediment deposition rates by a selected target value (the ER-L), and treating the result as the load to the system. If that logic were extended to all waterbodies in the United States, there would be DDT TMDLs for every single system regardless of need, as every system that had sediment deposition would also be assigned an associated DDT load equal to the sediment deposition rate multiplied by the sediment target. Because TMDLs calculated in this fashion are wholly unrelated to ecological conditions, human health concerns, or the overall physical dynamics of these systems, some of them will be very high, and others will be very low, and whether the TMDL is high or low will have nothing to do with the actual state or impairment of the system. These TMDLs do not correspond to the actual, site-specific assimilative capacity of either the bottom sediments or the waterbody itself.

Finally, aside from the major methodological problem described above, the sediment TMDLs are derived from two parameters that have been heavily criticized. The sediment deposition rates are from a model that has not been properly calibrated or validated.[5] This lack of calibration and validation has been pointed out by many of the commenters, including the Regional Water Board's peer reviewers. Also, the low target levels (ER-Ls and fish tissue levels) are well below levels that are relevant for managing a harbor system in a sound manner[6].

I have worked extensively throughout the United States with the use of screening level values, such as ER-Ls, on behalf of both the regulated and regulatory communities. It is well accepted in the scientific community, and I agree, that these screening values are inappropriate and impractical to use for managing contaminated sediments and for determining and managing waste load allocations to harbor systems. As recognized by the State Board's Water Quality

[4] They are incorrect for the purpose of any subsequent load allocations where those allocations are treated as loads to the waterbodies.

[5] Our check of the deposition values reveals orders of magnitude variations that do not make sense. There is a 700-fold range in sediment deposition across areas from Fish Harbor (the lowest) to Los Angeles River Estuary (the highest) that do not comport with our understanding of the likely relative variation in deposition rates for these areas.

[6] Extensive comments have been made by stakeholders on the inappropriate use of these low values without considering associated ecological, health, and economic impacts.

Control Plan for Enclosed Bays and Estuaries – Part 1, Sediment Quality, screening levels such as an ER-L are not intended to be used for as sediment targets as was done in the Channel/Harbor TMDL.

Exhibit C

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The Sea Surface Microlayer: Biology, Chemistry and Anthropogenic Enrichment

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Abstract—Recent studies increasingly point to the interface between the world's atmosphere and hydrosphere (the sea-surface microlayer) as an important biological habitat and a collection point for anthropogenic materials. Newly developed sampling techniques collect different qualitative and quantitative fractions of the upper sea surface from depths of less than one micron to several centimeters.

The microlayer provides a habitat for a biota, including the larvae of many commercial fishery species, which are often highly enriched in density compared to subsurface water only a few cm below. Common enrichments for bacterioneuston, phytoneuston, and zooneuston are 10^2–10^4, 1–10^2, and 1–10, respectively. The trophic relationships or integrated functioning of these neustonic communities have not been examined.

Surface tension forces provide a physically stable microlayer, but one which is subjected to greater environmental and climatic variation than the water column. A number of poorly understood physical processes control the movement and flux of materials within and through the microlayer. The microlayer is generally coated with a natural organic film of lipid and fatty acid material overlying a polysaccharide protein complex.

The microlayer serves as both a source and a sink for materials in the atmosphere and the water column. Among these materials are large quantities of anthropogenic substances which frequently occur at concentrations 10^2–10^4 greater than those in the water column. These include plastics, tar lumps, polyaromatic hydrocarbons, chlorinated hydrocarbons, and potentially toxic metals, such as, lead, copper, zinc, and nickel. How the unique processes occurring in the microlayer affect the fate of anthropogenic substances is not yet clear. Many important questions remain to be examined.

CONTENTS

1. INTRODUCTION

MOST BIOLOGICAL and chemical processes of importance occur at surfaces or interfaces between differing environments. The sea surface microlayer (upper 0–1 mm) represents such an interface. It covers 71% of the world's surface and controls the exchange of natural and man-made substances between the atmosphere and hydrosphere. Processes occurring in the microlayer make it far more important than its thin slice of the water column might indicate (Fig. 1). Indeed, it may have been at this interface that organic molecules organized into the first semblances of life over three billion yrs ago (FOX, 1965; PONNAMPERUMA and GABEL, 1968).

Today the air-sea interface serves as a point of concentration for many substances of anthropogenic origin such as heavy metals, petroleum hydrocarbons, plastic particles, pesticides and PCBs. The microlayer also provides a habitat for a diverse and abundant flora and fauna (the neuston) with much greater biological activity than the underlying water column. This intense activity could bring about chemical transformations of both natural and man-made materials in the marine environment. Finally, the surface microlayer is important for the reproduction

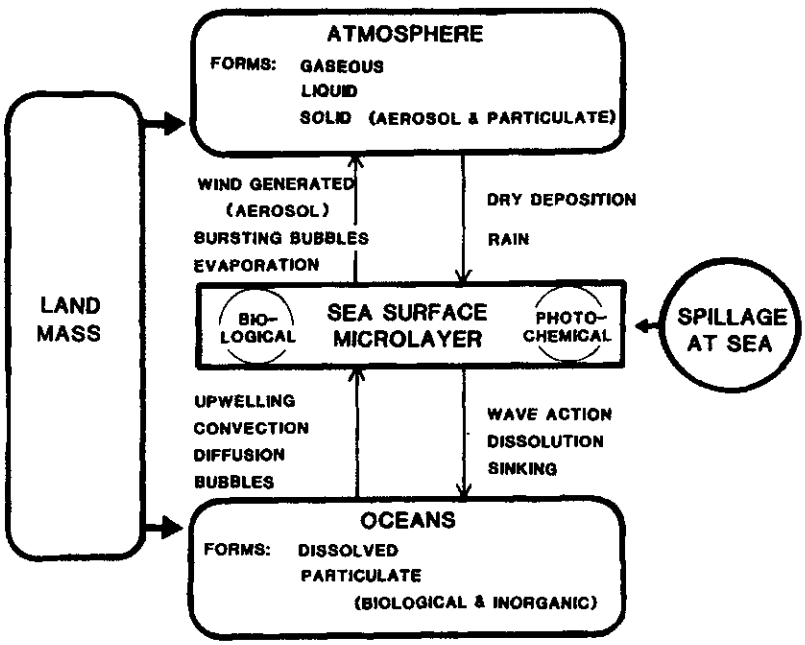

FIG. 1. Sources and sinks of natural and man-made materials and the sea surface microlayer (from, LISS, 1975).

of many fish, shellfish and crustacae, including those of commercial importance whose eggs and larval stages often concentrate in and depend upon the surface microlayer (ZAITSEV, 1971; CASTGANA, 1977).

Several papers have reviewed the physics (WANGERSKY, 1976), chemistry (BLANCHARD, 1974; MAC INTYRE, 1974; LISS, 1975), biogeochemistry (LION and LECKIE, 1981b), biology (ZAITSEV, 1971), and environmental significance (PARKER and BARSOM, 1970) of the sea surface microlayer. In this paper we update our current state of knowledge of the sea surface microlayer, provide a conceptual model of the processes taking place, evaluate the possible impact of man's activities on these processes, and suggest some areas of needed research.

1.1. *Sampling the surface microlayer*

Many techniques have been used to sample aquatic surface microlayers (HAMILTON and CLIFTON, 1979; GARRETT and DUCE, 1980). Each collects a somewhat different depth and type of biological or chemical sample and this has led to difficulty in comparing results of different investigations. The depth of the surface layer sampled by the different techniques spans seven orders of magnitude (Table 1). The screen and glass plate samplers have been the most commonly used techniques for microbiological and chemical investigations of the microlayer. Towing of skimmer nets is generally used for collecting zooneuston (DAVID, 1963; ELDRIDGE, BERRY and MILLER, 1977). The advantages and disadvantages of the different methods has been reviewed elsewhere (GARRETT and DUCE, 1980; VAN VLEET and WILLIAMS, 1980). Samples of the water column are generally collected at the same time (often from 10 cm depth) through tubes or subsurface opening and closing devices. Biological and chemical comparisons are then made between the microlayer and water column by an enrichment factor (EF) equal to the concentration in the microlayer divided by the concentration in the water column.

Different microlayer sampling techniques preferentially collect carbohydrates, proteins or lipids from organic surface films. Thus, the chemical nature of the surface film collected often differs depending upon the collection technique used. HATCHER and PARKER (1974) compared the collection and recovery efficiency of four surface microlayer samplers under controlled laboratory conditions. They concluded that for shallow depth sampling, the glass plate and drum were superior to the tray and screen samplers in efficiency. Membrane filters give the greatest efficiencies (near 100%, with respect to oleic acid) when small quantities of organic film are needed (VAN VLEET and WILLIAMS, 1980). Comparison of membrane filters and teflon sheets or plates indicates that bacterioneuston occupy sites in or just below the surface microlayer and are sampled most efficiently by means of the hydrophobic membrane filter technique (KJELLEBERG, STENSTRÖM and ODHAM, 1979).

2. BIOLOGY OF THE SEA SURFACE MICROLAYER

The air/water interface of both freshwater and marine environments provides a habitat for representative organisms from most major divisions of the plant and animal kingdom which either live, reproduce, or feed on the surface microlayer. These "neustonic" organisms, first described from freshwater (NAUMANN, 1977) use at least four methods to colonize the surface film: physical attachment to the surface film, tactic movements, secretion of mucilaginous extracellular buoyant material, and bubble floatation (HARDY, 1971).

TABLE 1. AQUATIC SURFACE MICROLAYER SAMPLING METHODS.

Sampler	Depth sampled	Typical samples collected	Reference
Metal screen	~ 300–400 μm	Microbiology and lipids and fatty acids	Garrett, 1962; 1967
Tray	~ 500–800 μm		Parker and Wodehouse, 1971
Glass plate	20–100 μm	Chemical and microbiological	Harvey and Burzell, 1972
Bubble generator	0.5–10 μm	Fractionated chemical and microbiological aerosol over sea surface	MacIntyre, 1968; Fasching *et al.*, 1974; Pattenden, Cambray and Playford, 1981
Polyethylene screen		Metals	Duce *et al.*, 1972
Quick freeze onto plastic film	1 mm	Water and particles	Hamilton and Clifton, 1979
Perforated teflon plate	50–100 μm	Glycoproteins and other organics	Larsson *et al.*, 1974
Prism	~ 30 nm	Organics	Baier, 1972
Electron microscope grid	?	Bacterioneuston	Young, 1978
Teflon disc	?	Hydrocarbons and fatty acids	Miget *et al.*, 1974
Skimmer nets	1–10 cm	Zooneuston	David, 1963; Eldridge *et al.*, 1977; Zaitzev, 1971
Membrane filters	?	Bacterioneuston and organics	Van Vleet and Williams, 1980
Rotating ceramic drum	60 μm	Bacterioneuston and organics	Harvey, 1966
V-shaped tube	Qualitative	Sea foam and convergent slicks	Szekielda *et al.*, 1972

2.1. *Bacterioneuston*

Compared to the water only a few cm below the sea surface, the microlayer blooms with bacteria (SIEBURTH, 1963, 1965, 1971; SIEBURTH, *et al.*, 1976; TSYBAN, 1971; HARVEY, 1966; MORITA and BURTON, 1970; BEZDEK and CARLUCCI, 1972). These bacterioneuston are commonly 10^2–10^4 more abundant than the bacterioplankton of the water column. For example, microlayer samples collected by membrane filters or teflon sheets or plates from the west coast of Sweden yielded enrichment factors of between 1–10^4 for bacteria and from 10^2 to 10^4 for yeasts and molds (KJELLEBERG and HÅKANSSON, 1977). In a Swedish fjord microlayer enrichments of bacterioneuston were greater than 10^2 at all stations (KJELLEBERG, STENSTRÖM and ODHAM, 1979).

Enriched levels of dissolved organic carbon often found in surface microlayers (see Section 3.2. below) apparently provide the nutrient source for these abundant bacterioneuston populations (SIEBURTH, *et al.*, 1976). The organic compounds are believed to originate from exudate material released by plankton and brought to the surface by rising bubbles, floatable particulates, and migrating and excreting phagotrophic protists.

The few studies performed on the biochemical activities of bacterioneuston report differing results. SIEBURTH (1971) found that the dominant surface film isolate *Pseudomonas sp.* was 95% lipolitic, 94% proteolitic, and 28% amylolitic, while a much lower percentage of water column bacteria were able to attack lipids and proteins. KJELLEBERG and HÅKANSSON (1977) reported the reverse case, with lower concentrations of lipolitic bacteria in the surface film. This was believed to result from photo-oxidation, whereby the relative amount of saturated fatty acids is higher in the surface film compared to the subsurface water. Bacterioneuston from the equatorial Pacific showed low viability on plates and low biochemical activity compared to bacterioplankton, presumably as a result of the inhibitory effects of high ultraviolet radiation at the surface (MARUMO, NOBUO and NAKAI, 1971).

Particulate surfaces serve as important sites for heterotrophic bacterioneuston activity in the sea surface microlayer. LION, HARVEY, YOUNG and LECKIE (1979) found that the majority of bacterioneuston from a salt marsh were associated with high concentrations of particulate matter in the surface microlayer, and PAERL (1973) suggested that bacterioneuston use particulate associated organics found in microlayers as a source of nutrients.

Bacterioneuston populations both consume and produce a wide variety of organic substances and as LISS (1975) suggests: "The existence of processes of this type, coupled with the high microorganism density at the sea surface argue for the importance of biological activity in the microlayer in bringing about the transformation of both natural and man-made materials in the marine environment".

2.2. *Phytoneuston*

Autotrophic production in the microlayer depends upon a great variety of microagal taxa (phytoneuston). Large microlayer phytoneuston enrichments have been found in sheltered bays and lagoons. Samples from a temperate marine lagoon contained 106 taxa of chrysophyta, chlorophyta, and euglenophyta dominated by neustonic pennate diatoms, and at times phytoflagellates (HARDY, 1971). Such photosynthetic neuston play an important part in the productivity of many waters, where they frequently occur at densities 10–100 times greater than the underlying phytoplankton (HARDY, 1973). In a Georgia salt marsh, 21–43% of the total water column productivity was concentrated in the upper 0.55 mm which was inhabited by

large numbers of microalgae, primarily, pennate diatoms. The mean productivity (moles $O_2/m^3/hr$) was up to 3,000 times greater in the surface microlayer (GALLAGHER, 1975).

Even offshore phytoneuston/phytoplankton ratios may be substantial. Screen samples of the surface film from the equatorial Pacific contained populations of diatoms (predominantly *Nitzschia sp.*) 10.5 times denser than the water 10 cm deep, but much of the biota did not appear in good physiological condition, presumably due to the strong tropical solar ultraviolet in the surface layer (MARUMO, NOBUO and NAKAI, 1971). Screen and rotating drum samples collected near Marseille had surface enrichments of 5–8 x for chlorophyll and 1.5–17 in ATP activity compared to a depth of 0.5 m (DAUMAS, LA BORDE, MARTY and SALIOT, 1976).

The behaviour of neuston may provide a link for the transfer of materials from the microlayer to the water column and vice versa. The phytoneuston interact with the phytoplankton community by diurnal vertical phototactic migrations. For example, in the North Sea, the dinoflagellates *Prorocentrum micans* and *Cerantium furca* have been found to move from the water column and to actively accumulate in the surface film during mid-day (WANDSCHNEIDER, 1979). Positive phototaxis was also responsible for mid-day accumulations of marine eugenloids and dinoflagellates in surface microlayers (HARDY, 1971) (Fig. 2). Laboratory studies could aid in clarifying the relationships between neuston and plankton. Thus far such studies are rare, but natural phytoneuston cummunities, dominated by diatoms, can be duplicated with only minor differences in laboratory flow-through microcosms (HARDY and VALETT, 1981).

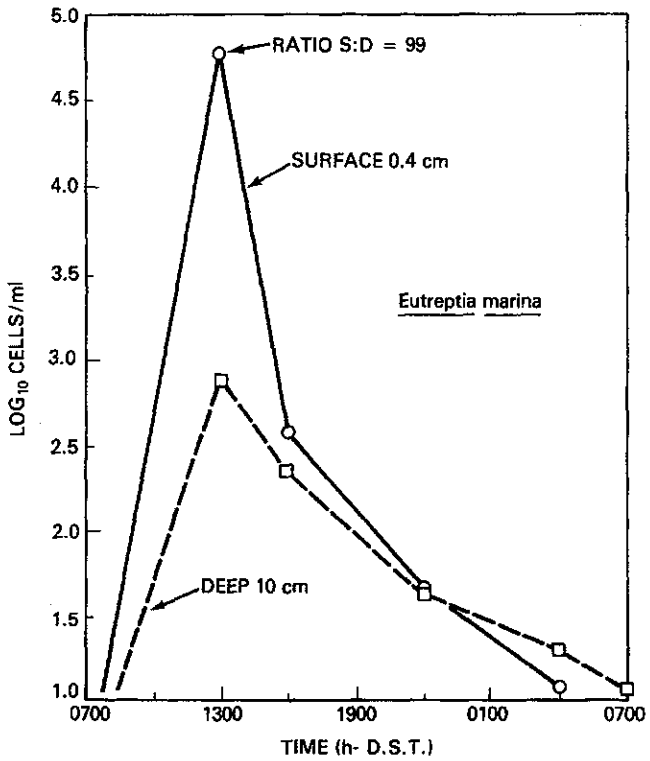

FIG. 2. Positive phototactic migrations resulted in a microlayer density of microalagae (Eugenoids) 100 times greater than the sub-surface water. (Based on data of HARDY, 1971).

2.3. *Zooneuston*

The secondary productivity of the microlayer depends upon a great diversity of small animals (zooneuston). These have been divided into three categories: (a) euneuston – organisms with maximum abundance in the immediate vicinity of the surface where they remain day and night; (b) facultative neuston – organisms which concentrate at the surface only during certain times and (c) pseudoneuston – maximum concentrations of these organisms occur at deeper layers, however, the range of their vertical distribution reaches the surface layer at least during certain hours (ZAITSEV, 1971; HEMPHEL and WEIKERT, 1972).

Like some phytoneuston, zooneuston can also be linked to the water column by diurnal vertical migration. Catches with a neuston net off Charleston, South Carolina revealed 29 species which were significantly more abundant in the surface water during night, whereas 12 species were greater during daylight hours (ELDRIDGE, BERRY and MILLER, 1978). Marine ciliates such as *Mesodenium rubrum* also undergo vertical positive phototactic migration from the water column to the surface film during mid-day (HARDY, 1971). The vertical migration of this ciliate could enhance photosynthesis of algal symbionts or allow for grazing on bacterioneuston, but the exact ecological significance of the migration is not yet understood. The phototaxis of several hyponeustonic crustaceans has been shown to respond primarily to blue and green monochromatic light and to decrease at wave lengths longer than 5.5 μm (MACQUART-MOULIN, 1975).

Many species of fish have larval or juvenile stages which inhabit the upper cm of the surface water. In the subtropical and boreal northeastern Atlantic Ocean facultative neuston organisms thrive in deeper layers during daytime, but at night join the feeding of the euneuston at the surface. Diurnal migrations occur, so that during daytime, a small number of euneuston species occupy the upper layer along with a high number of pseudoneuston species. In the evening, many facultative and pseudoneuston organisms move from the water column to the microlayer and apparently feed on neustonic organisms (HEMPEL and WEIKERT, 1972).

Populations of marine amoebae, heliozoans, tintinnids, and other protozoans may graze on bacterioneuston (DAVIS, CARON and SIEBURTH, 1978; ZAITSEV, 1971). Juvenile fish feed actively on live neuston as well as detrital material in the surface microlayer (HEMPEL and WEIKERT, 1972). However, the trophic relationships of the neuston and the degree of dependence of larval fish on phytoneuston and zooneuston communities has not been described in detail.

It has recently been recognized that the surface film is an important habitat for the larvae of commercial species, e.g., high concentrations of larval blue marlin (*Makaira nigricans*) congregate at the sea surface off the coast of South America (BARRTLETT and HAEDRICH, 1968). In the spring, off the eastern U.S. Coast, larvae of menhaden, hake, mackeral, cod, bluefish, lobster, blue crab and others have been found in much greater concentrations in the surface microlayer than in subsurface water (CASTAGNA, 1977). Oil spills or concentrations of toxic materials in the surface film (see Section 4 below) could have serious impacts on such neustonic larval populations and result in a detrimental recruitment to the commercial fisheries.

2.4. *Summary – biology*

Bacteria, microalgae and intervetebrates together form neustonic communities that depend upon the unique chemistry of the air/sea interface and, in turn, may affect the microlayer chemistry by their own metabolic activities. Although studies have not yet examined the

question, neustonic communities have the potential to serve as important transfer sites, either accelerating or slowing the fluxes of elements or compounds between the atmosphere and the water column and vice versa. This could occur as a result of chemical biotransformations in the microlayer or through trophic transfer to the plankton or nekton that feed on neuston organisms.

3. PHYSICS AND CHEMISTRY OF THE SEA SURFACE MICROLAYER

The sea surface microlayer represents a unique physical and chemical environment quite different from that of the subsurface water column. The presence of organic films, as well as the surface tension forces of the interface itself, provide an area of physical stability where compounds, particulate materials and organisms can concentrate. On the other hand, it is a climatically unstable environment subjected to greater extremes of temperature, salinity and solar energy than the water column. Studies point to a number of processes that may be involved in creating this unique physical/chemical environment, but considerable further study will be required before we can begin to understand the interaction, complexity or quantitative importance of these processes or their significance to air/sea transport or neuston communities.

3.1. *Physical characteristics*

In comparison to the water column, the sea surface microlayer can be characterized as a more physically stable, but climatically variable environment. The microlayer undergoes rapid environmental changes. Seasonal and diurnal fluctuations in temperature and salinity are generally greater than in subsurface water (HARDY, 1971). Physical stability results from strong surface tension forces. Normal oceanic waves and ripples cause periodic changes in the thickness of the microlayer, but generally leave the microlayer intact. Breaking waves will disrupt the microlayer temporarily, but whitecaps cover only 3–4% of the ocean surface at any one time (MAC INTYRE, 1974). Langmuir circulation tends to concentrate organic materials to form surface films, and if disturbed or mixed, these films rapidly reestablish their integrity. Formation and reorientation of organic surface films at the air/water interface has been estimated to occur in only about 0.2 sec (DRAGCEVIC and PRAVDIC, 1981). The surface pressure (lowering of the surface tension by the presence of organic films) can be conveniently measured by spreading concentrations of a polar compound such as dodecyl alcohol on the water surface. When this is done, estuarine areas and nearshore protected waters are often found to have surface tensions considerably below normal (ADAM, 1937; HARDY, 1973). Visable banded sea slicks occur frequently in coastal areas. These bands result from the dampening of capillary waves due to the presence of surface films which lower the surface pressure to 0.5–1.0 dynes/cm. The bands are thought to result from a four-fold compression of the surface film by horizontal convergent forces (BARGER, DANIEL and GARRETT, 1974).

To understand the processes governing the exchange of materials between the atmosphere and oceans, knowledge of the integrity and kinetics of formation of organic surface films is necessary. Materials can move from the benthic sediments and water column by upwelling, convection, diffusion, or bubble formation and collect at the sea surface. Transport from the sea surface to the atmosphere takes place through the formation of wind-generated aerosols, via the bursting of bubbles, or through evaporation of volatile compounds (MAC INTYRE, 1974). Both transport by bubbles from the water column and atmospheric deposition are considered potentially important contributors of substances to the sea surface microlayer (Fig. 3). For example, particulate aggregation associated with transport by bubbles may

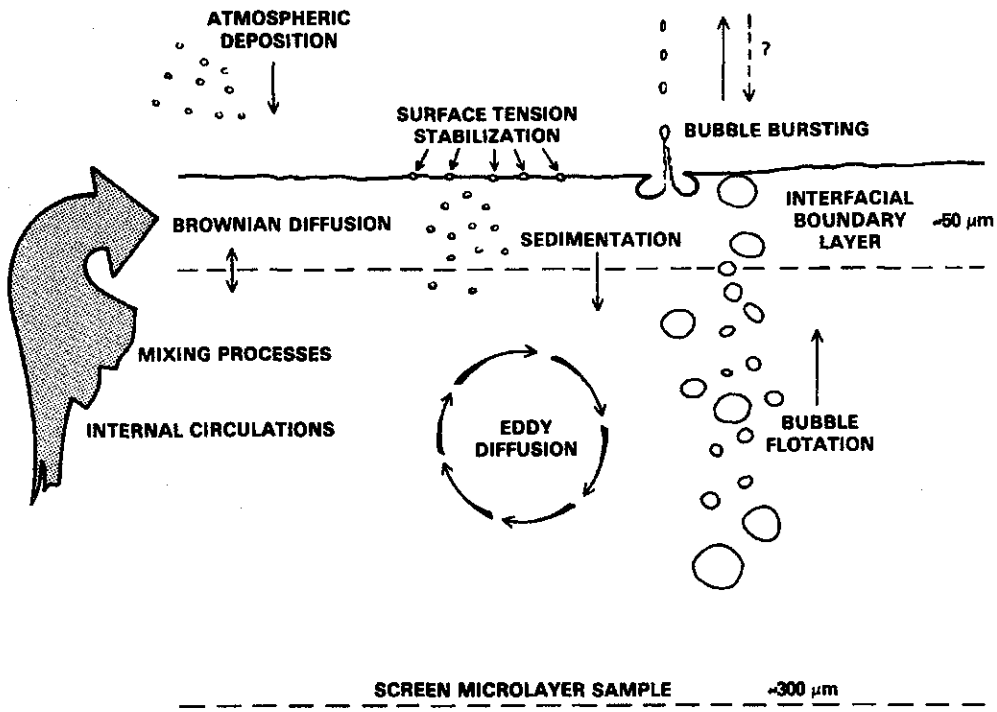

FIG. 3. Transport processes for particulate matter in the microlayer. The screen microlayer sample (~ 300 μm) is divided into an upper hydrodynamic boundary layer (~ 50 μm) within which turbulence is damped and a lower region which behaves like subsurface water and is well mixed by eddy diffusion (from HUNTER, 1980).

contribute to the rapid removal of particles (WALLACE, LOEB and WILSON, 1972) and trace metals (WALLACE and DUCE, 1978), including those of atmospheric origin, from the water column. Small particles (0.2–1.2 μm) are very important because they act as nuclei for the scavenging and growth of organic materials during the bubbling process (BATOOSINGH, RILEY and KESHWAR, 1969). Experimental bubbling of seawater collected from estuarine, continental shelf, slope and open ocean sites showed that about half of the original particulate organic carbon and nitrogen from the water column can be adsorbed and transported by bubbles to the surface froth. During this bubble scavenging, little or no conversion of dissolved to particulate organic carbon occurs; rather, smaller particles simply tend to aggregate into larger particles. The resultant larger particles may have a greater sinking rate and thus increase the overall rate of particulate organic carbon settling to deeper water (WALLACE and DUCE, 1978). However, the exact processes by which rising bubbles scavenge dissolved organic or colloidal materials from the water column remain incompletely understood and the subject of some controversy. Only further experimental work will clarify the importance of bubble formation in supplying materials to the microlayer, the water column or the atmosphere (e.g., see GARRETT, 1981 and JOHNSON and COOK, 1981).

From the literature and from calculations of some of the physical processes thought to control particles and particulate trace metals in the sea surface microlayer, HUNTER (1980) suggests that gravitational sedimentation is the major mechanism for removal of soil-sized (4–8 μm) dust particles. Browian movement and diffusion are relatively unimportant in

determining microlayer residence times. Mixing processes may be important for smaller colloidal-sized particles, but for larger particles sedimentation will exceed upward mixing. Surface stabilization of particles by interfacial forces may not be great for most mineral surfaces such as clays, metal oxides and carbonates which are readily wettable. However, many high-energy surfaces placed in seawater absorb natural organic surfactants from solution giving rise to organically coated particles with lower surface energies. This stabilization of particles by organic coatings is difficult to quantify, but organic-rich particles could have residence times in the microlayer appreciably enhanced.

3.2. *Organic chemistry*

Several studies have examined the organic chemical composition of the surface microlayer and compared it to subsurface water. Microlayer to subsurface ratios of organic matter, up to 8 and averaging approximately 2, have been found by many investigators (GOERING and MENZEL, 1965; WILLIAMS, 1967; NISHIZAWA, 1971; BARKER and ZEITLIN, 1972; QUINN and WADE, 1972).

Several studies indicate that the organic enrichment consists primarily of lipids and fatty acids although in some estuarine areas phenolic materials may be important (CARLSON and MAYER, 1980). GARRETT (1967) collected microlayer samples by the screen technique, from a total of 37 widely separated locations off the Atlantic and Pacific coasts of the U.S. and off Panama. He found that chloroform extracts of the samples contained free and combined fatty acids having from 11 to 22 carbon atoms and aliphatic alcohols such as dodecanol. Considerable quantities of lipid material have been found on the sea surface off the west coast of Sweden, even when no sea slicks were observed. Triglycerides, free-fatty acids, and wax esters were the predominating constituents (LARSSON, ÖDHAM and SÖDERGREN, 1974). Organic material, collected from the air above the sea surface and extracted with chloroform, also contains at least five fatty acids, with the relative proportions of each being similar to those found in sea surface material (BARGER and GARRETT, 1970).

Sterols in the C-25 and C-30 range, originating primarily from plankton, have been found in microlayer screen samples at enrichments of up to 15 and averaging about 2. They are also present in aerosols above the sea surface (BARBIER, TUSSEAU, MARTY, and SALIOT, 1981). The fatty acid composition of the lipid surface film appears to be quite specific and it has been suggested that this might be useful for characterization of the biomass from which the film originates. Preliminary work suggests that surface films produced by cod, herring, gray back and plaice proved to be specific enough for species discrimination (LARSSON, ODHAM and SÖDERGREN, 1974).

LISS (1975) pointed out that the earlier techniques used by GARRETT and others analyzed, at most, 25% of the total organic carbon in the surface microlayer with the majority of compounds being almost completely uncharacterized. Others suggested that polypeptide and polysaccharide compounds are important at the interface (MAC INTYRE, 1974; BAIER, GOUPIL, PERLMUTTER and KING, 1974) and that the lipid materials either result from pollution, or represent extracts of organisms in the samples. Indeed, BAIER, GOUPIL, PERLMUTTER and KING (1974) found that films from thousands of freshwater and marine samples were primarily glygoproteins and proteoglycans ranging in thickness from 100 to 300°A, and probably of biological exudate origin. The involvement of lipids or hydrocarbons at non-polluted sites was minimal. They concluded that, "The degrees and mechanisms of ion binding to these films and their influence on material transport to the atmosphere remain to be determined".

The effect of rainfall on the integrity of organic surface films is the subject of some controversy. BAIR, GOUPIL, PERLMUTTER and KING (1974) indicate that natural surface films are maintained during rain, but laboratory experiments using freshwater and an artificial organic film indicate that significant (20–75%) amounts of organic film are lost from the surface during rainfall and also suggest that the transfer of surface film substances to the atmosphere could be quite large during rainfall (GREEN and HOUK, 1979). Further work is needed on the effects of rain, including acidic rain, on microlayer processes.

3.3. *Inorganic chemistry*

Both inorganic and organic phosphorus frequently concentrate in aquatic surface microlayers (GOERING and MENZEL, 1965; WILLIAMS, 1967; NISHIZAWA, 1971). Studies also point to the importance of bubbling by the action of wind and waves in the presence of surface active molecules in producing higher concentrations of phosphorus in microlayers (LISS, 1975). With respect to nitrogen, the order of enrichment is approximately ammonia > particulate organic nitrogen > nitrate > dissolved organic nitrogen (LISS, 1975), but our present knowledge of the mechanisms producing such enrichment leaves much to be desired. Dissolved iodine species, however, do not appear to concentrate in the sea surface microlayer (CHAPMAN and LISS, 1980). Many trace metals are highly enriched in the microlayer (see Section 4.2. below).

3.4. *Summary – physical/chemical*

The disparities in microlayer chemical composition found by different workers probably result from two primary causes. First, the patterns of biological and chemical enrichment may be highly clumped in their distribution and problems of sampling scale have not been adquately addressed. Second, the numerous sampling techniques (see above) each collect a different type of sample. The biology and chemistry have not been examined together. In our estimation, much of the data may be resolved by a model in which the upper layer consists of a monomolecular lipid film of 10–20°A in thickness, below which is a polysaccharide protein layer ranging in thickness from 100 to 300°A and a closely associated layer of abiotic particulate matter, bacterioneuston and yeasts and molds to a depth of about 1 μm. Deeper layers may consist of microalgae (phytoneuston), ciliates, copepods and other zooneuston (Fig. 4).

4. ANTHROPOGENIC ENRICHMENT OF THE MICROLAYER

The sea surface microlayer covers 71% of the earth's surface and serves an important role in the interchange of materials between the atmosphere and the oceans (Fig. 1). Man's energy production processes, particularly fossil-fuel combustion, are likely to impact the sea surface microlayer. Gaseous air pollutants, particulate-bound metals and hydrocarbons deposit from the atmosphere to the air/sea interface through dry deposition and rainfall. Petroleum and other hydrophobic pollutants from riverine, coastal point sources, and spills concentrate at and may enter the world's oceans through the microlayer.

4.1. *Hydrocarbons*

Airborne particulate matter has been found to be highly enriched in anthropogenic and potentially toxic or carcinogenic polyaromatic hydrocarbons (PAH's) (PITTS, LOKENSGARD,

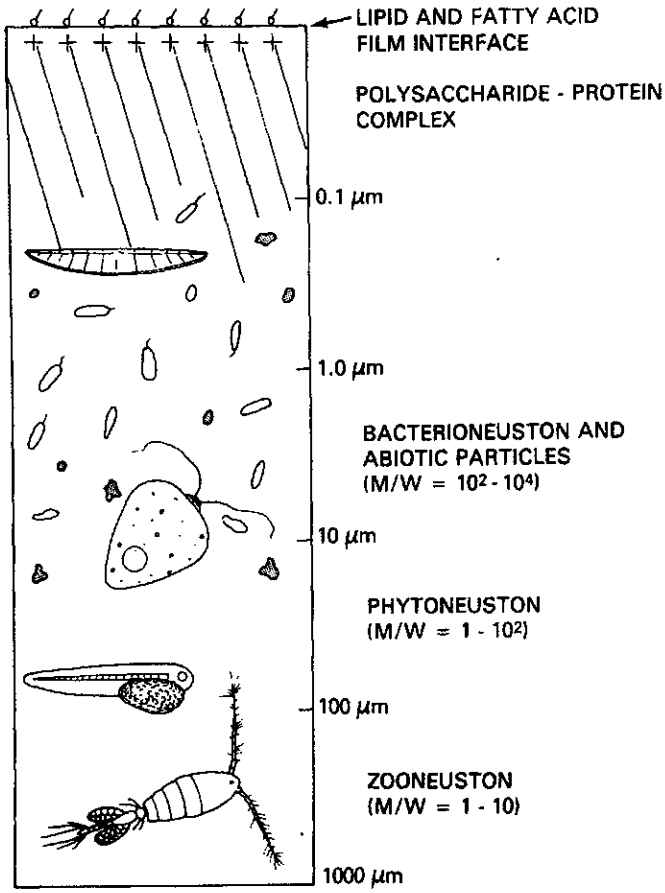

FIG. 4. Conceptual model of the sea surface microlayer ecosystem. M/W = typical microlayer to water concentration ratios based on a number of studies.

RIPLEY, VAN CAUWENBERGHE, VAN VAECK, SHAFFER and THILL, 1980; KATZ and CHAN 1980; and GREENBURG, YOKOYAMA, GIORGIO, and CANNOVA, 1980). The microlayer appears to be a repository for these PAH's. Such organic pollutants concentrate on particulate material and deposit in surface microlayers. For example, concentrations of polyaromatic hydrocarbons in the Lake Michigan microlayer range from 0.15 to 0.45 μg/L – a 10^6 enrichment compared to the concentration in air. Two of the important aromatics are benzo[a]anthracene and benzo[a]pyrene (STRAND and ANDREN, 1980).

Recent measurements indicate that chlorinated hydrocarbons and pesticides are present in the atmosphere even in remote oceanic areas (ATLAS and GIAM, 1981). Pesticides and PCBs are frequently enriched by 10^1–10^3 in surface films relative to subsurface water (DUCE, QUINN, OLNEY, PIOTROWICZ, RAY and WADE, 1972; BIDLEMAN and OLNEY, 1974). SEBA and CORCORAN (1969), for example, found that the surface film of Biscayne Bay, Florida contained concentrations of DDT more than 2670 times greater than the subsurface water.

Petroleum-derived hydrocarbons, tar and plastic particles are often found in microlayer samples. The ubiquitousness of petroleum lumps or "tar balls" on the sea surface was recognized

as early as 1970 (HORN, TEAL and BACKUS, 1970). In the Pacific, several surveys indicate that petroleum tar balls originate from the tanker route southwest of Japan and move in the surface layer around the north Pacific through the Koroshio subtropical gyre system (SHAW and MAPES, 1979). Pelagic oil aggregates (tar balls) of the eastern Atlantic contain their own associated neustonic periphyton, including microalgae and several invertebrate species (BENZHITSKII, TRETYAKOVA and KOIEFSNIKOVA, 1978). An area off the Mediterranean Coast of France, when sampled by both rotating drum and screen samplers, contained a microlayer enrichment of *n*-alkanes between 4 and 30× (DAUMAS, LABORDE, MARTY and SALIOT, 1976). Plastic particles occur in the microlayer of both the Atlantic (CARPENTER and SMITH, 1972) and the Pacific (WONG, GREEN and CRETNEY, 1974; SHAW and MAPES, 1979).

4.2. *Metals*

The microlayer serves as a collection point for metals such as copper, iron, nickel, lead, aluminum, zinc, chromium and mercury. In Narragansett Bay, enrichment factors for particulate matter in the upper 100–500 μm of water surface were lead, 5.4–5.8; iron, 4.3–29; copper 5–36; and nickel, 6–50 (DUCE, QUINN, OLNEY, PIOTROWICZ, RAY and WADE, 1972). In a San Francisco Bay salt marsh, lead concentrations were 6–14× in the microlayer compared to subsurface water and 83–97% of this trace metal was associated with particulate matter in the microlayer (LION, HARVEY, YOUNG and LECKIE, 1979). In convergence foams of Delaware Bay, concentrations of Cr, Cu, Fe, Hg, Pb and Zn were 10^4 greater than those in mean ocean water. Samples of the upper 150 μm of the surface near Hawaii had 6.7 and 6.1 times more copper and zinc, respectively, than the water 0.6 m deep. However, as the authors point out, the actual thickness of the microlayer is much less than 150 μm suggesting that their sampling methods may dilute the actual metal enrichments which may be closer to 10^3 (BARKER and ZEITLIN, 1972). On the other hand, no surface microlayer enrichment was found in screen samples collected in the northwest Atlantic (FITZGERALD and HUNT, 1974).

Because of the high enrichments of particulate materials and dissolved organic compounds at the air-sea interface (see Section 3.2.), trace metal speciation in the microlayer may be markedly different from that in the bulk seawater. These differences in chemical speciation, in turn, may have a strong influence on the potential transport of metals from the surface microlayer to the water column and could alter the possibilities for metal incorporation or toxicity in marine microbiota (Fig. 5). Computer modeling has been applied to trace metal equilibrium reactions to study the adsorption and complexation of metals in the microlayer. Computations suggest that cadmium and mercury would have little tendency to associate with surface active materials and concentrate in the microlayer, whereas lead and copper would be highly associated with surface active organic compounds and particulate matter, especially at higher surface film densities (LION and LECKIE, 1981a). This model generally agrees with recent field data describing metal accumulations in a salt marsh microlayer (LION and LECKIE, 1982) and the results of microcosm experiments in which the microlayer was enriched with atmospheric particules (HARDY, CRECELIUS and APTS, 1982).

Microlayer particulates, with their associated trace metals, may originate from the water column or from atmospheric particles settling on the sea surface. Trace metals from the latter source are relatively soluble in seawater (CRECELIUS, 1979) and this fact has important implications for the fate of trace metals introduced into the atmosphere by man's activities.

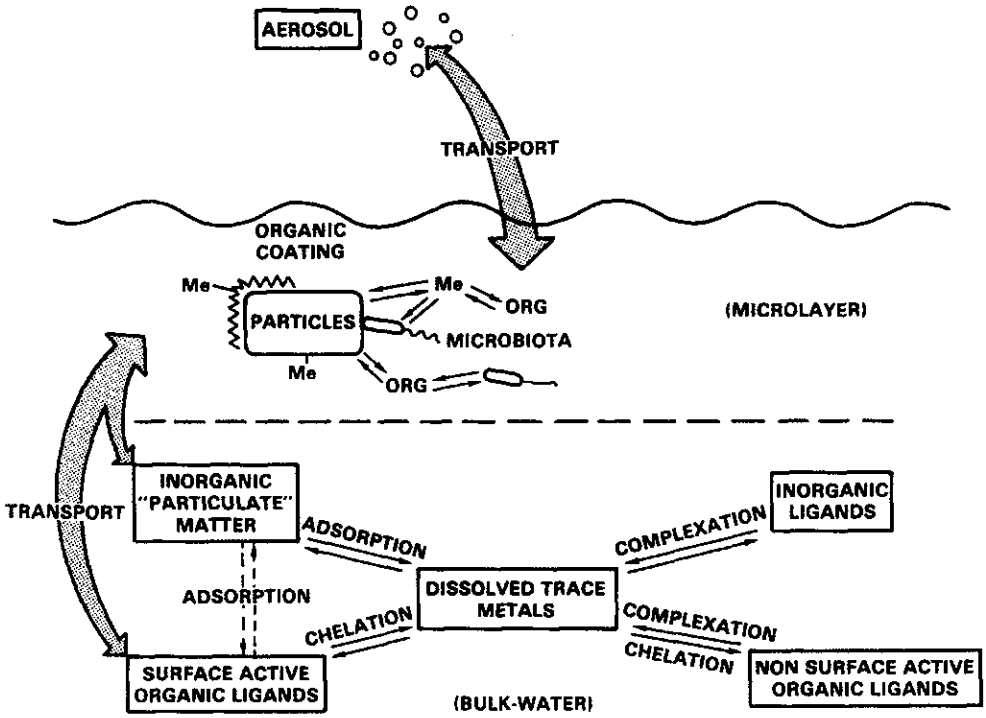

FIG. 5. Alternatives for the fate of trace metals at the air-sea interface (from LION and LECKIE, 1981).

As LISS (1975) points out, "such solubilization of airborne particulates at the sea surface will lead to rapid introduction [of pollutants] into marine food chains via the high concentrations of microorganisms found in the microlayer".

It is not known, at this time, whether or not neustonic organisms accumulate trace metal pollutants from the surface microlayer. Sea skaters (*Halobates robustus*), the only insects found on the open ocean, have been found to contain relatively high concentrations of cadmium and it has been suggested that they be utilized as indicator organisms for microlayer trace metal studies (CHENG, ALEXANDER and FRANCO, 1976). They have been shown in the laboratory to accumulate cadmium from the water (SCHULZ-BALDEZ and CHENG, 1979). However, neustonic copepods in the Mediterranean Sea contain body burden levels of Cr, Cu, Cd and Pd which are not greatly different from subsurface plankton communities (POLIKARPOV, OREGIONI, PARCHEVSKAYA and BENAYOUN, 1979).

The surface microlayer may act as an important agent for the concentration, cycling and transport of trace metals in lakes, streams, estuarine and salt marsh areas. For example, in a Delaware salt marsh out of the total metal fluxes, 10%, 19% and 23% of the copper, zinc and iron were carried by the surface microlayer (PELLENBARG and CHURCH, 1979). These were not extractable with organic solvents and were presumed associated with the inorganic phase (PELLENBARG, 1981).

Films on freshwater streams and lakes, formed largely from the decomposition of organics and exudates from trees, can be highly enriched in Fe and Mn compared to the subsurface water (POLJASEK and ZAJICEK, 1978). Recent evidence indicates that zinc, cadmium, lead

and copper occur in considerably greater concentrations in the surface microlayer than in the subsurface waters of Lakes Michigan, Ontario and Mendota. The presence, absence or relative development of films on the surface was positively correlated with the surface enrichment of (largely particulate-associated) trace metals believed to originate from deposition of atmospheric particulate matter (ELZERMAN, ARMSTRONG, and ANDREN, 1979). They concluded that, despite the small volume of the surface microlayer compared to the rest of the lake, interactions between materials in the surface microlayer (including trace metals, organic matter, particulate matter and microorganisms) could be influenced by the high concentrations (often 100 ppm) of trace metals with implications for the whole water system (EISENREICH, ELZERMAN and ARMSTRONG, 1979).

Some studies indicate that the contribution of air-bubble flotation to the microlayer trace metal enrichment is roughly comparable to the contribution of atmospheric deposition for a wide variety of particulate trace metals (WALLACE and DUCE, 1978). In contrast, other studies using the ratio $^{210}Po/^{210}Pb$, in both seawater and in surface microlayer slick samples, indicate that the subsurface water column rather than the atmosphere may be the largest source contributing to trace metal enrichments found in the surface microlayer (BACON and ELZERMAN, 1980), but further testing of this hypothesis is needed.

Atmospheric inputs constitute a significant route for trace metal inputs to the ocean near Bermuda. In turn, sea salt particles produced by bubbles bursting at the air-sea interface introduce quantities of zinc and copper to the atmosphere via the fractionation process which may be of the same magnitude as the deposition of atmospheric zinc and copper from crustal weathering and anthropogenic sources (DUCE, HOFFMAN, RAY, FLETCHER, WALLACE FASCHING, PIOTROWICZ, WALSH, HOFFMAN, MILLER, and HEFFTER, 1976).

A full discussion of atmospheric inputs of metals to the sea surface is beyond the scope of this paper. However, it is clear that large quantities of metals continually deposit on the surface of the ocean with deposition rates on the order of 10^{-2}–10^{-5} grams per m^2 per year (NAS 1978). The exact sources of these atmospheric metals, whether anthropogenic, e.g., from fossil fuel combustion particulates or natural, e.g., from volcanism or airborne dust, remains controversial. In some areas, lead, nickel, copper, and zinc appear to have significant anthropogenic origins (CAMBRAY, JEFFRIES and TOPPING, 1979; PATTERSON and SETTLE, 1974; DUCE, HOFFMAN, RAY, FLETCHER, WALLACE, FASCHING, PIOTROWICZ, WALSH, HOFFMAN, MILLER and HEFFTER, 1976; HUNTER, 1980; and HODGE, JOHNSON, and GOLDBERG, 1978), but other studies indicate that the natural environmental sources of lead, cadmium and mercury overwhelm the anthropogenic inputs (JAWOROWSKI, BYSIEK and KOWNACKA, 1981).

After entering surface waters, adsorption of metals on particulate matter may be largely controlled by the organic coatings on the particulates in seawater (BALISTRIERI, BREWER, and MURRAY, 1981). Bubble formation (see Section 3.1. above) may be important as a process for scavenging trace metals from the water column. Most atmospherically introduced particulate trace metals enter as particles with diameters less than 4 μm (CHESTER, ASTON, STONER and BRUTY, 1974). Their aggregation into larger particles during bubble scavenging could play an important role in transporting these metals to the water column (WALLACE and DUCE, 1978).

Atmospheric deposition can contribute a large proportion of the particulate matter to the microlayer, especially if the particles contain sufficient organic material for stabilization at the interface. Bubble floatation from the water column can also contribute significant quantities of particulate organic carbon and particulate trace metals to surface films. On the basis of

present studies, it appears that atmospheric deposition and bubble floatation contribute similar quantities of many substances to surface films, although in some areas atmospheric deposition may be the major source of microlayer enrichments (HUNTER, 1980). In the other direction, it is clear that, in the transport of metals from the ocean to the atmosphere, surface-active organic material in the microlayer plays a major role. Chemical fractionation occurs so that some metals are concentrated in the aerosal whereas others are preferentially left behind in the bulk seawater (DUCE and HOFFMAN, 1976). PATTENDEN, CAMBRAY and PLAYFORD (1981) analyzed metals in aerosols generated by a bubble-bursting sampler, collecting the upper 0.1–1 μm of the surface microlayer. Fractionation ratios* for lead, cobalt, zinc, and cesium were 140–410, up to 76, less than 50, and up to 500, respectively.

Bursting bubbles at the sea surface rather than wind driven sea spray, appears to be the major mechanism for the transport of sea salts and pollutants from the ocean to the atmosphere (WU, 1981). Bubble bursting and aerosol formation, in addition to resulting in chemical fractionation at the sea surface, can also produce enrichments of microorganisms in the ejected spray droplets. Aerosol enrichments of 26 for phytoplankton (SUTCLIFFE, BAYLOR and MENZEL, 1963) and 10–1000 for bacteria (BLANCHARD and SYZDEK, 1970) compared to the bulk seawater have been found. The problems associated with estimating the deposition of atmospheric particles to natural waters have been reviewed elsewhere (SLINN and SLINN, 1981; SLINN, HASSE, HICKS, HOGAN, LAL, LISS, MUNNICH, SEHMEL, and VITTORI, 1978; and SEHMEL and SUTTER, 1974).

Microlayer samples (0–300 μm) collected off the North Sea Coast of England were depleted in iron and manganese compared to subsurface water, but enriched in copper, zinc and lead. This situation is believed to result from the iron and manganese being associated with river-derived terrigenous minerals, which because of their relatively large particle size, settle rapidly out of the microlayer region. Copper, zinc, lead and nickel, on the other hand, are believed to be associated with very small organically-bound aggregates of colloidal minerals and/or organic detritus which enter the microlayer by a combination of bubble floatation, and/or atmospheric deposition. They then form relatively stable attachments at the air-sea interface by means of interfacial forces concentrating at levels which are substantially higher than their typical crustal abundance.

Microcosm studies utilizing atmospheric particulate matter also indicate that lead and zinc, introduced into the microlayer, remain highly enriched in the microlayer compared to the subsurface water. Concentration of these metals by microneuston does not appear to account for a large proportion of the microlayer metal enrichment (HARDY, CRECELIUS and APTS, 1982).

4.3. *Summary – anthropogenic enrichment*

The sea surface microlayer serves as a concentration point for anthropogenic substances both organic and inorganic. Organic compounds such as benzo[a]anthracene, benzo[a]pyrene, chlorinated pesticides and polychlorinated biphenyls have been identified in the atmosphere even in offshore oceanic areas. Their hydrophobic nature often leads to concentrations in the microlayer several orders of magnitude greater than in either the atmosphere or the water column. Petroleum enrichment of the microlayer is widespread. Potentially toxic metals such as lead, zinc, nickel and copper are often highly enriched in surface microlayers.

* $= \frac{\text{ratio of metal and Na concentrations in microlayer}}{\text{similar ratio in corresponding bulk seawater}}$

Chemical speciation of metals in the microlayer and their exchange with the water column and atmosphere is controlled by a number of processes which are not yet fully understood, but evidence indicates that solid surface adsorption and dissolved organic complexation reactions are probably important.

5. RESEARCH NEEDS

Our current concept of the sea surface microlayer is that of a biologically and chemically active boundary layer. This interface is generally physically stable, environmentally stressed, and often highly enriched in particulate matter, organic compounds, metals and biota compared to the water column. However, major questions of importance remain unresolved and in some cases completely unexamined.

(1) What is the actual depth of the microlayer in regard to its different chemical and biological components? Enrichment factors have frequently been calculated based on sampling techniques which are not representative of the actual depth distribution. For example, screen samples collect 300–400 μm of the surface. Enrichments calculated for organics or bacterioneuston, which may occupy only a small fraction of this depth, are in obvious error. Sample depth and collection efficiency should be well calibrated and appropriate to the fraction collected. Several different types of samplers may be desirable for differentiation of the chemical and biological composition of the microlayer.

(2) What effects do neuston communities have on the transfer rates of gases or compounds between the atmosphere and water column, or vice versa? How important are neuston as a food source for water column organisms? Is the organic film on the microlayer a result of the biological activities of neustonic populations, or are the populations present secondarily to use compounds that are deposited in the microlayer by other processes? LISS, (1975), concluded that, "Although organisms utilize and, hence, recycle the organic matter close to the interface, the real cause of the enrichment of the organic matter and organisms in the microlayer is the scavenging effect associated with the rising bubbles produced by wind and wave action".

(3) How important is the microlayer, in quantiative terms, either as a source or as a sink for anthropogenic materials from the atmosphere or water column? The removal mechanisms for pollutants found in the atmosphere are not well understood. Are the major sources of the observed microlayer enrichments for metals and organics natural or anthropogenic? Research is needed to quantify the flux rates of pollutants such as PAH's, other organics and metals across the air-sea interface. It is clear that the question of residence times of particles in the microlayer has not been adequately investigated. Further research is needed on the behaviour of atmospheric particulate matter as it enters the film and on biotransformation processes which affect the chemical speciation of such particles. How do organic coatings on natural air particles affect their residence time in the sea surface microlayer?

(4) How important are neuston communities on a global scale and what are the environmental determinants of these populations? Intensive field sampling programs should be undertaken to study neustonic populations and define their spatial and temporal distributions over several scales in different areas of the world's oceans. How are the often dense neuston communities related to variations in the physical and chemical environment of the microlayer? Most investigations have examined only one aspect of the microlayer environment. Biological, physical and chemical sampling needs to be undertaken simultaneously and multivariate analyzes applied. Only in this way can the functioning of the microlayer be understood as an integrated ecosystem.

All of these important questions remain, for the most part, unexamined. A great deal of research effort will need to be expended before we begin to understand, even rudimentally, how the processes occurring in the microlayer link the world's atmosphere and hydrosphere.

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Exhibit D

Framework for Addressing Technical Issues Associated with the TMDL

Introduction

This Framework identifies the key technical issues that the California Regional Water Quality Control Board, Los Angeles Region ("Regional Water Board") must address to develop a technically-defensible Total Maximum Daily Load ("TMDL") for the Dominguez Channel and Greater Los Angeles and Long Beach Harbor Waters (herein referred to as "The System") that is supported by the proper technical conditions. As defined by the U.S. Environmental Protection Agency, proper technical conditions for a TMDL include adequate modeling techniques, analytical methods, and data bases, all of which are lacking here. These proper technical conditions will continue to be lacking until the issues identified in this Framework are fully addressed. Without addressing these fundamental issues, the resulting TMDLs will continue to be either technically flawed or impractical or impossible to implement.

This Framework applies not only to TMDLs for DDT but also for other legacy contaminants. While not intended to be a comprehensive list of issues with the TMDL, or a list of legal issues with the TMDL, the issues have been organized around broad headings that relate to the following aspects of the TMDL development approach and process:

- Conceptual framework for TMDL development
- Current load estimates for The System
- Selection of TMDL derivation methods and input values
- Implementation considerations

Conceptual Framework for TMDL Development

Critical technical issues regarding the conceptual framework include:

- The conceptual framework used for The System areas involved deriving TMDLs solely for sediments rather than for waterbodies, resulting in confusion over what these TMDLs represent and how they are to be implemented. The sediment TMDLs also create an unbalanced management focus on sediments rather than on external sources of pollutants.
- The conceptual framework used for TMDL development for The System is inconsistent with that for other similar types of systems outside of the Los Angeles region.

Current Load Estimates to The System

Critical technical issues regarding the current load estimates to The System include:

- The sediment TMDLs and associated allocations ignore the fact that there are "clean" sediments entering the system, along with sediments leaving the system, and both are important parts of the mass balance and contribute to natural recovery processes. Dr. Susan Paulsen of Flow Science submitted comments on February 22, 2011 to the Regional Water Board that estimated the bypass through the Harbor for solids and contaminants. Dr. Paulsen used the ERDC modeling results to estimate that roughly 65% of inflowing sediment passes through the system without depositing to the sediment bed; Dr. Paulsen also estimated that a large fraction of the DDT loading to the watershed (72-97%) is simulated to pass through the system without depositing to the sediments.

- Loads from the atmosphere are not reliable and are inappropriately presumed to be equivalent to loads to the sediments resulting in incorrect loading estimates and, as a result, incorrect allocations. Dr. Susan Paulsen of Flow Science and Dr. Charles Menzie of Exponent have commented on this. Based on the ERDC modeling, a large fraction of the chemicals entering the Channel/Harbor system do not deposit in the sediments, but instead bypass the system and are carried out to sea. It is likely that an even larger fraction of chemicals that arrive in the system via atmospheric deposition will not fall to the sediments but will be transported away. Dr. Paulsen has described the processes that will act on these atmospherically-deposited chemicals in terms of particle sizes, mixing rates, and advection through the system. An additional process that is important for organic chemicals that land upon the sea surface (such as DDT), is that they can become trapped at the surface of the water within the thin film known as the sea-surface microlayer.[1] These chemicals are then subject to subsequent transport by winds as well as advection of underlying water.

Selection of TMDL Derivation Methods and Input Values

Critical technical issues regarding the selection of TMDL derivation methods and input values include:

- The sediment TMDLs for The System are derived from only two parameters – sediment deposition rate and a sediment target concentration. The derived sediment TMDLs do not take into account degree of impairment, site-specific ecological receptors, human receptors, or any other physical process or biological aspect of The System. Because these TMDLs do not account for system conditions (other than the modeled sediment deposition}, they do not reflect the realities of The System and the actual assimilative capacities of the relevant waterbodies, and could, in fact, have been developed for any system in the United States for which there is an estimate of sediment deposition.

- The modeled sediment deposition rates are not reliable because they are the result of models that have not been properly calibrated and validated to ensure that the results resemble real world conditions. Because the models have not been properly calibrated and validated, reliance

[1] The presence of these sea-surface microlayers and their importance as a reservoir for contaminants has been recognized for a long time as for example in: Hardy, J. T. 1982. The sea-surface microlayer: biology, chemistry, and anthropogenic enrichment. *Prog. Oceanogr*. 11:307-328.

on the values that result is highly suspect and not scientifically supported. Because the modeled sediment deposition rate is the primary factor for deriving the TMDLs (an issue that is described in more detail later), any error or uncertainty in this modeled value will result in a proportional error or uncertainty in the TMDL.

- Mass balance calculations were not performed and thus, there is no scientific evidence that the TMDLs reflect the actual inputs and outputs of the system. Therefore, the TMDLs have a false basis.

- The use of sediment screening-levels such as Effects Range – Lows ("ER-Ls") to support major risk management decisions for The System is not appropriate because screening values are not appropriate target values. Target values should be developed from stressor analysis carried out based on results of a screening analysis. By deriving extremely low TMDLs from screening values in the interest of protecting against certain types of risks, implementation of the resultant TMDL program will pose increased ecological, human health, and other risks that have not been evaluated and factored into the overall benefits.

- The TMDL did not rely on any system-specific information to establish linkage between sediments and fish tissues for The System but instead incorrectly assumed that there was a direct cause and effect relationship between sediment concentration and fish concentration. This presumed relationship was then incorrectly represented by using a Biota Sediment Accumulation Factor ("BASF") selected from another system that could be very different than The System.

- The TMDL development process does not rely on the California State Water Quality Control Board's SQO process. Instead, the TMDL relegates the SQO process to a confirmation stage, thereby creating a technical disconnect between the basis for TMDL development and the evaluation of efficacy of TMDL implementation.

Other important technical issues involving the selection of TMDL derivation methods and input values include:

- The sediment TMDLs do not take into account bioavailability processes which would explain why the screening levels such as ER-Ls are so much lower than regional sediment toxicity values that have been developed for the region and are available for use.

- The TMDL Staff Report and Response to Comments describe wildlife tissue target levels but these are not used for TMDL development and impairments are not identified. Therefore, this information introduces an unnecessary distraction and uncertainty into the TMDL process and should be removed from the materials.

Implementation Considerations

Critical technical considerations regarding implementation include:

- Because the TMDLs are specific to sediments and because loadings to sediments have not been properly estimated (e.g., atmospheric loadings), the sediments have been inappropriately made

the focus of management actions. This is a departure from what is done outside the Los Angeles region, where external inputs to the waterbodies are the focus of TMDL management efforts.

- Because the sediment TMDLs are specific to sediments in eleven particular areas and not to the overall system and associated waterbodies, these sediment TMDLs will be very difficult to relate to point and non-point sources.

- Because the derived sediment TMDLs ignore many ongoing recovery processes, the role of natural recovery for sediments (i.e., Monitored Natural Recovery ["MNR"]) is not given adequate attention, despite strong evidence that natural recovery is reducing external loadings for DDT and other legacy contaminants, and that recovery processes are occurring in The System.

- The role of maintenance dredging is not discussed in the TMDL, even though it is acknowledged by the scientific community to have a strong influence on allocations.

- Dredging to support sediment TMDLs could have adverse consequences for harbor management.

- Potential disposal options or capacities associated with the dredging described in the TMDL have not been considered and will likely be problematic.

Other important technical considerations regarding implementation include:

- Dredging cost estimates are based on out-of-date information and are therefore significantly underestimated.

- The TMDL document provides no discussion of the significant ecological costs and loss of ecological services associated with dredging.

- The TMDL did not cite or consider any recent sediment remediation guidance such as the Contaminated Sediment Remediation Guidance for Hazardous Waste Sites (USEPA 2005).

- Sediment fate and transport issues associated with dredging were not included in the TMDL analysis.

- The TMDL document is silent on the anticipated efficacy and the limitations of dredging.

Exhibit E

Environmental Defense Sciences

723 East Green Street, Pasadena, CA 91101 Tel: 626-744-1766 Fax: 626-744-1734

January 23, 2012

Mr. Samuel Unger, P.E.
Executive Officer
California Regional Water Quality Control Board
Los Angeles Region
320 W. 4th Street, Suite 200
Los Angeles, CA 90013

via e-mail: sunger@waterboards.ca.gov

Subject: **TMDL and Sediment "Carry Through"**

Dear Mr. Unger:

This letter follows up on comments made by Los Angeles Regional Water Quality Control Board (RWQCB) staff at the recent stakeholder meeting on January 9, 2012 regarding the proposed Total Maximum Daily Load for Toxic Pollutants in Dominguez Channel and Greater Los Angeles and Long Beach Harbor Waters (TMDL) in which I participated by telephone. In that meeting, staff, and specifically Dr. L.B. Nye, stated that "a lot of the sediment does carry through the Harbors," and is not deposited in the Harbors.

The purpose of this letter is to express my agreement with Dr. Nye's statement that sediment carries through the Harbors and comment upon the fact that the TMDL load allocations do not take into account the mass of sediment that passes out of the Harbors during major stormwater runoff events. This appears to be acknowledged in the Regional Board's Response to Comment 26.3a (iv), which states:

> "In addition, the allocations are written for the sediment depositing in the Harbor waterbodies, so pollutants and sediment that pass through the system are not included in the calculations."

This statement was confirmed by Dr. Nye at the January 9, 2012 meeting where she said, "Yes, sediment goes out to the ocean. Allocations are based on what deposits. That's the part we care about because that's the part that can affect fish."

Since there are in fact demonstrably large fluxes of sediment out of the Harbors, the net result is that the TMDL allocations for sediment-borne compounds are very much lower than would be the case had the flux of sediments out of the Harbors been included in the allocation computations. This arises because the TMDL load allocations are based upon the difference between two separate analyses of the average concentration of the bed sediments over a four year modeling period for which, in one case, loads are imposed and, in the other case, no contaminant load is included in depositing sediment. The problem is well illustrated by consideration of the PAH load allocations for the Consolidated Slip. In

one four year modeling run with load imposed the average sediment concentration of PAH is computed to be 32,373 micrograms per kilogram (µg/kg) of dry sediment; with no PAH loads imposed the average concentration in the sediments over the four year period is computed to be 32,240 µg/kg, or an increase of 133 µg/kg (0.41%) that is ascribed to the added load (see Table 5, page 70, Appendix III-Supplemental Technical Information). (Note that in both cases the modeled sediment concentration actually ***declines*** from about73,512 µg/kg to approximately 12,000 µg/kg over the four year period, as shown in Figures 8 and 9, page 71, Appendix III). Based on this very slight increase in the average sediment concentration between the two four-year modeling periods, the PAH stormwater allocation for the PAH TMDL (1.43 kg/yr) is computed to be 0.0041x1.43= 0.0059 kg/yr (see Table 6-10, Staff Report). The paradoxical result of the calculation is that had the difference between the two model runs been 40%, i.e., more sediment deposited, the stormwater allocation would have been 100 times higher. In other words, because the modeling indicates that most of the PAH in the stormwater is actually passing through the Harbors and not impacting the sediments the waste load allocations are very much smaller; i.e., the greater the flux through the Harbors the smaller the load allocation.

Sediment flocculation and deposition occur to some degree within the Harbors, as is recognized in the modeling but, as shown above, basing TMDL allocations solely on that portion of the mass that deposits is completely inappropriate. NPDES dischargers and nonpoint sources can release compound masses equal to the sum of the local deposition plus carry through and still satisfy water quality standards. The allocations should include the entire compound mass that can enter the water bodies and still result in attainment. That mass most certainly includes the compound that carries through the system without, as the RWQCB acknowledges, harming the subject water bodies.

According to Dr. Susan Paulsen, the RWQCB's own modeling indicated that up to 65% of the sediment that enters the Harbors does not deposit there, but passes through them. See: Comments of Dr. Susan Paulsen, Flow Science, on behalf of Signal Hill at 3.[1] Because the RWQCB's model was neither calibrated nor verified, actual sediment pass-through might be substantially different than 65%. But the TMDL calculation actually uses the modeled sediment deposition, so the RWQCB ought to acknowledge that its own best calculation shows that a substantial majority of sediment entering the Harbors may never deposit there. For particular compounds such as DDT, the RWQCB's own modeling, per Dr. Paulsen, shows up to 97% pass through. *Id*.

The substantial transport of sediment through estuaries and into the coastal ocean in Southern California is well documented in the scientific literature. Many studies show how fresh stormwater outflow laden with sediment floats on the surface of the ocean and extends many miles offshore. I have attached the following three articles for your consideration:

1. Hickey, Barbara M. "River discharge plumes in the Santa Barbara Channel", p. 65, 5th California Islands Symposium (Physical Oceanography) 1999.[2]

[1] Available at: http://www.waterboards.ca.gov/losangeles/board_decisions/basin_plan_amendments/technical_documents/66_New/11_0303/40%20Flow%20Science%2001.pdf

[2] Available at http://science.nature.nps.gov/im/units/medn/symposia/5th%20California%20Islands%20Symposium%20(1999)/Physical%20Oceanography/Hickey_River_Discharge_plumes_SB_Channel.pdf

2. Ahn *et al.,* "Coastal Water Quality Impact of Stormwater Runoff from an Urban Watershed in Southern California", *Environ. Sci. Technol.*, 2005, *39* (16), pp 5940–5953.[3]

3. Warrick *et al.,* "River plume patterns and dynamics within the Southern California Bight", USC Sea Grant Publication AR07 USC, pages 215-236.[4]

These scientific papers provide a description of the scope and mechanisms for stormwater transport of sediment to the coastal ocean in Southern California that are typical of all stormwater discharges in the area.

I would like to highlight the five attached figures that I have extracted from the above-cited articles. All of these figures provide visual evidence of the significant transport of solids through the system, or the "carry through." The first two of these figures show satellite images of the Southern California coastline, including the San Pedro Harbor area, and the extent of sediment plumes that emanate from the coastline following certain storm events. The next three figures are based on actual measurements of the turbidity (a measure of suspended solids, including sediments, in water) of the sea water off of the coast of Southern California and demonstrate that sediments are present in the offshore waters following stormwater runoff.

Attachment A is a reproduction of Figure 3 from a study of plumes in the Southern California Bight by Professor Barbara Hickey of the University of Washington that was presented at the 5th California Islands Symposium (1999). It shows satellite images of sea surface turbidity for the Southern California Bight for downwelling conditions (onshore winds, February 24, 1998; upper panel) and upwelling conditions (offshore winds, February 26, 1998; lower panel) following high surface water runoff. Sea surface turbidity offshore of all the river estuaries is clearly visible in these satellite-derived images, including San Pedro Bay in the bottom right of the images.

Attachment B is a reproduction of Figure 3B from a paper in the journal Environmental Science and Technology by Ahn *et al.* (*Environ. Sci. Technol.*, 2005, *39* (16), pp 5940–5953) showing Aqua true color satellite imagery of stormwater runoff plumes along the San Pedro Shelf, California, with nominal spatial resolution of 250 m. The sea surface plume of turbidity emanating from LA Harbor is clearly evident following a large precipitation event (51 mm) on February 25-26, 2004. The visible plume of high turbidity water with an apparent origin at the LA and Long Beach Harbors stretches more than halfway to Catalina Island.

The vertical structure of these plumes is made evident in the work done by Warrick *et al* in their studies of river plumes in Southern California (Reference 3 above). In these studies, salinity and light transmission referred to as beam-c (a measure of turbidity) were measured at the sea surface and at

[3] Available at http://pubs.acs.org/doi/abs/10.1021/es0501464

[4] Available at http://www.usc.edu/org/seagrant/Publications/PDFs/AR07_215_236.pdf

depth. Because they involved actual measurements on site, these studies cannot provide the synoptic picture visible in satellite images, but they do provide details not possible in the satellite images.

Attachment C is a reproduction of Figure 6 from the Warrick publication and it describes the results of on-site studies of river plumes in the Southern California Bight. This figure shows surface patterns of salinity and beam-c following high stormwater discharges into LA Harbor on March 23, 2005. The upper image represents the salinity of the surface waters inside and well outside LA Harbor on the San Pedro Shelf. The lower image is the beam-c distribution and areas of high turbidity can be seen to correspond to areas of low salinity.

These figures show that river plumes spread on the surface of the ocean and carry sediment with them and, in particular, that this certainly occurs for the stormwater flows out of LA and Long Beach Harbors. The sediment gradually flocculates as the double layer surface charge on the sediment particles is compacted in the ion rich seawater, which allows the particles to coagulate and form settlable particles. Sediment deposition is therefore dependent on the mixing of the freshwater and seawater, but this mixing is strongly inhibited by the density difference between the freshwater and seawater. The studies by Warrick *et al*. provide further evidence of these mechanisms.

Attachment D, a reproduction of Figure 4 from the Warrick *et al.* publication, shows a three-dimensional representation of the vertical and horizontal salinity and turbidity patterns in Santa Monica Bay following a flood discharge from Ballona Creek. It can be seen that the low salinity and high turbidity patterns are very similar and are located in a surface layer that has spread over the ocean waters.

The sharpness of the vertical gradient between the fresh upper layer and lower saline layer (the pycnocline) is made evident in **Attachment E**, which is a reproduction of Figure 4 from the Warrick *et al.* publication. The figure shows measured vertical profiles of salinity and turbidity occurring 4 km offshore from the Tijuana River. It can be seen that the vertical mixing is strongly inhibited by the density gradient. The distributions of high turbidity and low salinity are very similar. Note that this figure also shows a layer of high turbidity water near the sea floor, which is typical of ocean waters where the turbulence stirs the bottom sediments. While these figures show the regionally relevant Ballona Creek and the Tijuana River, it can be expected that similar processes will occur with the stormwater discharges from the Dominguez Channel and Los Angeles and San Gabriel River estuaries and their outflow from the Harbors, as shown in Attachments B and C.

In summary, satellite images and sea surface observations show that massive fluxes of sediment are carried through Southern California river estuaries and into the open ocean by stormwater runoff. Ocean studies confirm that these surface sediment plumes are slowly mixed with the ocean waters beneath them. As a result, there is flocculation and deposition of the sediment over a sustained period after stormwater is released to the ocean. As demonstrated by the referenced studies, and as reflected in the RWQCB's own modeling (upon which the RWQCB relies for other purposes), much of the sediment that enters the Harbor system is transported through the system and eventually settles on the outer continental shelf, or is carried even further away.

Because the TMDL calculations ignore these sediment fluxes, the sediment "carry through," (to use Dr. Nye's words), the allocations in the TMDL are set at values that may be orders of magnitude too

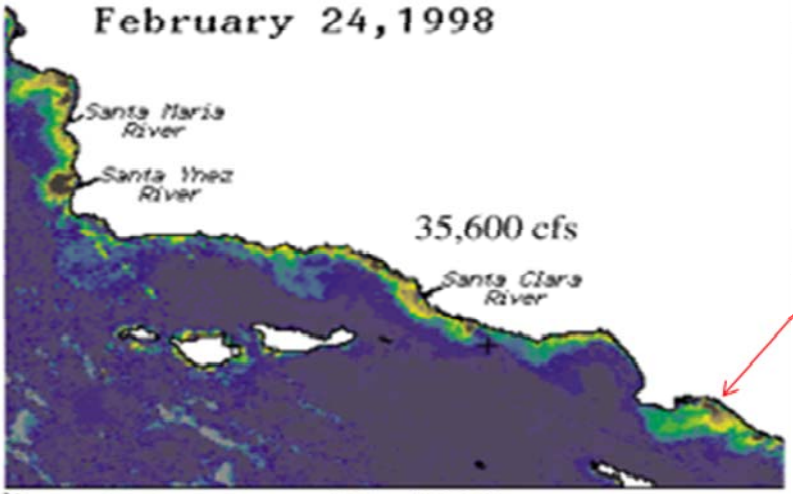
stringent. The TMDLs and allocations in the TMDL properly should be based on calculations of the assimilative capacity of the system that includes consideration of sediment, and associated compound mass, that passes out of the Los Angeles and Long Beach Harbors.

Sincerely,

E. John List, Ph.D., P.E.
Principal Consultant

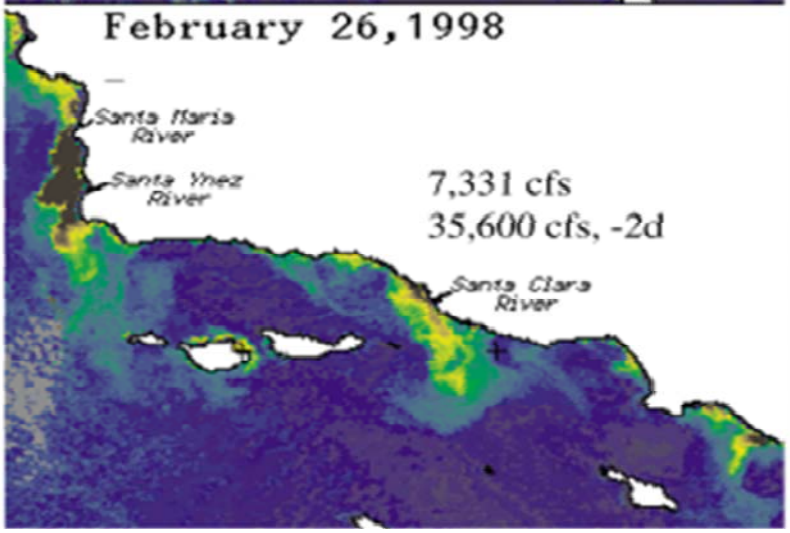
Attachments

cc: Charlie Hoppin, Chair, State Water Resources Control Board
Frances Spivy-Weber, Vice Chair, State Water Resources Control Board
Tam Doduc, Member, State Water Resources Control Board
Thomas Howard, Executive Director, State Water Resources Control Board
Dr. Peter Kozelka, United States Environmental Protection Agency, Region 9



ATTACHMENT A

San Pedro Bay



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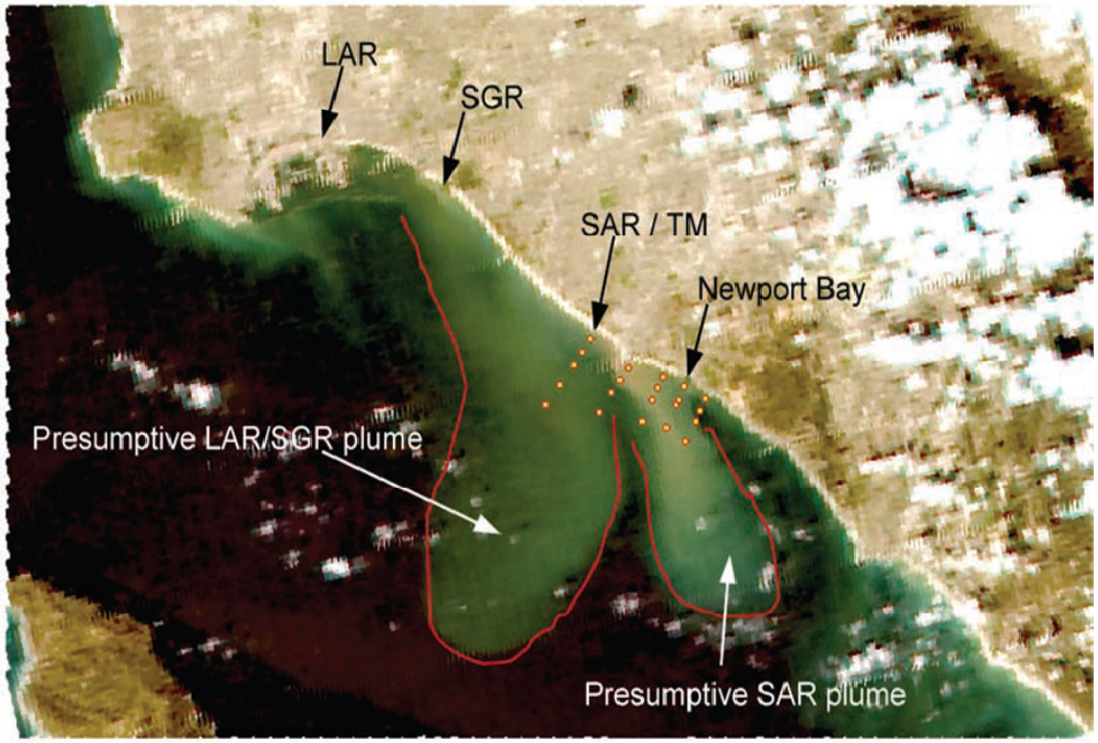
http://pubs.acs.org/doi/abs/10.1021/es0501464

ATTACHMENT B

(B) 27 Feb. at 12:35



Coastal Water Quality Impact of Stormwater Runoff from an Urban Watershed in Southern California. From Ahn et al --*Environ. Sci. Technol.*, **2005**, *39* (16), pp 5940–5953

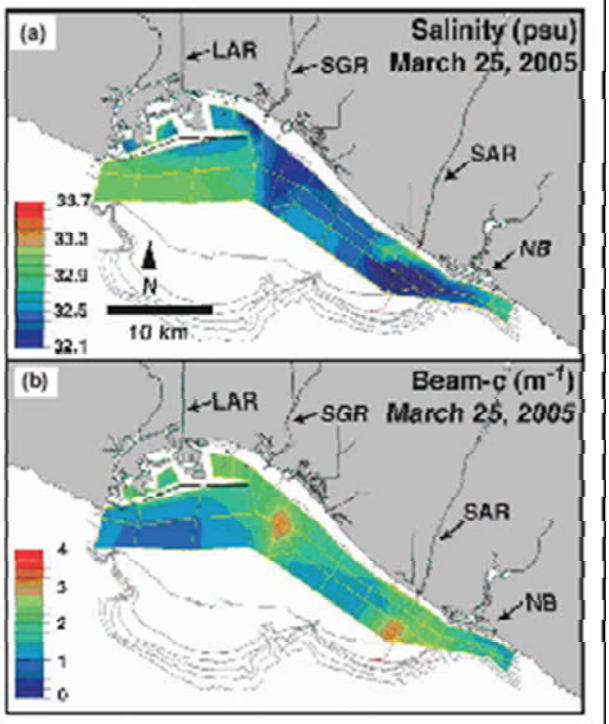


Figure 6. Surface measurements of salinity and beam-c data from the San Pedro Bay on March 25, 2005. Linear interpolation has been used to estimate parameter values between stations, which are located at the intersections of the yellow lines. LAR = Los Angeles River; SGR = San Gabriel River; SAR = Santa Ana River; and NB = Newport Bay.

ATTACHMENT C

River plume patterns and dynamics within the Southern California Bight

Jonathan A. Warrick1, Paul M. DiGiacomo2, Stephen B. Weisberg, Nikolay P. Nezlin, Michael J. Mengel3, Burton H. Jones4, J.Carter Ohlmann5, Libe Washburn5, Eric J. Terrill6 and Katie L. Farnsworth1

ATTACHMENT D

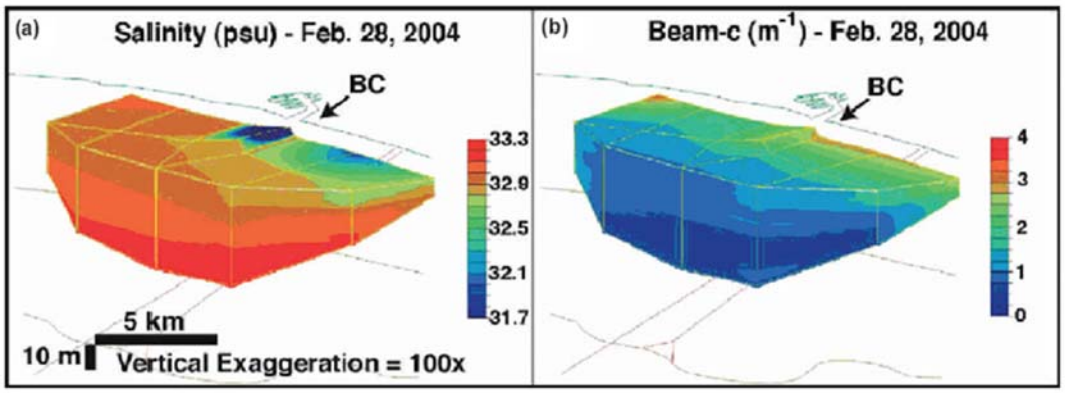


Figure 5. Three-dimensional presentation of salinity and beam-c data offshore of Ballona Creek (BC) showing the freshened and turbid river plume waters along the sea-surface. Linear interpolation has been used to estimate parameter values between stations, which are shown with vertical yellow lines and line intersections along the water surface.

From: River plume patterns and dynamics within the Southern California Bight
Jonathan A. Warrick1, Paul M. DiGiacomo2, Stephen B. Weisberg, Nikolay P. Nezlin, Michael J. Mengel3, Burton H. Jones4, J.Carter Ohlmann5, Libe Washburn5, Eric J. Terrill6 and Katie L. Farnsworth1

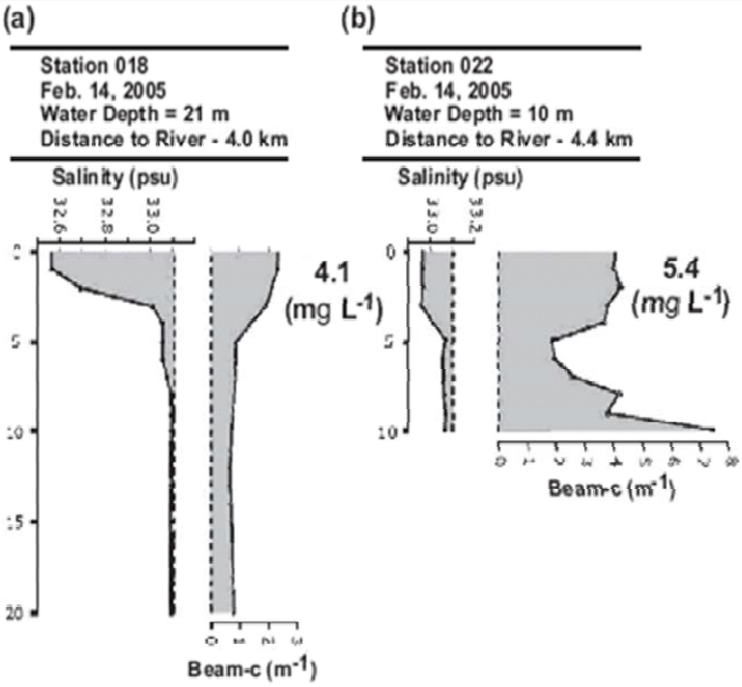


Figure 4. Salinity, beam-c and TSS data from CTD casts taken on February 14, 2005 offshore of the Tijuana River. TSS concentrations for 1 m water depth samples. Dashed lines represent reference levels of 33.1 psu salinity and 0 m^{-1} beam-c.

ATTACHMENT E

River plume patterns and dynamics within the Southern California Bight

Jonathan A. Warrick1, Paul M. DiGiacomo2, Stephen B. Weisberg, Nikolay P. Nezlin, Michael J. Mengel3, Burton H. Jones4, J.Carter Ohlmann5, Libe Washburn5, Eric J. Terrill6 and Katie L. Farnsworth1

Exhibit F

RIVER DISCHARGE PLUMES IN THE SANTA BARBARA CHANNEL

Barbara M. Hickey

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ABSTRACT

Satellite-derived images of ocean sea surface turbidity and in situ measurements of ocean salinity demonstrate that large areas of the coastal zone in southern California (as much as 8,000 km) can be impacted by discharge from coastal rivers. Such river plumes carry both dissolved and suspended material from California watersheds into the coastal ocean. River plumes can also substantially affect coastal current patterns, particularly in the upper ~5 m of the water column. Typical plumes from the Santa Clara River region, for example, cover a surface area of about 500 km^2 extending up to 50 km into the Santa Barbara Channel under northward regional wind conditions or 70 km southeast into the Santa Monica Basin under southward regional wind conditions. Individual plumes persist for about two to five days. Southward and offshore surface flows during upwelling-favorable wind conditions tend to spread plumes offshore of the river mouth. For example, the plume from the Santa Clara and Ventura rivers in the eastern Santa Barbara Channel frequently reaches the eastern Channel Islands during the strong upwelling events that generally follow major storms. Similarly, in high discharge years, the western Channel Islands are impacted by river discharge plumes that originate north of Point Conception.

INTRODUCTION

River plumes provide a primary mechanism by which material from coastal watersheds and storm runoff is distributed through the coastal zone. The presence of a river plume in a coastal region can also significantly change regional flow patterns, particularly in the upper ~5 m of the water column. Previous studies in the Southern California Bight have not addressed the structure and temporal variability of such features: river plumes occur only during major storms when measurements are difficult to obtain; and they occupy the shallowest portion of the coastal ocean, which is difficult to sample. This paper describes the spatial structure and temporal variability of river plumes that impact the Santa Barbara Channel. A complete discussion of this topic for the entire Southern California Bight is given in Hickey and Kachel (1999).

Significant progress has been made recently in understanding circulation in the Santa Barbara Channel (Hendershott and Winant 1996; Harms and Winant 1998). The large scale circulation patterns described by these studies are a result of wind, wind curl and pressure gradients along the coast. In the upper 5 m of the water column, direct wind forcing (frictional currents) is also important.

River plumes, when they occur, contribute additional complexity to the resulting circulation patterns. When coastal rivers discharge into the coastal ocean, they form a buoyant plume governed by nonlinear dynamics. In the northern hemisphere, and in the absence of ambient currents, such plumes bend toward the right on entering the ocean (e.g., model results in Chao 1988; Kourafalou et al. 1996). The region in which the plume turns is highly nonlinear. Farther downstream, the plume reattaches to the coast to form a (linear) coastal current that hugs the coastline. In the presence of ambient currents, the plume may bend to the left after it leaves the river mouth (e.g., the Columbia River plume in summer); or it may remain adjacent to the coast if the prevailing coastal flow is northward. River plumes are particularly sensitive to changes in local wind conditions, which directly affect flow in the surface Ekman layer (e.g., model results in Chao 1988; Kourafalou et al. 1996). This sensitivity has been demonstrated in the Columbia plume, which moves onshore or offshore as the wind changes direction from northward to southward on scales of two to three days (Hickey et al. 1998). The response time of the Columbia plume to such changes is less than six hours (Hickey et al. 1998). The spatial structure of surface currents during large storms, when plumes occur, is of particular consequence during oil spills and other marine emergencies.

During winter and spring seasons when the principal river discharge events occur, winds with a northward component are generally associated with storms, increased rainfall and northwestward to westward surface flow in the Santa Barbara Channel ("upcoast" flow) adjacent to the coast. Winds with a southward component during those seasons are generally associated with good weather, upwelling of cold water adjacent to the coast, and eastward to southeastward ("downcoast" flow) surface currents near the coast (Hickey 1992; Harms and Winant 1998).

MATERIALS AND METHODS

Time series of daily mean river discharge as well as suspended sediment yield for selected rivers were obtained from the United States Geological Survey (USGS).

Discharge data from 1998 were provided by the United Water Conservation District.

Wind data at a centrally located buoy (National Data Buoy Center Buoy 46025) were obtained from the "Data Zoo" maintained by Scripps Institution of Oceanography (SIO). Buoy location is shown in Figure 1. Comparison with wind data at other sites (Hickey 1992) as well as analysis of wind patterns within the Bight (Winant and Dorman 1997) show that winds from this site are sufficient to provide a general indication of environmental conditions in the nearshore Southern California Bight.

Satellite images of sea surface temperature, visible imagery, and surface albedo were obtained for selected dates from Ocean Imaging, Inc. Data have a nominal spatial resolution of 1 km. A combination of the first two satellite channels (detecting red and near infrared light, respectively) was used by Ocean Imaging, Inc. to construct a measure of sea surface turbidity using the algorithm of Stumpf and Pennock (1989).

RESULTS

Three major rivers (the Santa Clara and Ventura, the Santa Maria, and the Santa Ynez) have discharge plumes that can affect the Santa Barbara Channel (Figure 1). These discharge plumes are easily identified in satellite-derived images of sea surface turbidity (Hickey and Kachel 1999). The plume from the Santa Clara and Ventura rivers discharges into the channel near its eastern end. Roughly one-third of the plume volume originates from the Ventura River; the remaining two-thirds originates from the Santa Clara River (Hickey and Kachel 1999). The plume from the Santa Maria and Santa Ynez rivers enters the channel from its western end during periods of strong coastal upwelling.

River discharge data demonstrate that major floods from rivers in Southern California occur every few years (30% of the years since 1943) primarily during El Niño conditions (Hickey and Kachel 1999). During flood years, periods of high discharge generally occur for two to ten days on several occasions between January and April. During each storm, river discharge begins abruptly and tapers off over several days (Figure 2). Most rivers flood at roughly the same time. During the strongest El Niños, discharge can remain high for several weeks (Hickey and Kachel 1999). Between flood years, and during summer and fall in all years, southern California rivers are essentially dry.

During flood years, millions of tons of material can be delivered to the Southern California Bight in a very short period of time (one to two days), exceeding the mean annual output of the largest river on the U.S. west coast (the Columbia) (Figure 2 for 1993; see Hickey and Kachel (1999) for additional years. This material is derived from the river drainage basin, including agricultural lands, storm sewers, etc. Pollutants such as pesticides (e.g., DDT), PCB, and oil

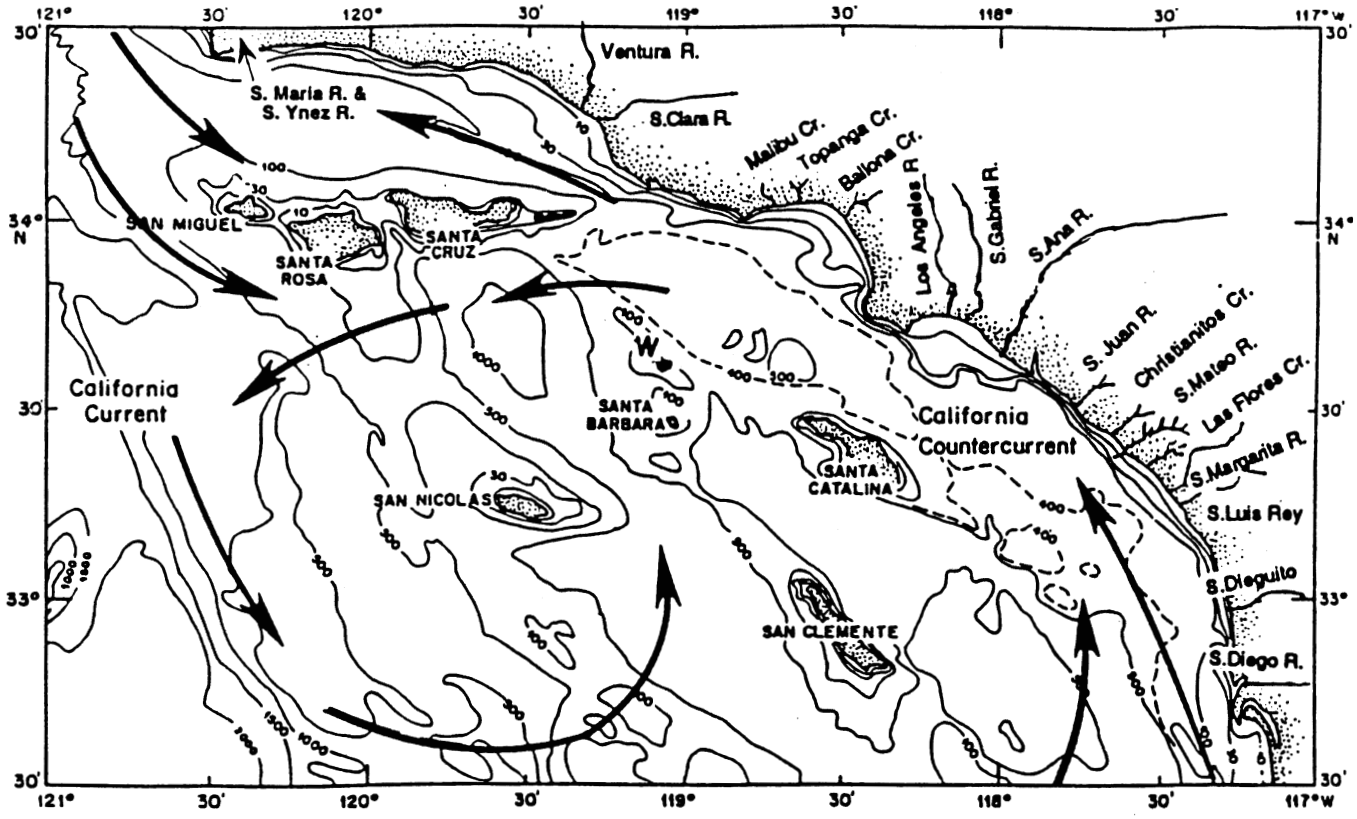

Figure 1. Location of gauged rivers in the Southern California Bight relative to coastline orientation and bottom topography. A schematic circulation pattern for large scale flow in the Bight near the sea surface is superimposed on the topography (from Hickey 1992).

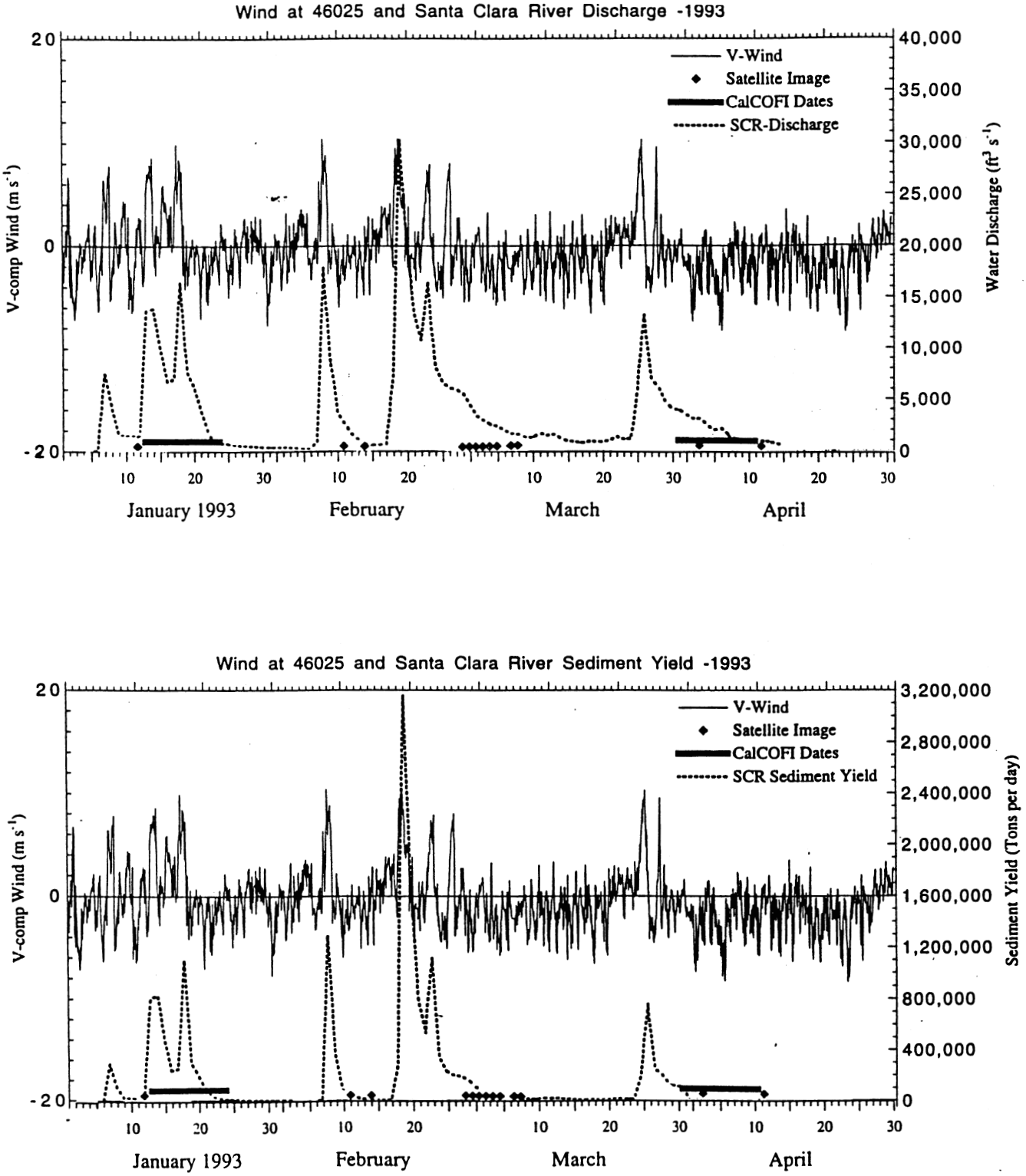

Figure 2. North–south component of wind and river discharge (upper panel) and wind and sediment yield (lower panel) during periods when satellite data were collected. Time is given in Pacific Standard Time. Dates of satellite images are shown as symbols along the x-axis. In general, southward wind is indicative of upwelling conditions and northward wind is indicative of downwelling conditions.

are transferred from their point of origin or temporary storage to coastal marshes or to the ocean.

The plume from the Santa Clara and Ventura rivers has two dominant orientations: upcoast tending or downcoast tending. Upcoast plumes are generally associated with the occurrence of upcoast winds, hence downwelling and onshore flow that tends to keep plumes confined to the coast (Figure 3, upper panel). Downcoast plumes are generally associated with downcoast winds, hence upwelling and offshore flow that tends to spread plumes off the coast and

to the south or southeast (Figure 3, lower panel). For both types of plumes, spatial structure is much less variable than the environmental conditions or recent and ongoing river discharge rate (Hickey and Kachel 1999). This suggests some limitation to growth of turbid plumes. In the images collected (winter to spring 1991, 1993, 1995, 1998), turbid plumes from the Santa Clara and Ventura rivers extended a maximum distance of about 60 km westward into the Santa Barbara Channel or 110 km southeast into the Santa Monica Basin (Hickey and Kachel 1999). Downcoast tending plumes are typically almost twice as long and more than twice as wide as the upcoast plumes, likely a result of enhancement of wind-driven flow as the Ekman layer is compressed by plume stratification. Thus, upwelling conditions are very effective at spreading fine-grained material away from river mouths. For example, the plume from the Santa Clara and Ventura rivers can envelop Anacapa Island during upwelling conditions following major floods.

Each major storm in southern California is generally followed by a strong upwelling event. During these upwelling events, turbid material from flooding rivers north of Point Conception (principally the Santa Maria and the Santa Ynez) enter the Bight from the west where they frequently envelop the western Channel Islands (Figure 3, lower panel). The intrusion of turbid water from north of Point Conception into the Santa Barbara Channel is consistent with silt content in surface sediments (Thornton 1984) as well as light transmission surveys (Drake 1972). Thus, upwelling events following major floods may be more efficient than actual storm conditions at moving finer grained particles away from river mouths along the coast and out to the Channel Islands.

The volume of freshwater discharged into the ocean during a typical five-day flood in the Santa Barbara Channel would occupy a 2 m high column of water over an area of about 10 to 100 km^2. The volume impacted by the discharge can be many times greater than the initial discharge volume. Lower salinity areas at the sea surface as great as 8,000 km^2 have been observed off the southern California coast during periods of highest discharge (Hickey and Kachel 1999). On one occasion, fresher water in the Santa Clara River region occupied an area of about 2,000 km^2. More typical low salinity areas in the Santa Clara region covered a surface area of about 500 km^2. Areas covered by turbid plumes from the Santa Clara River ranged from 100 to 1,500 km^2, although an area of about 3,000 km^2 was covered by the plume during strong upwelling following closest in time to a very high discharge event. Depth strata in which salinity is clearly influenced by river discharge range from the sea surface to 10 or 20 m from the surface (Hickey and Kachel 1999).

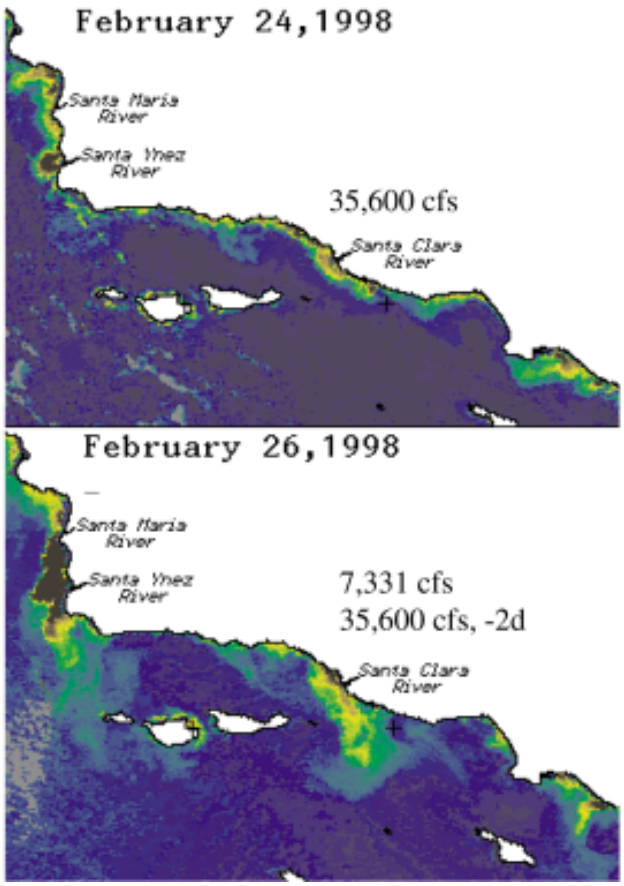

Figure 3. Satellite images of sea surface turbidity for the Southern California Bight for downwelling conditions (February 24, 1998; upper panel) and upwelling conditions (February 26, 1998; lower panel). Discharge from the Santa Clara River on the image dates and the value and date of any recent discharge maximum (subtract the number of days given from the image date) are listed. Turbidity scales are relative only.

DISCUSSION

This paper uses satellite-derived images of sea surface turbidity to provide information on the spatial structure and temporal variability of river plumes in and near the Santa Barbara Channel. Such information is important for providing an accurate picture of surface currents during storms on the California coast as well as for understanding how material in coastal watersheds is distributed to offshore coastal regions.

Results demonstrate that river plumes can readily distribute this material throughout a large portion of the coastal zone. During a particular flood, large particles may be deposited in the vicinity of the river mouth. Finer particles can be carried tens and hundreds of kilometers from the river mouth. Some of the fine material may form aggregates and settle more rapidly. While the particles are in the upper water column interactions with the biota can occur: particles may be consumed by marine animals and utilized by plants. These in turn are ingested so that any pollutants move up the food chain to birds and mammals. Marine birds, in particular, are often found at density fronts near the edges of river plumes because water convergence at the front increases food density.

Because sediment falls from the water column, the depth and area influenced by river turbidity may differ from that of water properties. Area influenced at the sea surface is likely smaller for turbidity than for salinity. However, turbidity could affect a larger area in the water column than salinity at deeper depths and the area influenced might be expected to increase with depth. Areas covered by turbid plumes shown in the majority of available satellite images may underestimate areas that would be covered at peak flood. On the other hand, fallout of particulates from the plume, as well as processes such as flocculation, which accelerate fallout rates (Baker and Hickey 1986), appears to limit the size of turbid plumes.

The greatest impact on the Channel Islands likely occurs during coastal upwelling, which spreads river discharge plumes from the eastern channel offshore toward Anacapa Island, and spreads discharge plumes from north of Point Conception into the western channel entrance where they encounter the western Channel Islands. Upwelling conditions cause plumes to thin and spread out so that the total surface area is many times that observed during the actual storms responsible for the rainfall that caused the river plumes.

Impacts on flow fields cannot be ascertained from satellite imagery. However, results from other studies (e.g., Hickey et al. 1998) and model results (e.g., Kourafolou et al. 1996) suggest that effects in the upper 10 m of the water column are significant. Current speeds of 10 to 20 cm s^{-1} above ambient flow would not be unreasonable. Moreover, current direction in the vicinity of the plume would likely be altered: for example, currents in the upper 5 to 10 m of the water column a few kilometers from a river mouth would tend to parallel density contours and be concentrated along density fronts. Hence, particularly during strong upwelling, current patterns in the upper water column might differ significantly from those observed in the absence of river plumes.

ACKNOWLEDGMENTS

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Exhibit G

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Coastal Water Quality Impact of Stormwater Runoff from an Urban Watershed in Southern California

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Field studies were conducted to assess the coastal water quality impact of stormwater runoff from the Santa Ana River, which drains a large urban watershed located in southern California. Stormwater runoff from the river leads to very poor surf zone water quality, with fecal indicator bacteria concentrations exceeding California ocean bathing water standards by up to 500%. However, cross-shore currents (e.g., rip cells) dilute contaminated surf zone water with cleaner water from offshore, such that surf zone contamination is generally confined to <5 km around the river outlet. Offshore of the surf zone, stormwater runoff ejected from the mouth of the river spreads out over a very large area, in some cases exceeding 100 km^2 on the basis of satellite observations. Fecal indicator bacteria concentrations in these large stormwater plumes generally do not exceed California ocean bathing water standards, even in cases where offshore samples test positive for human pathogenic viruses (human adenoviruses and enteroviruses) and fecal indicator viruses (F^+ coliphage). Multiple lines of evidence indicate that bacteria and viruses in the offshore stormwater plumes are either associated with relatively small particles (<53 μm) or not particle-associated. Collectively, these results demonstrate that stormwater runoff from the Santa Ana River negatively impacts coastal water quality, both in the surf zone and offshore. However, the extent of this impact, and its human health significance, is influenced by numerous factors, including prevailing ocean currents, within-plume processing of particles and pathogens, and the timing, magnitude, and nature of runoff discharged from river outlets over the course of a storm.

Introduction

Oceans adjacent to large urban areas, or "urban oceans", are the final repositories of pollutants from a myriad of point and nonpoint sources of human waste (*1*). Pollutants are transported to the urban ocean by surface water runoff (*1*−*4*), discharge of treated sewage through submarine outfalls (*5*), wet and dry deposition of airborne pollutants (*6*), and submarine discharge of contaminated groundwater (*7*). Until recently, effluent from sewage treatment plants was often the primary source of urban coastal pollution, including nutrients, pathogens, pesticides, and heavy metals (*8*). However, pollutant loading from many sewage treatment plants has declined over the past several decades because of improvements in civil infrastructure (e.g., separation of the storm and sanitary sewer systems to prevent combined sewer overflows), pollutant source control, and disposal/treatment technology (*9*). As a result, surface water runoff, in many cases, has supplanted sewage treatment plants as the primary source of pollutant loading to the urban ocean (*3*, *10*).

The focus of this study is the coastal water quality impact of surface water runoff during storms, or "stormwater runoff", from an urban watershed in southern California. The study was motivated by several considerations. First, beneficial use designations for the coastal ocean in southern California apply year-round and, consequently, watershed managers are legally required to develop stormwater management plans for reducing wet-weather impairments of the coastal ocean (*11*). The impact of stormwater runoff on coastal water quality is of particular concern in arid regions such as southern California because, on an annual basis, a large percentage (>99.9% according to Reeves et al. (*2*) and >95% according to Schiff et al. (*10*)) of the surface water runoff and associated pollution flows into the ocean during a few storms in the winter. Second, while recreational use of the coastal ocean in southern California is lighter in the winter, compared to the summer, winter ocean recreation is still very common, particularly among surfers who surf the large waves that often accompany storm events (R. Wilson, personal communication). Third, to the extent that particles in stormwater runoff are associated with pathogens and other contaminants, their discharge to the ocean during storms may serve as a source of near-shore pollution that persists long after the storm season is over (*10*, *12*). Finally, in many urban watersheds in southern California and elsewhere, the flow of stormwater runoff is highly regulated by civil infrastructure (e.g., dams) designed to minimize flood potential and maximize water reclamation. As will be demonstrated later in this paper, the regulated nature of stormwater runoff implies that the ocean discharge of stormwater runoff from urban watersheds can occur days after the cessation of rain, when the potential for human exposure to pathogens by marine recreational contact is significant.

This paper describes how stormwater runoff from several major rivers in southern California, with particular focus on the Santa Ana River in Orange County, impacts coastal water quality, as measured by turbidity, particle size spectra, total organic carbon, fecal indicator bacteria, fecal indicator viruses, and human pathogenic viruses. The present study is unique in the combination of data resources utilized, including data and information from routine surf zone water quality and wave field monitoring programs, an automated in-situ ocean observing sensor, shipboard sampling cruises, and satellite sensors. Further, this is the first wet weather study to examine the linkage between water quality in the surf zone, where routine monitoring samples are collected

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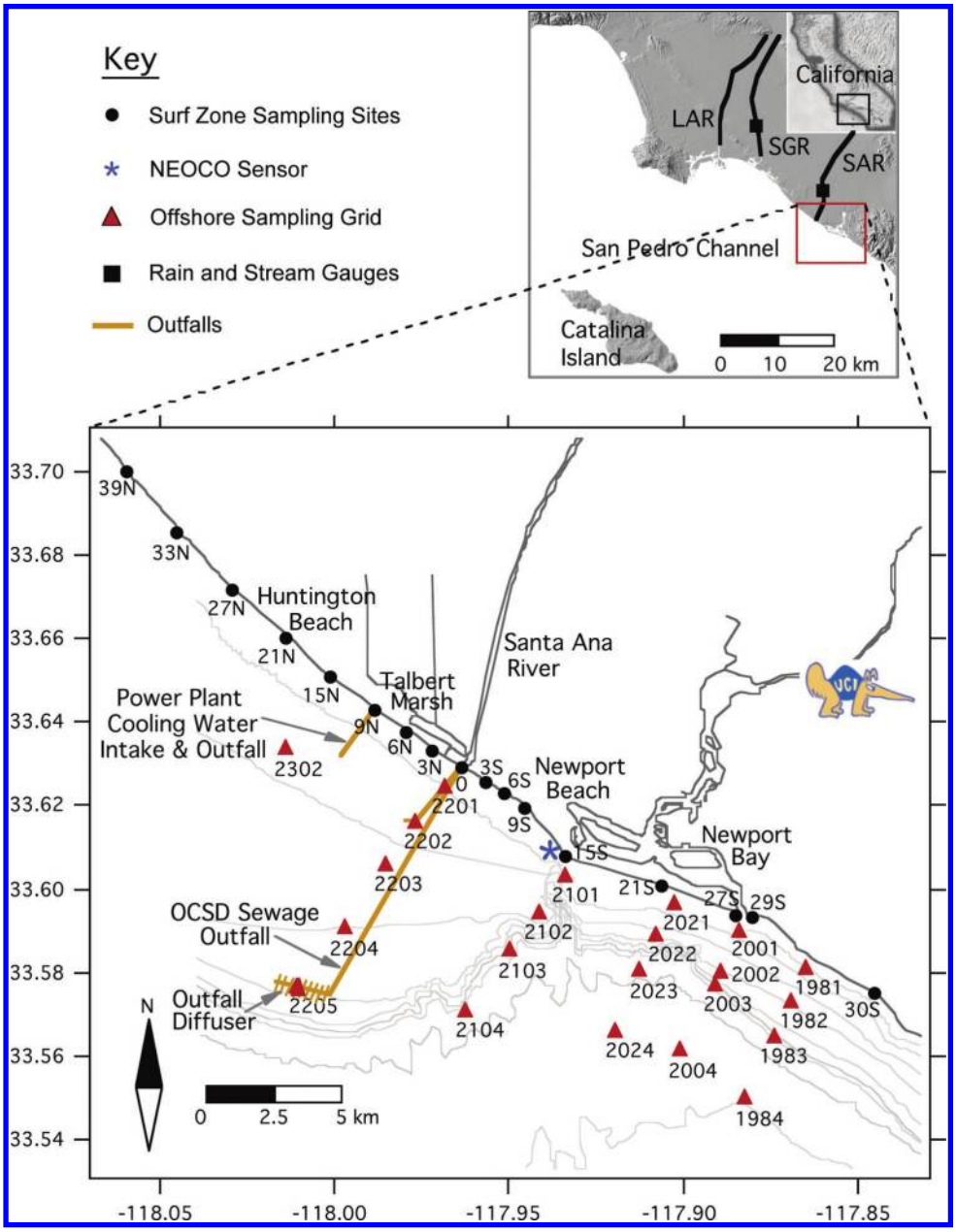

FIGURE 1. Map showing location of field site and sampling sites in the surf zone and offshore. Also shown are the locations of the NEOCO sensor on the end of the Newport Pier and the rain and stream gauges located on the Santa Ana River and the San Gabriel River. Abbreviations are Los Angeles River (LAR), San Gabriel River (SGR), Santa Ana River (SAR), Orange County Sanitary District (OCSD), and University of California, Irvine (UCI).

and most human exposure occurs, and water quality offshore of the surf zone. The work described in this study was carried out in parallel with a watershed-focused study that examined the spatial variability of fecal indicators, and the relationship between suspended particle size and fecal indicators, in storm runoff from the Santa Ana River watershed (*13*). Background information is available elsewhere on coastal water quality impairment at our Orange County field site (*2*, *14*−*18*) and the transport and mixing dynamics of sediment plumes as they flow into the coastal ocean from river outlets in southern California (*4*, *19*, *20*).

Materials and Methods

Rainfall and River Discharge. Weather information and Next Generation Radar (NEXRAD) images for planning the field studies and interpreting rainfall patterns were obtained online from the National Weather Service (http://www.nwsla.noaa.gov/). Precipitation and stream discharge data were obtained at two sites, one located where the Santa Ana River crosses 5th Street in the City of Santa Ana and another located where the San Gabriel River crosses Spring Street in the City of Long Beach (black squares in inset, Figure 1). These data were obtained, respectively, from the U.S. Army Corps of Engineers and the Los Angeles County Department of Public Works. Both of these gauge sites are located relatively close (within 11 km) to the rivers' respective ocean outlets, and hence streamflow measured at these sites will likely make its way to the ocean.

Surf Zone Measurements: NEOCO Data. Time series of water temperature, conductivity, chlorophyll, and water depth were obtained from an instrument package deployed at the end of the Newport Pier, where the local water depth is between 6.5 and 9 m (blue star in Figure 1). This instrument package is part of a recently deployed network of coastal

sensors in southern California called the Network for Environmental Observations of the Coastal Ocean (NEOCO). The NEOCO sensor package contains an SBE-16plus CTD (Sea-Bird Electronics, Inc., Bellevue, WA) and a Seapoint Chlorophyll Fluorometer (Seapoint Sensors, Inc.). These instruments are mounted on a pier piling at a depth of approximately 1 m (below mean lower low water) and are programmed to acquire data at a sampling frequency of 0.25 min^{-1}.

Surf Zone Measurements: Fecal Indicator Bacteria and Breaking Waves. The concentration of fecal indicator bacteria in the surf zone was measured at 17 stations (black circles along shoreline in Figure 1) by personnel at the Orange County Sanitation District (OCSD). The stations are designated by OCSD according to their distance (in thousands of feet) north or south of the Santa Ana River outlet (e.g., station 15N is located approximately 15 000 ft, approximately 5 km, north of the Santa Ana River outlet). Water samples were collected 5 days per week (not on Friday and Sunday) from 5:30 to 10:00 local time at ankle depth on an incoming wave, placed on ice in the dark, and returned to the OCSD (Fountain Valley, CA) where they were analyzed within 6 h of collection for total coliform (TC), fecal coliform (FC), and enterococci bacteria (ENT) using standard methods 9221B and 9221E and EPA method 1600, respectively. Results are reported in units of colony forming units per 100 mL of sample (CFU/100 mL). Wave conditions, including both the direction and height of breaking waves, were recorded by lifeguards at the Newport Beach pier (near surf zone station 15S, Figure 1) twice per day, once at 7:00 and again at 14:00 local time.

Offshore Measurements: Satellite Ocean Color Imagery. The satellite images used in this study were collected by NASA's Moderate-Resolution Imaging Spectroradiometer (MODIS) instruments. These instruments operate onboard two near-polar sun-synchronous satellite platforms orbiting at 705 km altitude: Terra (since February 24, 2000) and Aqua (since June 24, 2002). Terra passes across the equator from north to south at ~10:30 local time, while Aqua passes the equator south to north at ~13:30 local time. As such, all the images were acquired within 2 h before or after local noon or between 18:00 and 22:00 UTC. The MODIS sensors collect data in 36 spectral bands, from 400 to 14 000 nm. We utilized bands 1 (250-m spatial resolution, 620−670 nm), 3, and 4 (500-m resolution, 459−479 and 545−565 nm, respectively) to produce "true color" (i.e., RGB) images, with band 1 used for the red channel, band 4 for the green channel, and band 3 for the blue channel. Using a MATLAB program, the 500-m green (band 4) and blue (band 3) monochrome channels were "sharpened" to 250-m resolution using fine details from the higher resolution red channel (band 1). Then, the contrast of each of these monochrome channels was increased to emphasize maximum details in the coastal ocean region of interest. Finally, all three monochrome channels (i.e., red, green, and blue) were combined to form a single true color image. In all, 16 satellite images from February 23 to March 5 were acquired and processed for this study; four of them were selected as most illustrative, on the basis of their quality and observed features. The timing of these satellite acquisitions relative to the storms and sampling periods is indicated at the top of Figure 2.

Offshore Measurements: Sampling Cruises. The offshore monitoring grid (red triangles in Figure 1) was sampled during three separate cruises on February 23, February 28, and March 1, 2004, coinciding with a sequence of storm events in late February 2004. Table 1 provides a summary of activities performed during each cruise. A short description of the offshore sampling and analysis protocols is presented here; details can be found in the Supporting Information for this paper. All offshore water samples were analyzed for salinity and fecal indicator bacteria, specifically, total coliform (TC), *Escherichia coli* (EC, a subset of FC), and enterococci bacteria (ENT), using the defined substrate tests known commercially as Colilert-18 and Enterolert (IDEXX, Westbrook, ME) implemented in a 97-well quantitray format; results are reported in units of most probable number of bacteria per 100 mL of sample (MPN/100 mL). A subset of the offshore water samples was analyzed for total organic carbon (TOC) by U.S. EPA Method 415.1, fecal indicator viruses (F^+ coliphage) by a two-step enrichment method (U.S. EPA Method 1601), and human pathogenic viruses (human adenovirus and human enterovirus) by real-time quantitative polymerase chain reaction (Q-PCR), nested PCR, and reverse-transcriptase (RT)-PCR using published protocols (*21*−*25*). Details on the PCR protocols used here can be found in the Supporting Information for this paper.

Coincident with the collection of the offshore water samples, temperature, particle size spectra, and light transmissivity were measured using an LISST-100 (laser in situ scattering and transmissometry) analyzer (Sequoia Scientific, Inc., Bellevue, WA). The LISST-100 estimates the particle volume per unit fluid volume (ΔV) resident in 32 logarithmically spaced particle diameter bins ranging in size from d_p = 2.5 to 500 μm. At least 10 replicates of the particle size spectra were collected at each offshore station. Following the recommendation of Mikkelsen (*26*), ΔV was taken as the median of all replicate measurements. The LISST-100 data are presented in this paper in one of three ways: (1) particle size spectra represented by plots of $\Delta V/\Delta \log d_p$ against log d_p, (2) the number of particles per unit fluid volume or total number concentration (TNC), and (3) the number-averaged particle size, $\bar{d}$. The last two parameters were computed from the particle size spectra as follows (*26*, *27*):

$$\mathrm{TNC} = \sum_{i=1}^{32} \frac{6\Delta V_i}{\pi d_{p,i}^{\ 3}} \tag{1a}$$

$$\bar{d} = \sqrt[3]{\frac{6}{\pi}\frac{\sum_{i=1}^{32}\Delta V_i}{\mathrm{TNC}}} \tag{1b}$$

Results and Discussion

Rainfall and River Discharge. Over the period of study (February 18 through March 3, 2004), four rain events were recorded by the rain gauge on the Santa Ana River in the City of Santa Ana (black curve, top panel, top axis, Figure 2). The first event accumulated 16.0 mm of rain in the afternoon of February 21 (RE_1 in Figure 2), the second event accumulated 23.4 mm of rain in the afternoon of February 22 (RE_2), the third event accumulated 51.3 mm of rain in the evening of February 25 (RE_3), and the fourth event accumulated 6.8 mm of rain in the evening of March 1 (RE_4). The rain gauge located on the San Gabriel River in the City of Long Beach did not record RE_2 but recorded a fifth rain event on February 18 (red curve, top panel, top axis, Figure 2). The difference in rainfall recorded at the Santa Ana River and the San Gabriel River sites is a consequence of the spatial variability of rainfall near the coast (see Figures S1 and S2, Supporting Information, for NEXRAD maps acquired during RE_1 and RE_2). Records of stream discharge (in units of m^3/s) at the Santa Ana River and the San Gabriel River sites are also quite different (black and red curves, top panel, bottom axis, Figure 2). While rainfall and stream discharge are coupled at the San Gabriel River site (i.e., stream discharge increases shortly after locally recorded rain events, compare set of red curves in top panel, Figure 2), rainfall and stream discharge are frequently uncoupled at the Santa Ana River site. For example, the Santa Ana River discharge events DE_3 and DE_4 do not obviously correlate with records of local rainfall. Instead, these two discharge events can be traced to stormwater runoff generated from inland regions of the Santa Ana River watershed

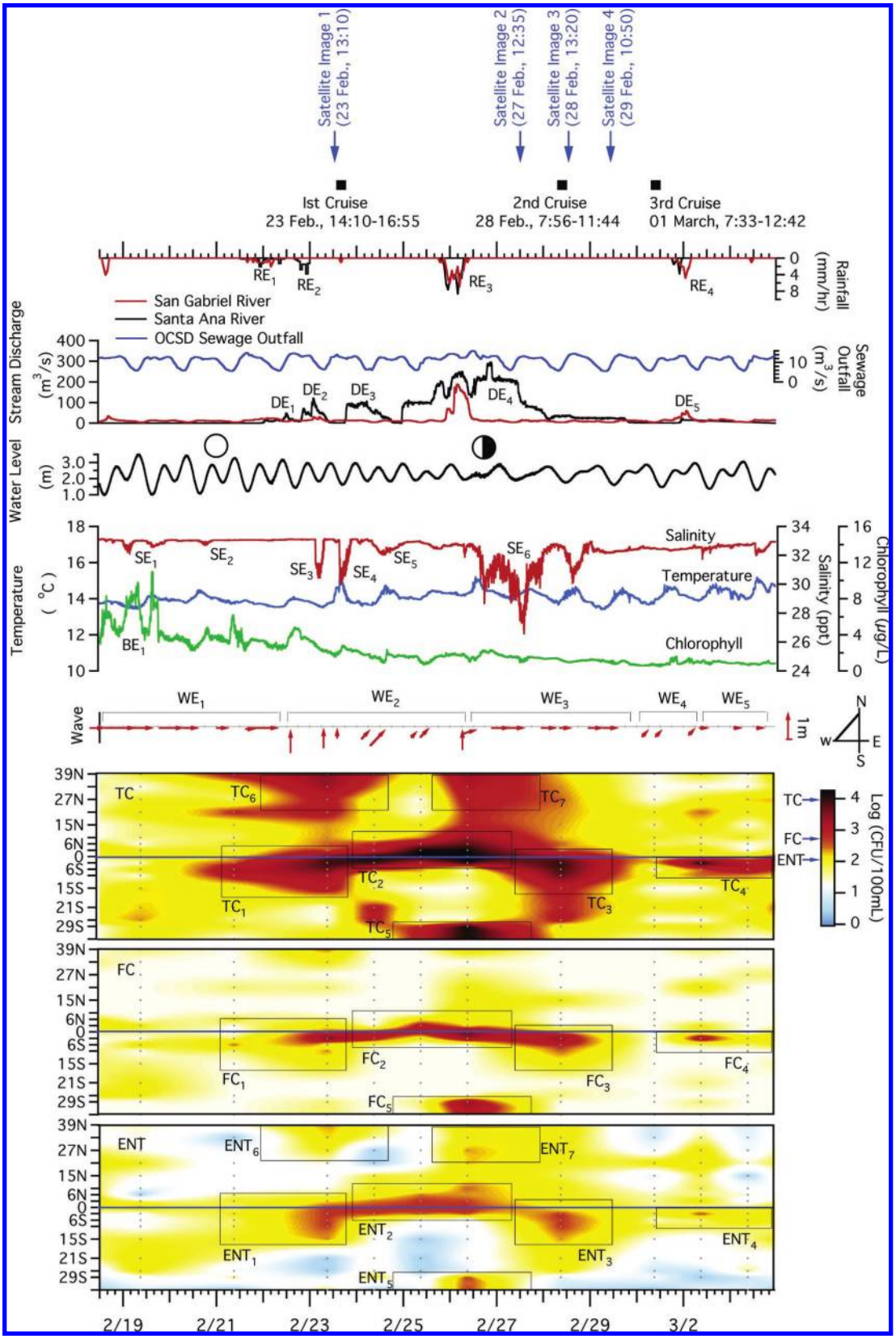

FIGURE 2. Time series measurements of rainfall, stream discharge at the Santa Ana River and San Gabriel River, and discharge of treated sewage from the OCSD outfall (top panel); water level, salinity, temperature, and chlorophyll measured at the NEOCO sensor (second and third panels); the direction and height of breaking waves at the Newport Beach Pier (fourth panel); and the concentration of fecal indicator bacteria in the surf zone (color contour plots, fifth through seventh panels). Shown at the top of the figure is the timing of the satellite images (blue lettering) and the offshore sampling cruises (black squares).

that was released from inland dams after the cessation of rain (*13*). For comparison, we have also included in the plot hourly volume discharge records (unit of m^3/s, blue curve, top panel, Figure 2) of treated sewage discharged from the Orange County Sanitation District (OCSD) sewage outfall (courtesy of OCSD).

TABLE 1. Summary of Analyses Performed during the Sampling Cruises

sampling parameters	methods	number of offshore sites sampled		
		February 23, 2004	February 28, 2004	March 1, 2004
conductivity[a]	Thermo Orion162A or CTD (SBE-32)	20	21	21
temperature[b]	thermocouple w/ LISST-100 or CTD (SBE-32)	20	21	21
total coliform, *Escherichia coli*, enterococcus[c]	Colilert and Enterolert (IDEXX)	20 (+2 sets of fractionated samples)	21 (+6 sets of fractionated samples)	21
total organic carbon[d]	EPA 415.1	17 (+2 sets of fractionated samples)		
human adenoviruses & enteroviruses[5]	nested PCR RT-PCR	2	6	
fecal indicator viruses (F^+coliphage)[e]	two-step enrichment	2	6	
particle size spectra	LISST-100 (light diffraction)	20	16	21
transmissivity	LISST-100	20	16	21

[a] Measured using a Thermo Orion 162A conductivity meter on February 23 and a CTD instrument (SBE-32) on February 28 and March 1. [b] Measured using a thermocouple bundled with an LISST-100 on February 23 and a CTD instrument (SBE-32) on February 28 and March 1. [c] Samples collected by UCI and analyzed by OCSD on February 23 and collected and analyzed by OCSD on February 28 and March 1. Fractionated samples collected and analyzed by UCI on February 23 and 28. [d] Collected by UCI and analyzed by Del Mar Analytical (Irvine, CA). [e] Carried out on the fractionated samples and measured using a real-time PCR for enterovirus and a nested PCR for adenovirus.

Surf Zone Measurements: NEOCO Data. Water level, salinity, temperature, and chlorophyll measurements at the NEOCO sensor, located on the end of the Newport Pier at the offshore edge of the surf zone, are presented in Figure 2 (second and third panels). The largest rain event (RE_3) and the largest discharge of stormwater runoff from the Santa Ana River (DE_4) occurred during a neap tide when the daily tide range was small (see quarter moon and water level measurements in the second panel, Figure 2). The other rainfall and stream discharge events occurred during periods of time when the daily tide range was larger, either during the transition from spring to neap tide (RE_1, RE_2, DE_1, DE_2, DE_3) or during the transition from neap to spring tide (RE_4, DE_5).

Salinity recorded at the NEOCO sensor is characterized by a series of low salinity events, relative to ambient ocean water salinity of 32.5−33.0 ppt (salinity events SE_1−SE_6, Figure 2). These low salinity events may be caused, at least in part, by stormwater discharged from the Santa Ana River (e.g., SE_6 appears to be related to DE_4). However, correlating discharge and the low salinity events is complicated by the fact that once river water is discharged to the ocean, its offshore transport is controlled by a complex set of near-shore currents (*28*). These near-shore currents, and their impact on the spatial distribution of stormwater runoff plumes, are explored in the next several sections. Temperature and chlorophyll records at the NEOCO sensor appear to be relatively unaffected by rainfall or discharge from the Santa Ana River. Surf zone temperature exhibits a diurnal pattern consistent with solar heating (i.e., temperatures are higher during the day and lower at night). Chlorophyll measurements indicate a bloom event occurred early in the study period (bloom event 1, BE_1), but this bloom event mostly dissipated prior to the rain and discharge events that occurred later. While the chlorophyll fluorometer was being maintained during this period, we cannot rule out the possibility that the downward trend in the chlorophyll signal is related to instrument fouling.

Surf Zone Measurements: Wave Data and Along-Shore Currents. Wave conditions, including the direction and height of breaking waves, were recorded twice per day by lifeguards stationed at the Newport Pier (surf zone station 15S, Figure 1). These wave data, which are plotted in the fourth panel of Figure 2, can be divided into five events, depending on whether waves approach the beach from the west (WE_1, WE_3, and WE_5) or from the south to southwest (WE_2 and WE_4). Because this particular stretch of shoreline strikes northwest−southeast (see Figure 1), waves approaching the beach from the west are likely to yield a down-coast surf zone current (i.e., directed to the southeast). Likewise, waves approaching the beach from the south are likely to yield an up-coast surf zone current (i.e., directed to the northwest) (*28*, *29*).

This expectation is consistent with the salinity signal measured at the NEOCO sensor, which is located approximately 5 km down-coast of the Santa Ana River ocean outlet. The onset of low salinity event SE_6 at the NEOCO sensor coincides very closely in time with the change in wave conditions from WE_2 to WE_3 and a likely change in the direction of the surf zone current from up-coast to down-coast (Figure 2). Discharge from the Santa Ana River was particularly high during this period (discharge event DE_4 overlaps wave events WE_2 and WE_3). Hence, the onset of SE_6 was probably triggered by a change in the direction of wave-driven surf zone currents from up-coast during WE_2 to down-coast during WE_3 and a consequent down-coast transport of stormwater runoff entrained in the surf zone from the Santa Ana River during DE_4.

Employing the same logic, low salinity events SE_3−SE_5, which occurred during a period when waves were out of the

south to southwest, may have originated from stormwater discharged by river outlets or embayment located down-coast of the NEOCO sensor (e.g., the Newport Bay outlet). Low salinity events SE_1 and SE_2, which occurred during a period when waves were out of the west, may have originated from stormwater discharged by outlets located up-coast of the NEOCO sensor, although no significant discharge from the Santa Ana River was recorded during this period of time.

Some of these low salinity events may have originated from the cross-shore transport of lower salinity water from offshore, perhaps from surface runoff plumes or submarine wastewater fields associated with local sewage outfalls (*16*), or from the submarine discharge of low salinity groundwater (*7*). While the power-plant cooling water intake and outfall appear to affect local circulation patterns offshore of Huntington Beach (*30*), the power-plant effluent consists of pure ocean water and therefore is very unlikely to be a source of the low salinity events documented in Figure 2. It is theoretically possible that the OCSD sewage outfall is a source of SE_1 and SE_2, although there is nothing unusual about the sewage discharge rates observed during these two periods of time (compare SE_1 and SE_2 with the blue curve, top panel, Figure 2).

Surf Zone Measurements: Fecal Indicator Bacteria. The concentrations of the three fecal indicator bacteria groups (TC, FC, and ENT) in the surf zone are presented as a set of color contour plots in Figure 2 (bottom three panels). Fecal indicator bacteria concentrations were log-transformed to visualize the temporal and spatial variability associated with these measurements. For comparison, the California single-sample standards for the three fecal indicator bacteria (10^4 for TC, $10^{2.602}$ for FC, and $10^{2.017}$ for ENT, all CFU or MPN/100 mL) are indicated by a set of arrows on the scale bar in the figure. The concentration of fecal indicator bacteria was frequently elevated around the ocean outlet of the Santa Ana River (near surf zone station 0), particularly during and after rain events when stormwater was discharging from the river. For example, during stormwater discharge events (DE_3 and DE_4), water quality around the Santa Ana River outlet was very poor (see water quality events TC_2, FC_2, and ENT_2 in Figure 2). During this period of time, fecal indicator bacteria concentrations around the Santa Ana River outlet frequently exceeded one or more state standards, in some cases by as much as 300−500% (depending on the fecal indicator group).

The spatial distribution of fecal indicator bacteria in the surf zone around the Santa Ana River outlet appears to be controlled by local wave conditions, in a manner consistent with the earlier discussion of wave-driven surf zone currents. When waves approach the beach from the west and down-coast currents are likely to prevail, the concentration of fecal indicator bacteria in the surf zone is higher on the down-coast side of the ocean outlet (compare WE_1 with TC_1, FC_1, ENT_1 and WE_3 with TC_3, FC_3, ENT_3). Likewise, when waves approach the beach from the south and up-coast currents are likely to prevail, the concentration of fecal indicator bacteria in the surf zone is higher on the up-coast side of the ocean outlet (compare WE_2 with TC_2, FC_2, ENT_2). The exception is a short period of time when relatively small waves (wave height < 0.5 m) approach the beach from the southwest and the concentration of fecal indicator bacteria is higher on the down-coast side of the river (compare WE_4 with TC_4, FC_4, ENT_4). This exception can be rationalized by noting that waves out of the southwest break with their crests parallel to the beach, and hence the direction of long-shore transport in the surf zone is likely to be unpredictable under these conditions. The apparent time delay between change in wave direction (e.g., from WE_1 to WE_2) and change in the spatial distribution of fecal indicator bacteria around the Santa Ana River outlet (e.g., from TC_1 to TC_2) is, at least in part, a sampling artifact. Wave height and direction were recorded twice per day while fecal indicator bacteria concentrations in the surf zone were sampled at most once per day (the gray dots in the color contour plots indicate the timing of surf samples at each station).

Stormwater runoff discharged from the Santa Ana River appears to severely impact water quality in the surf zone over a fairly limited stretch of the beach (<5 km either side of the river between surf zone stations 15N and 15S). This spatial confinement of stormwater plumes in the surf zone, which is particularly evident for FC and ENT, could be the result of physical transport processes (e.g., dilution by rip cell mediated exchange of water between the surf zone and offshore) or nonconservative processes (e.g., the removal of fecal indicator bacteria from the surf zone by die-off or sedimentation) (*28*, *29*). An analysis of historical fecal indicator bacteria measurements at Huntington Beach concluded that the length of surf zone impacted by point sources of fecal indicator bacteria, such as the Santa Ana River, is influenced more by rip cell dilution and less by nonconservative processes such as die-off (*31*). The decay length scale reported here of 5 km is very close to the length scale predicted by rip cell dilution alone (2−4 km, assuming a rip cell spacing of 0.5 km) (*31*). Hence, die-off probably plays a secondary role, compared to dilution, in limiting the distance over which water quality is impaired in the surf zone by stormwater runoff from the Santa Ana River.

Fecal indicator bacteria events also occur in the surf zone at the northern (events TC_6, TC_7, ENT_6, ENT_7) and southern (events TC_5, FC_5, and ENT_5) edges of our study area. Possible sources of these fecal indicator bacteria events include stormwater discharged from the Huntington Harbor and Newport Bay Harbor located at the extreme northern (5 km up-coast of station 39N) and southern (stations 27S and 29S) ends of the study site and, possibly, from river outlets located outside of the study area (e.g., the Los Angeles River and San Gabriel River, see inset in Figure 1). Boehm and co-workers (*32*, *33*) suggested that the OCSD sewage outfall might be a source of fecal indicator bacteria in the surf zone at Huntington Beach, particularly during dry weather summer periods. However, compared to the Santa Ana River, the sewage outfall probably had a negligible impact on surf zone water quality at Huntington Beach and Newport Beach during the storm events sampled in this study. This conclusion is based on the following evidence. First, during our study period, sewage effluent discharged by OCSD was chlorinated and the fecal indicator bacteria concentrations in the final effluent (mean of 6000, 400, and 100 MPN/100 mL for TC, EC, and ENT, $n = 17$, C. McGee, personal communication) were significantly below the concentration of fecal indicator bacteria measured in stormwater runoff from the Santa Ana River (mean 17000, 5000, and 8000 MPN/100 mL for TC, EC, and ENT, $n = 30$, Surbeck et al. (*13*)). Second, the peak discharge rate from the OCSD outfall (ca. 13 m^3/s) is much smaller than the peak discharge rate of stormwater runoff from the Santa Ana River (ca. 300 m^3/s) (compare blue and black curves, second panel, Figure 2). Third, the sewage effluent is discharged 6 km offshore of the surf zone through a 1-km-long diffuser located at the end of OCSD's submarine outfall at a water depth of approximately 60 m (hatched region of the outfall pipe in Figure 1). By contrast, stormwater runoff from the Santa Ana River is discharged into the ocean directly at the surf line.

Offshore Measurements: Satellite Ocean Color Imagery. The spatio-temporal distributions of offshore stormwater runoff plumes sampled during this study are revealed by MODIS true color satellite imagery of a 100-km stretch of the coastline centered around our field site (Figure 3). The monitoring grid sampled during the offshore cruises is depicted on the satellite images by yellow dots. The timing of the satellite passes, relative to rain events, discharge events,

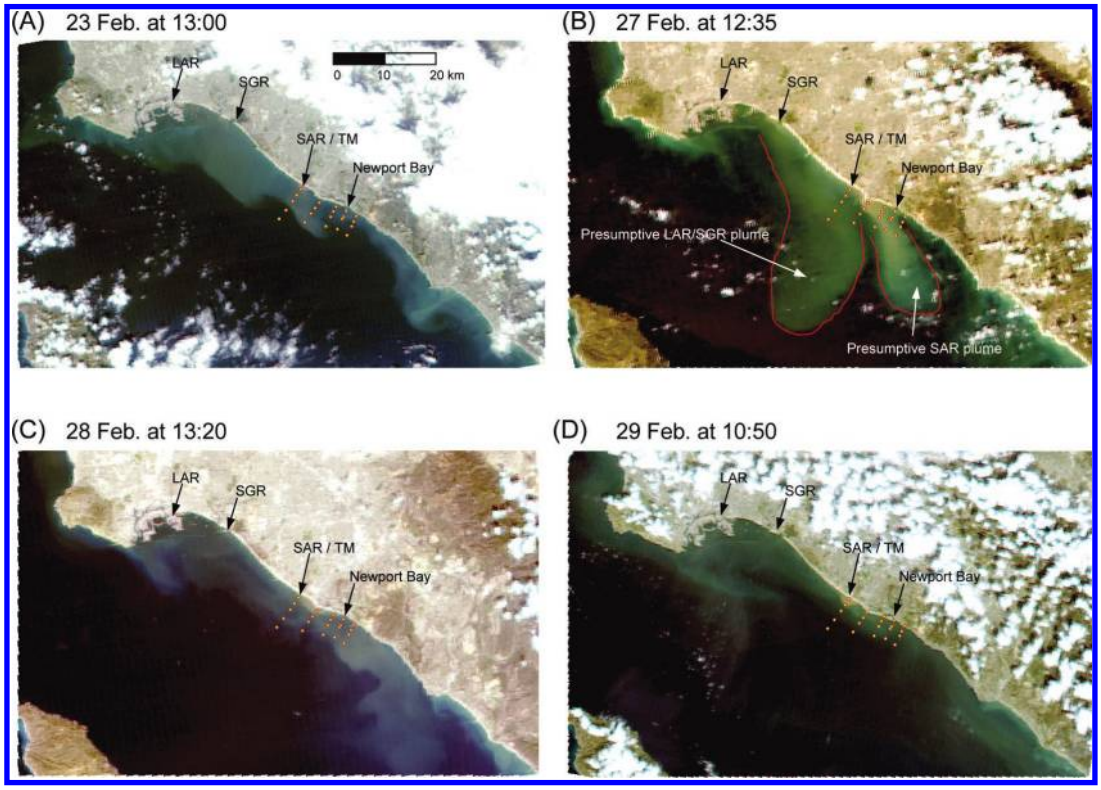

FIGURE 3. MODIS Terra and Aqua true color satellite imagery of stormwater runoff plumes along the San Pedro Channel, California, with nominal spatial resolution of 250 m. Yellow dots indicate location of field sampling stations offshore of Huntington and Newport Beach; black arrows denote the Los Angeles River (LAR) outlet, San Gabriel River (SGR) outlet, Santa Ana River/Talbert Marsh (SAR/TM) outlet, and Newport Bay outlet. (A) MODIS-Aqua, February 23, 2004, at 21:00 UTC (13:00 local time), (B) MODIS-Aqua, February 27, 2004, at 20:35 UTC (12:35 local time), (C) MODIS-Aqua, February 28, 2004, at 21:20 UTC (13:20 local time), (D) MODIS-Terra, February 29, 2004, at 18:50 UTC (10:50 local time).

wave events, surf zone water quality events, and offshore sampling cruises, is indicated at the top of Figure 2.

Generally speaking, in this collection of true color imagery the stormwater runoff plumes appear to be characterized by a band of turbid water turquoise to brown in appearance that is observed along the entire imaged region, although both cross-shelf and along-shore gradients in the color signature are evident. Following the rain events on February 21−22 (total of 39.4 mm, see RE_1 and RE_2 in Figure 2), a MODIS Aqua imagery from February 23 demonstrates the cross-shelf extent of the runoff plume to be variable, ranging from under 1 km in some places to more than 10 km offshore of the Los Angeles River and San Gabriel River (Figure 3A). At our study site, which is centrally located within this broad region, a distinct and apparently heavily particulate-laden runoff plume was observed in the vicinity of the Santa Ana River outlet and nearby station 2201 (see Figure 1 for numerical designation of offshore sampling sites). The Santa Ana River plume extended offshore past station 2203, with an apparent turn down-coast (i.e., southeast), continuing past stations 2104 and 2024. During this time, breaking waves were out of the south and the transport direction of fecal indicator bacteria in the surf zone was directed up-coast, opposite the apparent transport direction of stormwater plumes offshore of the surf zone (compare timing of satellite image 1 with WE_2 and fecal indicator bacteria events TC_2, FC_2, and ENT_2, Figure 2). It also appears that a portion of the Los Angeles River and the San Gabriel River stormwater plumes may have advected south and comingled with the Santa Ana River stormwater plume. Further south, offshore particulate loadings off the Newport Bay outlet (station 2001) do not appear to be as large as those off the Santa Ana River outlet.

A MODIS image on February 27 revealed two distinct plumes of considerable size and offshore extent (Figure 3B). This satellite acquisition preceded by 1 day the sampling cruise on February 28 (described in the next section), followed the large precipitation event on February 25−26 (total of 51.3 mm, see RE_3 in Figure 2), and followed the large discharge event from the Santa Ana River (DE_4, in Figure 2). The plume to the northwest in this image appears to be associated with the Los Angeles River or the San Gabriel River outlets, with an approximate areal extent of 450 km^2. The plume to the southeast appears to be distinct from the former plume and likely originated from the Santa Ana River outlet, with an approximate areal extent of 100 km^2 (the presumptive Los Angeles River, San Gabriel River, and Santa Ana River plumes are delineated by red lines in Figure 3B). The February 27 Santa Ana River stormwater plume is considerably larger in size than the one observed on February 23 (compare Figure 3A and 3B), consistent with the very large volume of water discharged from the Santa Ana River just prior to this satellite acquisition (approximately 4×10^7 m^3, see DE_4 in Figure 2). Further, the Los Angeles River, San Gabriel River, and Santa Ana River runoff plumes on February 27 differed from those on February 23 in that they penetrated farther offshore (30 km compared to 10 km) and thus potentially transported more sediments into the deep waters of the San Pedro Channel.

The jetlike appearance of the presumptive Los Angeles River, San Gabriel River, and Santa Ana River stormwater runoff plumes in Figure 3B has been observed elsewhere in the Southern California Bight, for example, off the Santa Clara River discharge (*4*, *29*), and is potentially the result of inertia-driven flow. At the time of this second satellite acquisition, breaking waves out of the west, and along-shore transport in the surf zone and offshore of the surf zone, appear to be directed down-coast (compare timing of satellite image 2 with WE_3 and fecal indicator events TC_3, FC_3, and ENT_3).

Subsequent MODIS true color imagery on February 28 (Figure 3C) and February 29 (Figure 3D) indicates that both

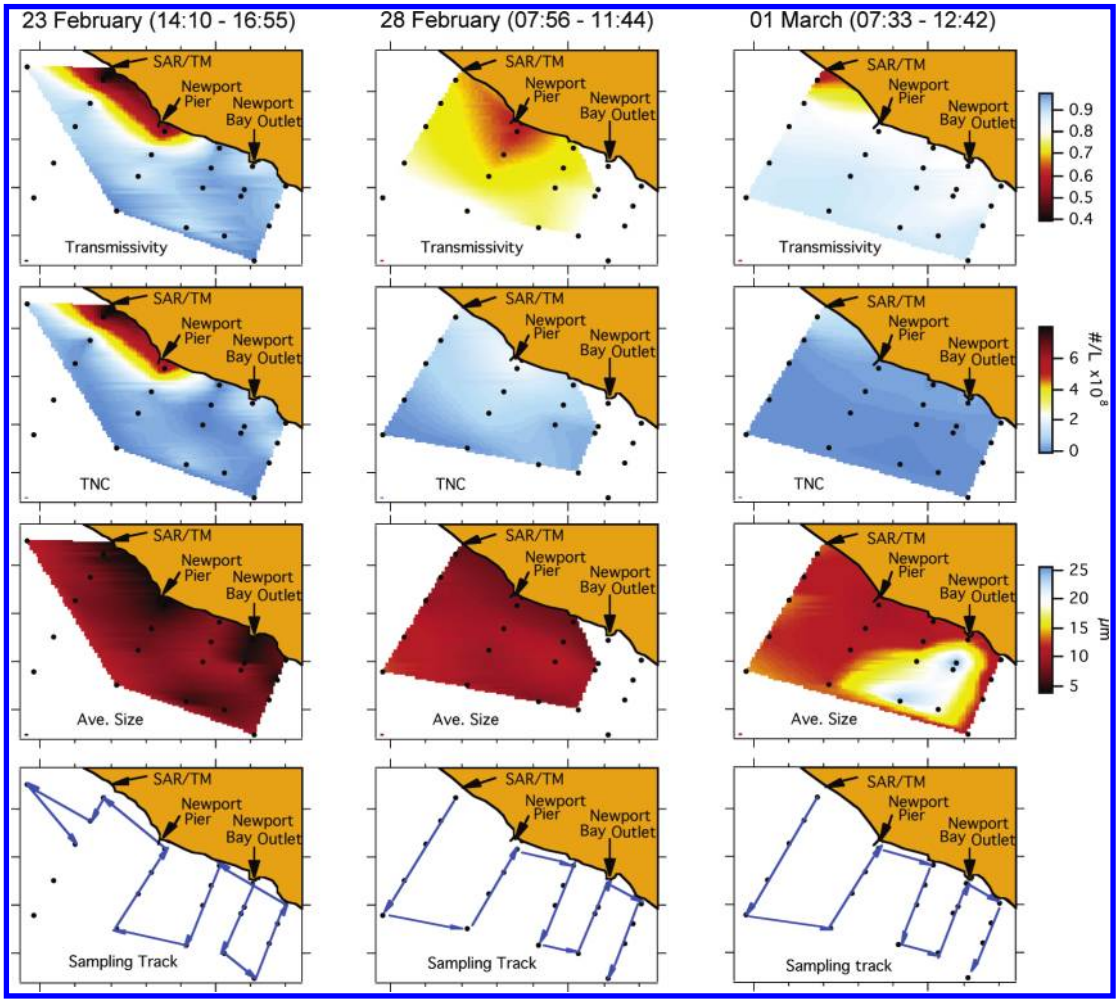

FIGURE 4. Particle measurements collected during the three sampling cruises. The bottom row of panels indicates the sampling track. TNC is an abbreviation for total particle number concentration. TNC and number-averaged particle size were calculated from measured particle size spectra using eq 1a, b.

the Los Angeles River/San Gabriel River and the Santa Ana River runoff plumes had significantly decreased in size, consistent with reduced flow out of the respective rivers (compare stream discharge curves with timing of satellite images 2 and 3, Figure 2). However, particulate matter appeared to remain high in the general vicinity of the Santa Ana River outlet. Whereas this zone of elevated particulate matter extended south to at least station 2021 on February 27−28, by February 29 it had receded somewhat and was fairly localized around station 2201. Unfortunately, no satellite imagery was available the following day (March 1) to complement the third sampling cruise, given persistent regional cloud cover that day.

Offshore Measurements: In-Situ Turbidity and Number-Averaged Particle Size. In-situ turbidity measurements collected during the three offshore cruises are presented as a series of color contour plots in Figure 4. During the February 23 cruise, a region of high turbidity, as evidenced by low transmissivity and high TNC, is evident offshore of, and to the south of, the Santa Ana River outlet (left-hand column of panels, Figure 4). The number-averaged particle size is depressed in this same region, as well as in the region offshore of the Newport Bay outlet. During subsequent cruises, the ocean became progressively less turbid closer to shore (although not necessarily offshore), as evidenced by increasing transmissivity and decreasing TNC, and the number-averaged particle size progressively increased (second and third columns, Figure 4). These results suggest that, offshore of the surf zone, particle size was steadily increasing and particle concentrations were steadily decreasing following the rain and stream discharge events that ended on, or before, the evening of February 27. The above turbidity patterns are generally consistent with the plume signatures and gradients observed in the true color satellite imagery (Figure 3), although some differences exist which could result from the offset timing (up to several hours) between the acquisition of the satellite images and the field measurements. As a technical aside, the number-averaged particle size ($\bar{d}$, see eq 1b) and the median particle size (d_{50}) follow similar trends (i.e., they both rise and fall together), although the magnitude of d_{50} was approximately 16-fold larger (Figure S3, Supporting Information). For the results presented here, $\bar{d}$ was chosen because it emphasizes changes in the small end of particle size spectra.

Offshore Measurements: Fecal Indicator Bacteria. Water quality test results from the three offshore cruises are presented as a set of color contour plots in Figure 5. During the February 23 cruise, the concentration of fecal indicator bacteria exceeded the California single-sample standards for TC, ENT, and EC in several samples collected just offshore, and to the south, of the Santa Ana River and Newport Bay outlets (left-hand column of panels in Figure 5). Nevertheless, the highest concentrations measured offshore of the surf zone are generally lower, in many cases by several orders of magnitude, compared to the highest concentrations measured in the surf zone (compare concentration scales for EC, FC, and ENT in Figures 2 and 5). The difference in offshore and surf zone fecal indicator bacteria concentrations is even

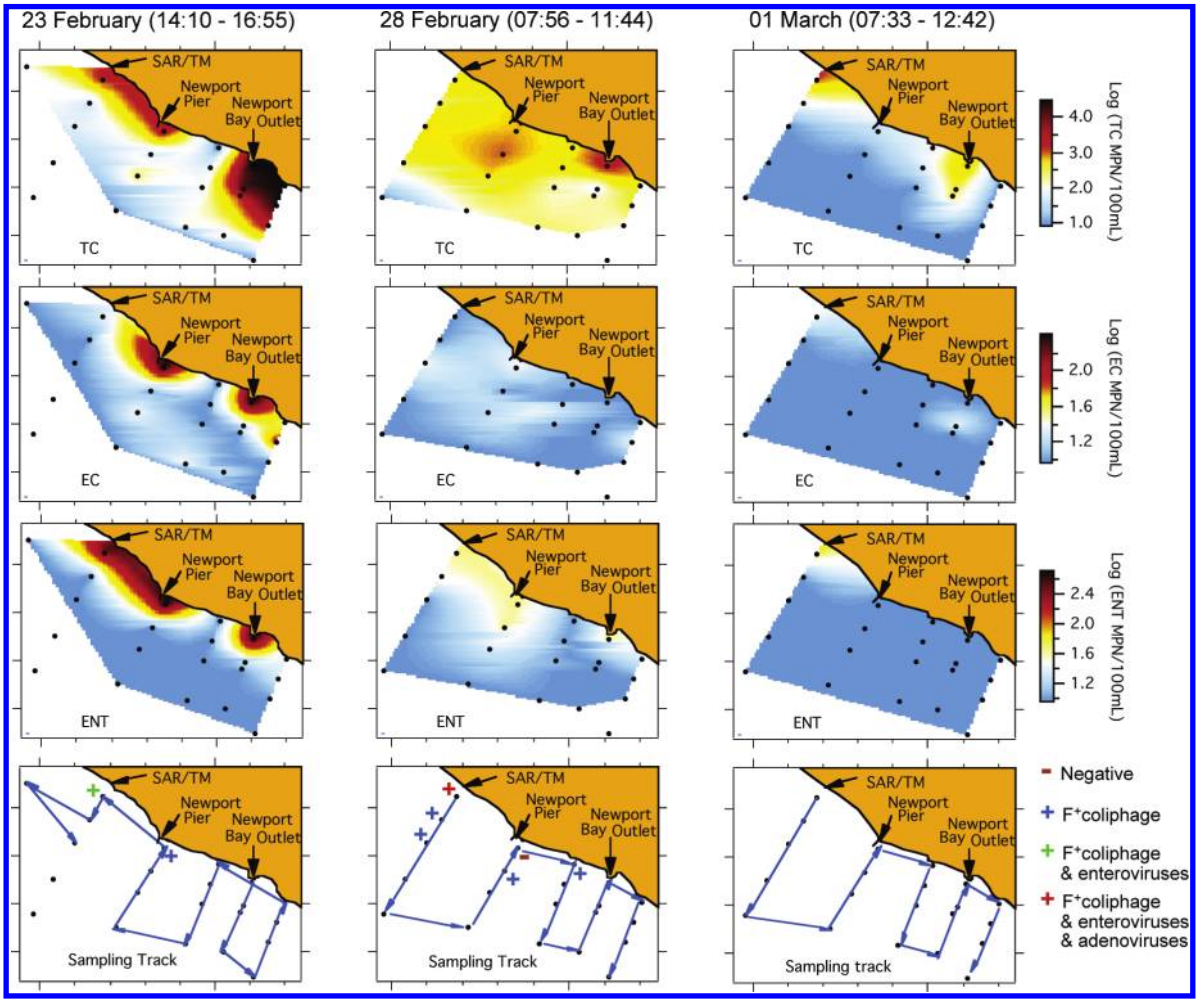

FIGURE 5. Fecal indicator bacteria concentrations measured during the three sampling cruises. The bottom row of panels indicates the sampling track (blue arrows) and the detection of F^+ coliphage and human viruses. SAR/TM is an abbreviation for the outlet of the Santa Ana River and Talbert Marsh.

more pronounced during the later cruise dates. For example, none of the samples collected during the February 28 and March 1 cruises exceeded state standards for fecal indicator bacteria, yet several of the samples collected from the surf zone during the same time period exceeded single-sample standards for one or more fecal indicator bacteria groups (compare concentrations measured during the second cruise date with TC_3, FC_3, and ENT_3 and concentrations measured during the third cruise date with TC_4, FC_4, and ENT_4, Figures 2 and 5).

Offshore Measurements: F^+ Coliphage and Human Viruses. Offshore samples tested positive for F^+ coliphage (n = 8, see Table 1), with the exception of a single sample collected on the February 28 cruise from offshore of the Newport Pier (blue, green, and red plus symbols, bottom panels, Figure 5). Human adenoviruses and enteroviruses were detected by real time Q-PCR, nested PCR, and RT-PCR in a sample collected from station 2201 located directly offshore of the Santa Ana River outlet during the February 28 cruise (red plus, middle bottom panel, Figure 5). The concentration of human adenoviruses in this sample is estimated to be 9.5×10^3 genomes per liter of water, which is approximately equivalent to 10 plaque forming units per liter of water, according to a laboratory study comparing Q-PCR results with plaque assay (*35*). Human enteroviruses were also detected in a sample collected directly offshore of the Santa Ana River outlet (station 2201) on the February 23 cruise (green plus, bottom left panel, Figure 5). While relatively few samples were tested for human viruses (n = 8), these results demonstrate that human viruses are present in surface water offshore of the Santa Ana River outlet following storm events, even when the fecal indicator bacteria concentrations are below state standards (e.g., station 2201 during the February 28 cruise, Figure 5). These results are consistent with previous observations that human pathogenic viruses and fecal indicator viruses persist longer than fecal indicator bacteria in ocean water (*36*). Direct PCR measurement of pathogenic viruses in highly turbid water is challenging because of PCR inhibition (*35*).

Offshore Measurements: Relationship between Fecal Indicator Bacteria, Turbidity, and Number-Averaged Particle Size. Turbidity has been suggested as a possible proxy for water quality (*37*, *38*). However, on the basis of our offshore data, turbidity per se appears to be an inconsistent proxy for the concentration of fecal indicator bacteria. For example, during the February 23 cruise, there is good coherence between turbidity and TC, EC, and ENT concentrations off the Santa Ana River outlet and Newport Pier (compare transmissivity and TNC with fecal indicator bacteria results, left-hand column of panels, Figures 4 and 5). However, turbidity is low off of the Newport Bay outlet where the bacteria concentrations are particularly high. In addition, there are no consistently robust relationships between shipboard measurements of fecal indicator bacteria and shipboard measurements of TOC, temperature, or salinity (see Figure S4, Supporting Information). The number-averaged particle size, on the other hand, comes close to matching the along-shore spatial pattern of fecal indicator

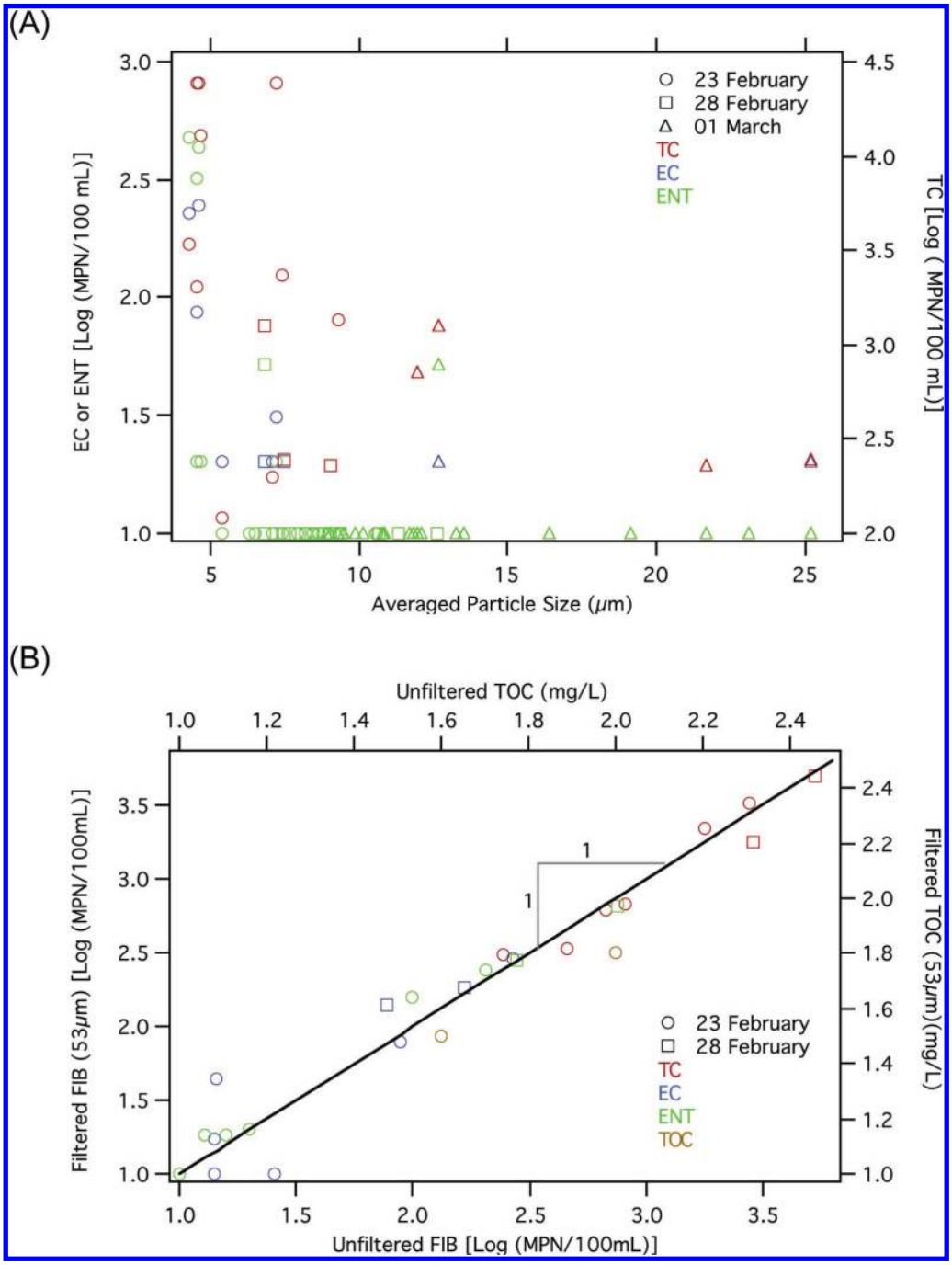

FIGURE 6. (A) Cross plots of log-transformed fecal indicator bacteria concentrations measured in samples collected during the three offshore cruises, against the corresponding number-averaged particle size. (B) Cross plots of log-transformed fecal indicator bacteria concentrations and TOC concentrations measured in samples collected during the three offshore cruises, before and after filtration through a 53-μm sieve. The one-to-one line corresponds to the case where the concentrations are the same before and after filtration.

bacteria measured during the February 23 cruise. Specifically, elevated fecal indicator bacteria concentration appears to correlate with depressed number-averaged particle size (compare fecal indicator bacteria and number-averaged particle size results for the February 23 cruise, left-hand column of panels, Figures 4 and 5). When all of the fecal indicator bacteria data collected during the three cruises are aggregated and plotted against number-averaged particle size, an inverse relationship between these two parameters emerges; specifically, samples with elevated fecal indicator bacteria concentrations also exhibit small number-averaged particle size (Figure 6A). Moreover, the concentration of fecal indicator bacteria in water samples collected during the first two cruises is the same, within error, before and after filtration through a 53-μm sieve (Figure 6B), implying that fecal indicator bacteria are either adsorbed to particles smaller than 53 μm or are not particle-associated. TOC also appears to pass through the 53-μm sieve (Figure 6B) as do human viruses and fecal indicator viruses (data not shown). The co-occurrence of small particles and indicators of fecal pollution (fecal indicator bacteria, fecal indicator viruses, and human pathogenic viruses) does not necessarily imply that the latter are adsorbed to the former. The inverse relationship evident in Figure 6A, for example, may reflect a temporal evolution of stormwater plumes as they age, from a predominance of small particles and high concentrations of fecal indicators initially, to larger particles and lower concentrations of fecal indicators later.

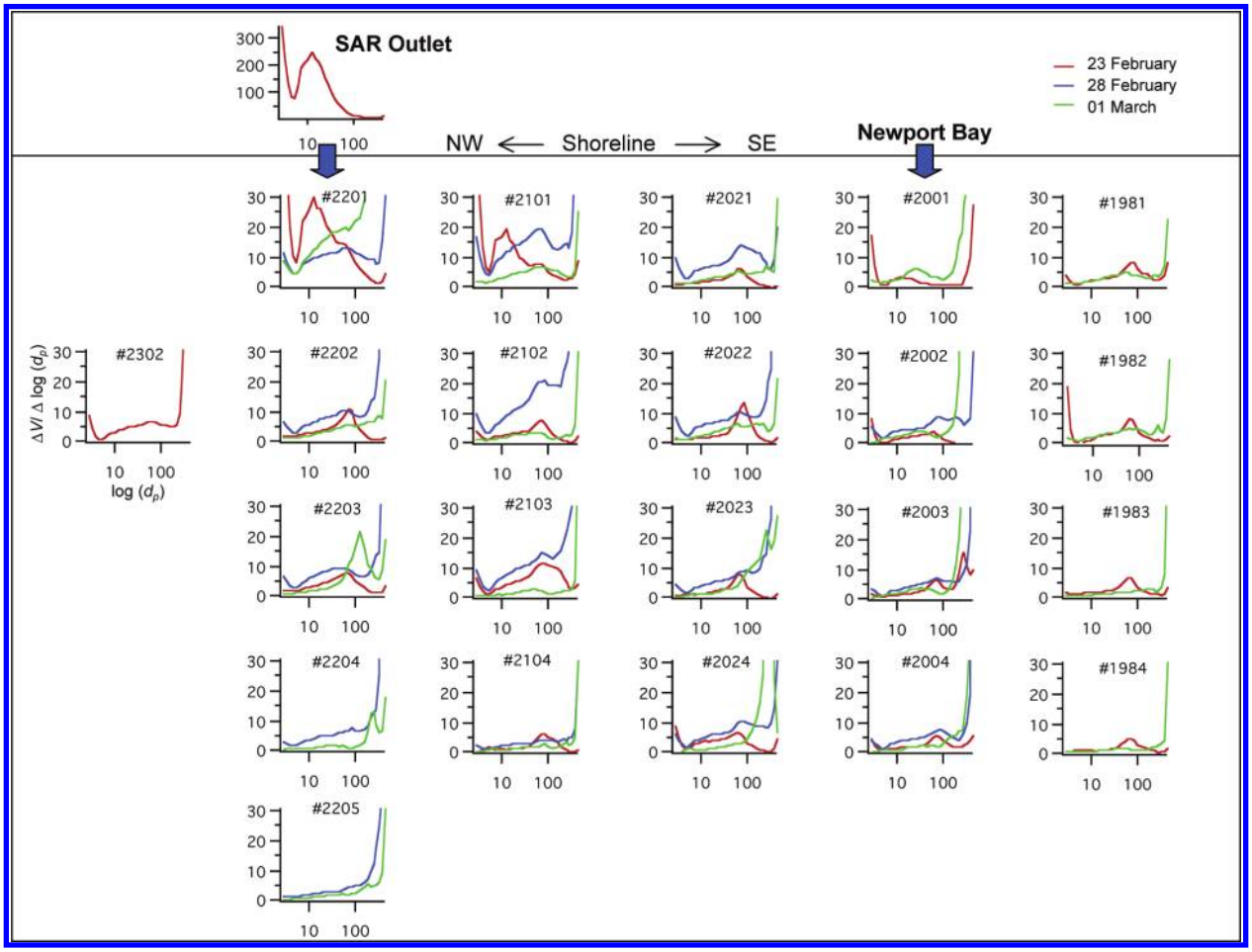

FIGURE 7. Particle size spectra measured during the three offshore cruises; numbers at the top of each panel denote the station number where the particle size spectra were measured (see Figure 1). The vertical axis in each plot represents the particle volume resident in logarithmically spaced particle diameter bins; the horizontal axis represents the diameter of the particles (in μm). These plots are arranged so that the stations progress from onshore to offshore (top to bottom) and up-coast to down-coast (left to right). The single plot labeled "SAR Outlet" corresponds to a particle size spectrum measured in stormwater runoff flowing out of the Santa Ana River outlet, just upstream of where it flows over the beach and into the ocean.

Offshore Measurements: Particle Size Spectra. Particle size spectra acquired during the three cruises are presented in Figure 7. Each plot displays the normalized particle volume (vertical axis) detected in 32 logarithmically spaced particle diameter bins ranging in size from 2.5 to 500 μm (horizontal axis). The particle size spectrum measured at a particular offshore location and time appear to be related to the specific stormwater plume the particles are associated with and, possibly, the elapsed time stormwater has spent in the ocean. Stormwater flowing out of the Santa Ana River during the February 23 cruise, for example, is characterized by two modes at the small end of the size spectrum, one in the <5 μm bin and another in the 10−50 μm bins (set of red curves, Figure 7). These modes are present in stormwater runoff sampled at several locations in the Santa Ana River watershed (*13*), in samples collected at the ocean outlet of the Santa Ana River (panel labeled "SAR Outlet" at top of Figure 7), and in samples collected just offshore (red curve at station 2201, Figure 7) and down-coast (red curve at station 2101, Figure 7) of the Santa Ana River outlet. Particles discharged from the Santa Ana River appear to dilute and merge into a background turbidity characterized by a single broad mode in the 50−300 μm size range (evident in the red curves at most stations, Figure 7).

Referring to Figure 3A and the earlier discussion of this satellite image, the 50−300 μm mode observed on February 23 may be characteristic of a large runoff plume originating from one or more up-coast sources of stormwater runoff, most likely the Los Angeles River or the San Gabriel River. Several factors can lead to artifacts in the particle size spectra estimated from the light-scattering instrument deployed in this study (*39*). However, in our case this caveat is mitigated somewhat by the observation that particle volume fractions calculated from the particle size spectra are strongly correlated (Spearman's rank correlation $Sp = 0.90$, $p = 0.02$) with independent measurements of total suspended solids (data not shown).

During the second and third cruises, the particle size spectra progressively coarsen with the result that, by March 1, virtually all of the particle volume is associated with the largest size bin (>500 μm, green curves in Figure 7). The observed temporal evolution in particle size spectra, from high turbidity and multiple modes at the lower end of the particle size spectrum to low turbidity and a single mode at the large end of the particle size spectrum, may reflect decreasing particle supply (i.e., reduced stormwater discharge from major river outlets) coupled with within-plume coagulation of particles into larger size classes and, ultimately, removal of the largest particles by gravitational sedimentation. Coagulation time scales estimated from these particle size spectra measurements are short (minutes to hours or longer) compared to time scales associated with the generation and offshore transport of stormwater plumes (hours to days), and hence coagulation cannot be ruled out as an important mechanism at our field site (see Supporting Information for details on the time scale calculations).

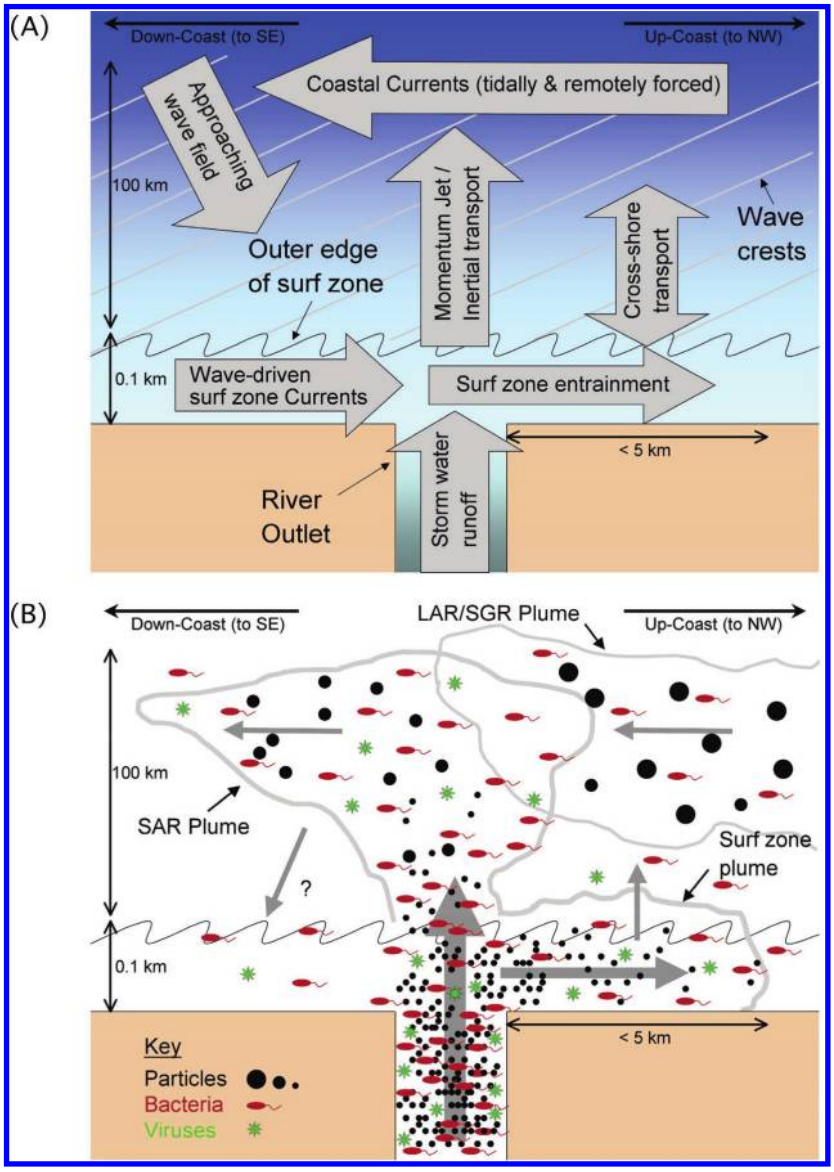

FIGURE 8. (A) Transport mechanisms that can affect the offshore distribution of contaminants discharged from river outlets. (B) Schematic representation of the spatial distribution of particles (black circles of varying size), fecal indicator bacteria (red symbols), and F^+ coliphage and human pathogenic viruses (green symbols). Abbreviations are SAR (Santa Ana River), SGR (San Gabriel River), and LAR (Los Angeles River).

Whether coagulation, in fact, plays a role in the fate and transport of particles and particle-associated contaminants in stormwater plumes will likely depend on the coagulation efficiency (i.e., the fraction of particle−particle collisions that result in sticking events) and shear rates present at a given location and time (*40*, *41*). Alternatively, the observed temporal coarsening of particles in the offshore may reflect changes in the particle size spectra of the stormwater runoff before it enters the ocean, from a predominance of smaller particles during the peak of the hydrograph, to a predominance of coarser particles during the falling limb of the hydrograph. Further studies are needed to determine whether observed coarsening of the offshore particle size spectra is caused by within-plume coagulation or by temporal evolution of the particle size spectra in stormwater runoff before it enters the ocean.

Data Synthesis. Results presented in this paper are represented schematically in Figure 8, including potential offshore transport mechanisms (panel A) and the resulting distribution of particles, bacteria, and viruses (panel B). As stormwater is discharged from the river outlet and flows over the beach, a fraction is entrained in the surf zone and the rest is ejected offshore in a momentum jet. Measurements of fecal indicator bacteria in the surf zone suggest that, once entrained, contaminants are transported parallel to shore by wave-driven currents, in a direction (i.e., up- or down-coast) controlled by the approaching wave field. When waves strike the beach so that a component of wave momentum is directed up-coast (the scenario pictured in Figure 8), fecal indicator bacteria in the surf zone are carried up-coast of the river outlet. Conversely, when waves strike the beach so that a component of wave momentum is directed down-coast, fecal indicator bacteria in the surf zone are carried down-coast of the river outlet. The buildup of water in the surf zone from breaking waves drives a cross-shore circulation cell, which can transport material between the surf zone and offshore of the surf zone. At our field site, this cross-shore circulation appears to limit the length of beach severely polluted with fecal indicator bacteria to <5 km around the river outlet, by diluting contaminated surf zone water with cleaner water from offshore. While the transport processes described here are based on measurements of fecal indicator bacteria in the surf zone, it is likely that other contaminants in stormwater runoff, in particular, human viruses and toxic

contaminants associated with suspended particles (*13*, *42*), will behave similarly.

Further offshore, stormwater runoff plumes are common and readily detected through a variety of geophysical parameters (e.g., salinity, transmissivity, surface color). A clear linkage between these parameters and fecal indicator bacteria could not be established here. However, fecal indicator bacteria did appear to be associated with the smallest particle sizes, on the basis of both fractionation studies (Figure 6B) and the inverse relationship observed between fecal indicator bacteria concentrations and number-averaged particle size (Figure 6A). Particle size spectra in the offshore plumes coarsen with time post-release, and fecal indicator bacteria concentrations steadily drop (see the schematic representation of particle size in the various offshore plumes, Figure 8B). These results have several implications. First, they suggest that high concentrations of fecal indicator bacteria in the surf zone at our field site are probably not brought into the study area by coastal currents from distal sources (e.g., the Los Angeles river or the San Gabriel river). Second, cross-shore transport of water between the surf zone and offshore of the surf zone, for example, by rip cell currents, is likely to improve surf zone water quality by diluting dirty river effluent entrained in the surf zone with relatively clean ocean water from offshore.

While the concentrations of fecal indicator bacteria in the offshore plumes are generally below surf zone water quality standards, particularly during the latter two cruises, fecal indicator viruses (F^+ coliphage) were detected in nearly all offshore samples tested, and human adenoviruses and enteroviruses were detected in several offshore samples, including two collected offshore of the Santa Ana River outlet (station 2201 on February 23 and 28, see Figure 5). It is likely that the virus results presented here represent a conservative estimate of viral prevalence, because a limited numbers of samples were tested ($n = 8$). In addition, the presence of PCR inhibitors in stormwater reduces the efficiency of PCR detection of human pathogenic viruses, as mentioned earlier. At present, there are no water quality standards for fecal indicator viruses and human pathogenic viruses, largely because epidemiological data are not available to link adverse human health outcomes (e.g., gastrointestinal disease) to recreational ocean exposure to these organisms. However, the offshore detection of human pathogenic viruses begs several questions: First, do these viruses constitute a human health risk, either by contaminating the surf zone directly (see arrow with question mark, indicting the possible transfer of contaminants from offshore into the surf zone, Figure 8B) or by sequestering in offshore sediments? Second, given the fact that the Santa Ana River has separate storm and sanitary sewer systems, what is the source of human fecal pathogens in the wet weather water runoff? Many studies have shown that human fecal pathogens are associated with storm runoff from urban areas located throughout the United States (*25*, *43*−*45*), so the association between stormwater runoff and human fecal pathogens observed here is certainly not unique. Possible sources of human pathogens in stormwater runoff from urban areas include leaking sewer pipes, illicit sewage connections to the stormwater sewer system, homeless populations, and so forth.

Taken together, the results presented in this paper demonstrate that stormwater runoff from the Santa Ana River is a significant source of near-shore pollution, including turbidity, fecal indicator bacteria, fecal indicator viruses, and human pathogenic viruses. However, relationships between variables (e.g., between turbidity and fecal indicator bacteria and between fecal indicator bacteria and human viruses) vary from site to site (at the same time) and from time to time (at the same site) suggesting that the sources, fate, and transport processes are contaminant specific. The apparent exception is the inverse relationship observed between fecal indicator bacteria and number-averaged particle size, although further studies are needed to determine if this result is generalizable to other storm seasons and coastal sites and, if so, to determine the underlying mechanism at work. The relationship between water quality parameters (e.g., fecal indicator bacteria), turbidity, and other field proxies, such as number-averaged particle size, salinity, and colored dissolved organic matter, are the focus of ongoing and future regional studies, including as part of a coastal water quality observing program within the Bight '03 Project (http://www.sccwrp.org/regional/03bight/bight03_fact_sheet.html), as well as other investigations being carried out as part of the Southern California Coastal Ocean Observing System (SCCOOS).

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Supporting Information Available

Sampling and analysis protocols, calculation of the orthokinetic coagulation time scales, and additional figures. This material is available free of charge via the Internet at http://pubs.acs.org.

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Exhibit H

River plume patterns and dynamics within the Southern California Bight

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Abstract

Stormwater river plumes are important vectors of marine contaminants and pathogens in the Southern California Bight. Here we report the results of a multi-institution investigation of the river plumes across eight major river systems of southern California. We used *in situ* water samples from multi-day cruises in combination with MODIS satellite remote sensing, buoy meteorological observations, drifters, and HF radar current measurements to evaluate the dispersal patterns and dynamics of the freshwater plumes. River discharge was exceptionally episodic, and the majority of storm discharge occurred in a few hours. The combined plume observing techniques revealed that plumes commonly detach from the coast and turn to the left, which is the opposite direction of Coriolis influence. Although initial offshore velocity of the buoyant plumes was ~50 cm s^{-1} and was influenced by river discharge inertia (i.e., the direct momentum of the river flux) and buoyancy, subsequent advection of the plumes was largely observed in an alongshore direction and dominated by local winds. Due to the multiple day upwelling wind conditions that commonly follow discharge events, plumes were observed to flow from their respective river mouths to down-coast waters at rates of 20 - 40 km d^{-1}. Lastly, we note that suspended-sediment concentration and beam-attenuation were poorly correlated with plume salinity across and within the sampled plumes (mean R^2 = 0.12 and 0.25, respectively), while colored dissolved organic matter (CDOM) fluorescence was well correlated (mean R^2 = 0.56), suggesting that CDOM may serve as a good tracer of the discharged freshwater in subsequent remote sensing and monitoring efforts of plumes.

Introduction

Southern California's coastal watersheds (Figure 1a) drain a highly modified landscape with 54% of the watershed area dammed and many of the channels straightened, leveed or channelized (Willis and Griggs 2003). These modifications, combined with the Mediterranean climate, lead to episodic river discharge, with large winter storms contributing the majority of annual water and sediment budgets (Inman and Jenkins 1999). These river systems also provide large loadings of pollutants and pathogens to the coastal ocean, surpassing loadings from municipal wastewater discharges for most constituents and as such merit detailed investigation (Schiff *et al.* 2000, Dojiri *et al.* 2003, Ahn *et al.* 2005, Warrick *et al.* 2005, Stein *et al.* 2006).

The plumes from these river discharge events can extend 10's km from the shoreline (Mertes and Warrick 2001, DiGiacomo *et al.* 2004, Nezlin and DiGiacomo 2005, Nezlin *et al.* 2005). Nezlin *et al.* (2005) found that plume areas defined by SeaWiFS radiometer-data were strongly correlated to antecedent precipitation. The maximum extent of these plumes occurs one - three days following precipitation, and multiple day plume persistence was found for all of the major river plumes (Nezlin *et al.*

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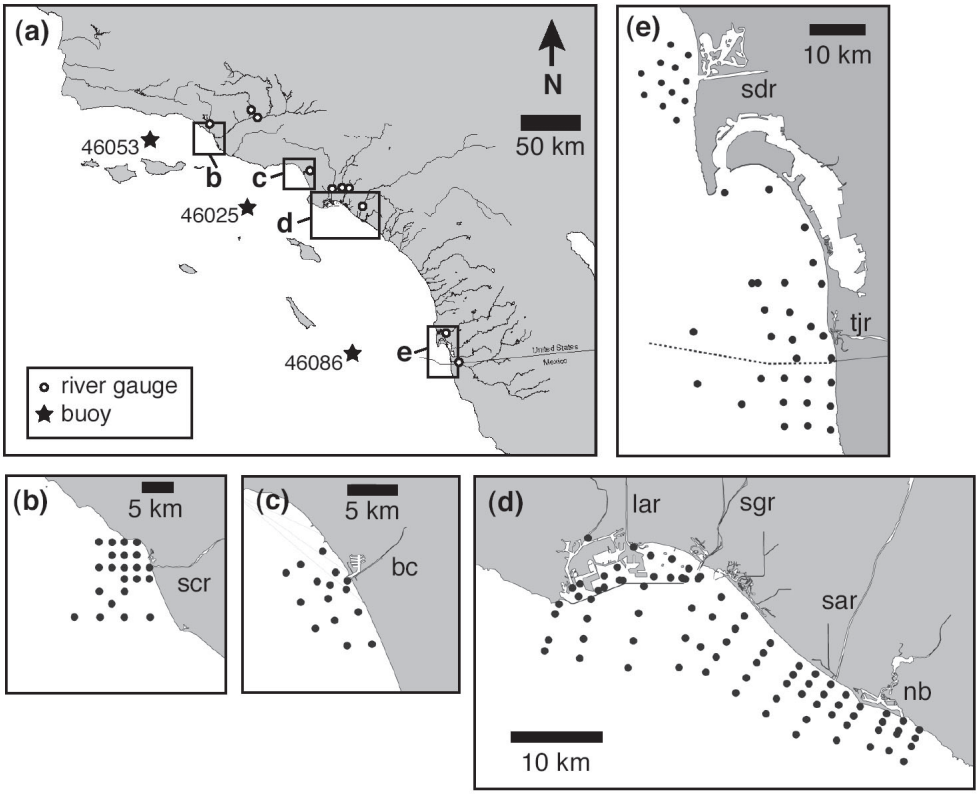

Figure 1. The Southern California Bight study area with the four sampled regions (a). Ship-based plume sampling stations for each of the four regions (b-e). Rivers within each region are also identified: scr = Santa Clara River (b); bc = Ballona Creek (c); lar = Los Angeles River; sgr = San Gabriel River, sar = Santa Ana River; and nb = Newport Bay (d); and sdr = San Diego River and tjr = Tijuana River (e).

2005). However, significant plume size variability is found across the California watersheds in both time and space (Mertes and Warrick 2001, Warrick and Fong 2004, Nezlin and DiGiacomo 2005, Nezlin *et al.* 2005).

Jones and Washburn (1997), Washburn *et al.* (2003) and Warrick *et al.* (2004a) have shown that the freshwater from southern California rivers quickly stratifies into a buoyant plume when it reaches the ocean. Warrick *et al.* (2004b) suggest that the movement of Santa Clara River plume near the river mouth is strongly influenced by the river discharge inertia, i.e., the momentum induced by the mass flux from the river. These river plumes are also likely subject to buoyancy, wind and tidal forcing, which will dictate dispersal patterns and dynamics (e.g., Stumpf *et al.* 1993, Garvine 1995, Pinones *et al.* 2005, Whitney and Garvine 2005). Better understanding of plumes in the Southern California Bight is needed to track and understand the potential health and ecological implications of the discharged pollutants.

Finally, satellite-derived ocean color products have been valuable tools to investigate the lateral movement of southern California river plumes, and most of these investigations utilize turbidity or suspended-sediment products as proxies to track plumes (e.g., Mertes and Warrick 2001, Nezlin *et al.* 2005). Although these river plumes are commonly quite turbid, sediment mass balances suggest that little of the discharged sediment resides in the buoyant plume due to rapid settling near the river mouth (Warrick *et al.* 2004a). It is necessary and valuable, then, to evaluate which satellite-based measurements may best track the freshwater plumes.

Here we present the results of a multi-organization study to describe post-storm runoff plumes from the eight largest river systems in southern California. Each of these systems was assessed for up to five days following each of two storms during 2004 and 2005. We combine *in situ* and remotely sensed data to evaluate plume dispersal patterns and rates and the forcing function(s) responsible for these transformations. Emphasis is placed on identifying transport and transformations processes that could be generalized across systems and discharge events.

METHODS

The study involved sampling four geographic regions that represent the river mouths of the largest southern California watersheds (Figure 1). These regions included (from the north): the eastern Santa Barbara Channel (Santa Clara and Ventura Rivers); Santa Monica Bay (Ballona Creek); the San Pedro Shelf (Los Angeles, San Gabriel and Santa Ana Rivers); and the southern Bight (San Diego and Tijuana Rivers). These regions and river systems were chosen because they represented a broad distribution of watershed land use and river types (open space, agricultural and urban) and because they covered the broad geographic extent of southern California.

Here, we provide a summary of the methods used to investigate the river plumes; details of the data collection methods, quality assurance/quality control program, and raw data are published in the Bight'03 Water Quality Study Final Report (Nezlin *et al.* 2007a). The primary method of investigation was shipboard profiling of the plumes with an enhanced CTD system (conductivity, temperature, depth, dissolved oxygen, pH, transmissometer, chlorophyll fluorometer, and CDOM fluorometer), hereafter referred to as CTD+. Water turbidity was computed from transmissometer observations as the beam attenuation coefficient at 660 nm (hereafter referred to as beam-c). CDOM fluorescence was linearly calibrated with up to 100 ppb of quinine sulfate dehydrate (QSD). Water samples were obtained with 5-liter Niskin bottles attached to the CTD+ carousel and triggered remotely. Sampling occurred on regularly spaced grids for each region, which are shown in Figure 1. The primary intent of the grids was to sample the nearshore discharge areas and assess water quality there, not necessarily to track plumes as they advected away from the river mouth regions. Some stations were positioned further offshore so that they provided "non-plume" profiles for comparative purposes. Profiles were obtained to within 2 m of the seabed or to a depth of 60 m for sites deeper than 60 m. Water samples were taken at 1m water depth for most sites and at a sub-surface depth(s) below the buoyant plume for a limited number of sites. Samples were analyzed for total suspended solids, chlorophyll, macronutrients (Si, N, P), bacteria and toxicity. Here we focus primarily on the measurements of salinity, temperature and suspended solids; the remaining data will be presented in subsequent publications.

The sampling plan called for sampling two events across each region, and three days of sampling during each event as conditions permitted (to be nominally conducted on Days 1, 3 and 5 following the discharge peak). One ship was dedicated to each region, except for the San Pedro Shelf where three monitoring vessels were utilized coincidentally and the Tijuana River where two ships were used. However, not all sites were sampled in the proposed fashion largely due to limitations from weather and sea-state (Figures 2 and 3). Further, sampling of the Tijuana River plume was conducted during an event not sampled at the remaining sites (Figure 3), due to a storm that was directed largely toward the southern portion of the study area. The resulting sampling effort consisted of 574 CTD+ stations and 705 water samples during a total of 36 ship-days.

Ancillary data were also collected or utilized to supplement the shipboard sampling. River discharge observations were obtained from United States Geological Survey (USGS) gauging stations, stations operated by Los Angeles County Department of Public Works (LACDPW), and a daily discharge gauge for the Tijuana River operated by the International Boundary and Water Commission (Figure 1). USGS sites provided discharge rates at 15-minute intervals and included the following sites: Ventura River (USGS station 11118500), Santa Clara River (sum of USGS 11113000 and 11109000), Santa Ana River (USGS 11078000), and the San

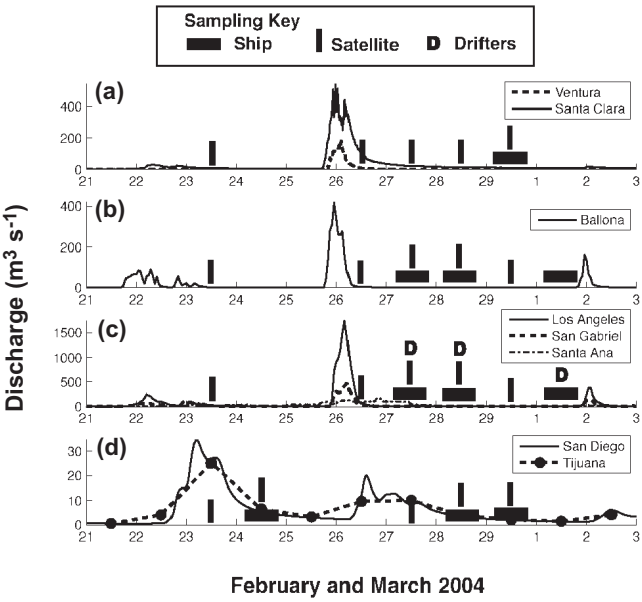

Figure 2. Discharge and sample timing for the first event sampled.

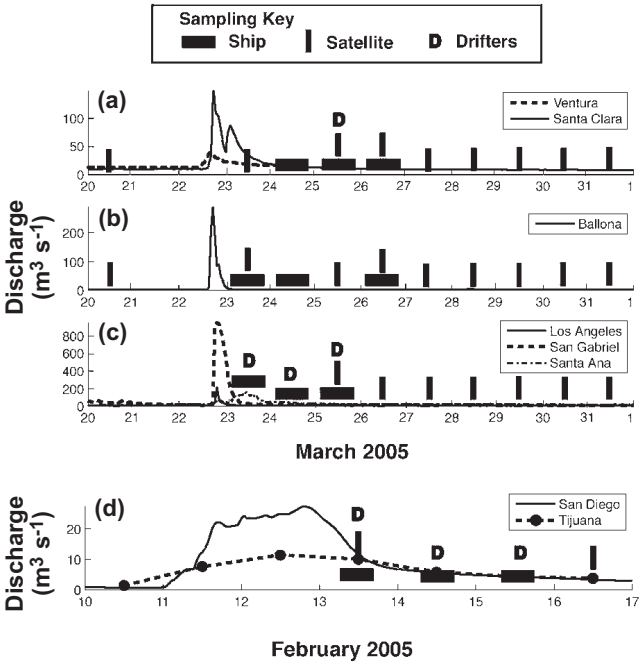

Figure 3. Discharge and sample timing for the second event sampled. Note that the Tijuana River (d) was sampled on a different schedule than the other systems (a - c).

Diego River (USGS 11023000). LACDPW stations provided discharge rates at 1-hour intervals and included Ballona Creek (station F38C), Los Angeles River (F319), and San Gabriel River (sum of F354 and F42B).

Hourly averaged wind speed and direction were obtained from a number of the NDBC buoys, including 46053 (East Santa Barbara Channel), 46025 (Santa Monica Basin) and 46086 (San Clemente Basin; Figure 1). These data were used to evaluate the influence of wind speed and wind stress on the river plumes, where wind stress (τ_w) was computed by the iterative quadratic formulation of Large and Pond (1981) for each hourly measurement.

Satellite ocean color imagery was obtained from the NASA Moderate Resolution Imaging Spectroradiometers (MODIS) on the Aqua and Terra platforms. These sensors provided daily or better coverage of the Southern California Bight study area, although clear-sky images were obtained for only about half of the days of interest and largely on days following river discharge peaks (Figures 2 and 3). Here we present "true-color" representations of the multi-band data provided by each sensor to qualitatively track the combined sediment, CDOM and phytoplankton manifestations of the buoyant plume. Quantitative satellite-derived products (e.g., a412, bb551, chlorophyll-a) are discussed in a companion paper to better understand the impacts of the plumes.

Surface currents were obtained from the tracks of high resolution drifting buoys drogued at 1 m depth (Ohlmann *et al.* 2005). The drifters, with known water following capabilities, record their position every 10 minutes using GPS. Individual drifter tracks give an indication of how river plume water moves in the coastal ocean. The relative motion of drifter pairs allows for quantification of plume dispersion. Sets of up to 21 drifters were released within the river plumes just beyond the surf zone at the Santa Clara River (1 day), Santa Ana River (6 days) and the Tijuana River (3 days). The drifters were typically released in the morning and retrieved before sunset. If a drifter was clearly about to enter the surf zone, thus being subject to damage, it was retrieved and re-deployed offshore of the river mouth. The individual drifter tracks along with flow information determined from the position data can be viewed on the web at (www.drifterdata.com).

Lastly, high-frequency (HF) radar was used for the Santa Clara/Ventura and Tijuana River systems to track surface currents during the sampled events. The northern HF radar array is part of the UCSB Ocean Surface Currents Mapping Project, which consists of 4 sites to characterize surface currents in the Santa Barbara Channel (http://www.icess.ucsb.edu/iog/realtime/index.php). The Tijuana River region is included in the San Diego Coastal Ocean Observing System (SDCOOS) administered by Scripps Institution of Oceanography (SIO; http://sdcoos.ucsd.edu/).

Plume Freshwater Volume Calculations

The volume of freshwater residing in the plumes each day can be estimated by spatially integrating the reduced salinity measurements across the sampling grid (*cf.* Gilbert *et al.* 1996). For each profile a freshwater fraction (F_{fw}, in m of freshwater) was calculated by:

$$F_{fw} = \int_z \{[S_0 - S(z)] \,/\, S_0\}\, dz \qquad (1)$$

where S_0 is a reference salinity (in psu), S is the measured salinity (in psu) at depth z (in m). We selected S_0 from the profiles outside of the influence of the plumes either laterally or from the waters

underlying the plumes. Unique values of S_0 were calculated for each event within each of the 4 regions; however similar values of 33.0 psu during 2004 and 33.1 psu during 2005 were obtained for all of the sites. Uncertainty in these values of S_0 was approximately 0.1 psu, which induced less than 10% error across the freshwater volumetric calculations. To compute freshwater volumes we assumed that F_{fw} changed linearly between each station. Further, if $S_{(z)}$ was greater than S_0 for any depth, we set the quantity [S_0 - $S_{(z)}$] equal to zero.

Results

General Plume Patterns

Two events were sampled for each river mouth region during the winters of 2004 and 2005 (Figures 2 and 3). The 2004 event resulted in approximately twice the discharge rates and volumes of the 2005 events. Both events were modest sized, however, as the peak discharges were equivalent to approximately 2- and 1.5-year recurrence interval events based on longer discharge records. Therefore, the sampled events were slightly smaller than the "annual" recurrence events (i.e., the 2.3-year recurrence event) for each river.

Ship-based sampling occurred within one to five days of the discharge events (Figures 2 and 3). However, the 2004 event was generally more difficult to sample due to sea-state. Sampling for the Santa Clara River during 2004 was only possible on the fourth day following peak discharge (Figure 2a). Sampling of Ballona Creek was very limited on February 27, 2004 due to sea-state and only 4 stations were sampled. The 2005 efforts resulted in sampling immediately following discharge and for three full days of sampling for each region (Figure 3).

Two representative profiles of salinity and beam-c from the Tijuana River plume are shown in Figure 4. Both profiles were obtained approximately four km from the river mouth on February 14, 2005, and both show a freshened buoyant plume in the upper three to five m of the water column. Similar plume observations were obtained throughout the other study areas. These buoyant surface plumes also had elevated beam-c compared to waters immediately underneath the plume (Figure 4). The waters immediately above the seabed differ considerably, however: the shallower station (Figure 4b) reveals an ~5 m nephloid layer above the seabed, which was a common characteristic of many of the shallow profiles,

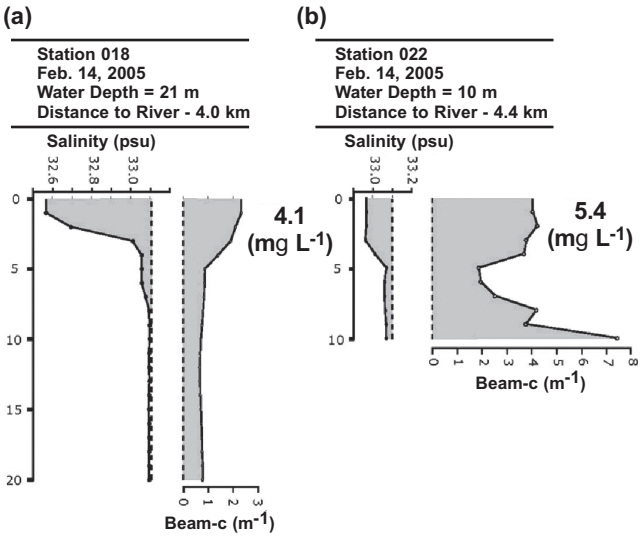

Figure 4. Salinity, beam-c and TSS data from CTD casts taken on February 14, 2005 offshore of the Tijuana River. TSS concentrations for 1 m water depth samples. Dashed lines represent reference levels of 33.1 psu salinity and 0 m^{-1} beam-c.

while the deeper profile did not (Figure 4a). It is instructive, however, to also contrast the buoyant plumes: the deeper station (Figure 4a) had lower salinity (i.e., more freshwater) while having lower suspended sediment (i.e., beam-c and TSS) than the shallow station (Figure 4b). This suggests that the river water and sediment were not mixing in a simple conservative manner with respect to a single river endmember water type. Below we show that this one observation from the Tijuana River plume was typical of a generally poor relationship between salinity and sediment concentration in stormwater plumes over the entire Southern California Bight.

Spatial mapping of the salinity and beam-c data from each site revealed synoptic characteristics of the buoyant plume properties. For example, data from Ballona Creek on February 28, 2004 show a buoyant plume with lowest salinities immediately offshore of the river mouth, and these low salinities continue to the southern side of the river mouth, which is in the opposite direction of Coriolis influence (Figure 5a). In contrast, the highest beam-c on the same day was measured close to shore and away from the river mouth (Figure 5b). The three-ship monitoring effort along the San Pedro Shelf on March 25, 2005 revealed that low salinity/high beam-c waters extended many kilometers along- and across-shore from the river mouths (Figure 6). Further, it appears that a portion of this broad plume

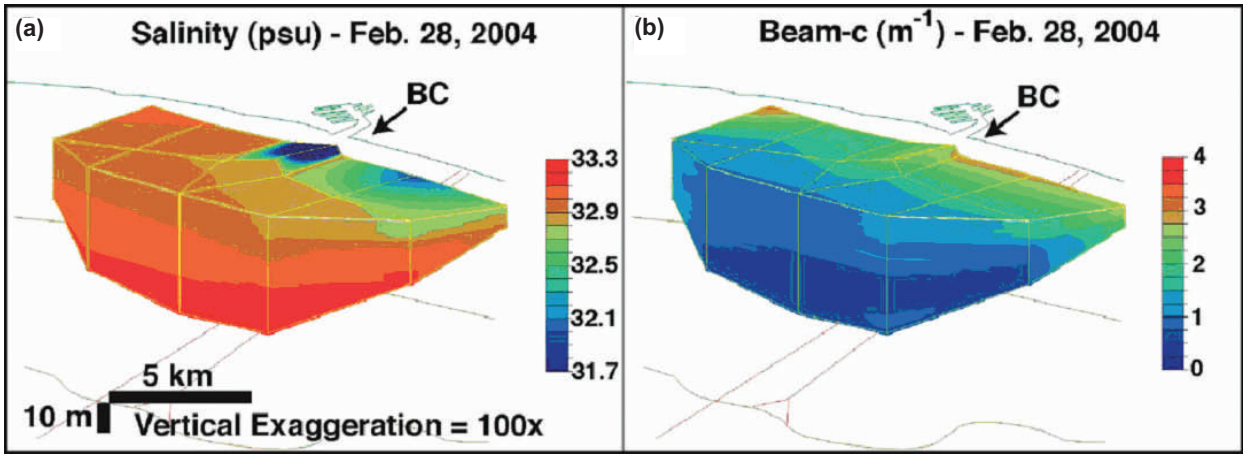

Figure 5. Three-dimensional presentation of salinity and beam-c data offshore of Ballona Creek (BC) showing the freshened and turbid river plume waters along the sea-surface. Linear interpolation has been used to estimate parameter values between stations, which are shown with vertical yellow lines and line intersections along the water surface.

was detached from the coastline, because two regions of low salinity and high turbidity on this date were observed approximately five km offshore of the coast and laterally offset from the river mouths (Figure 6).

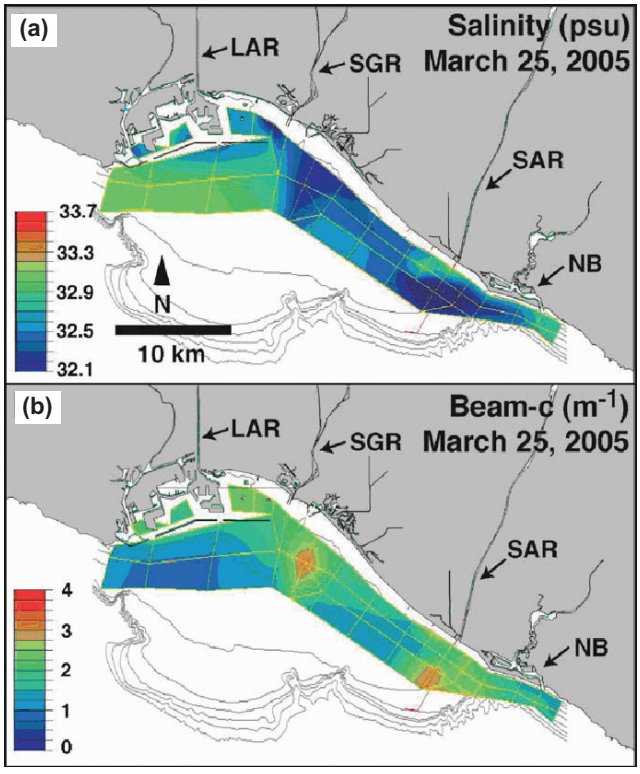

Figure 6. Surface measurements of salinity and beam-c data from the San Pedro Bay on March 25, 2005. Linear interpolation has been used to estimate parameter values between stations, which are located at the intersections of the yellow lines. LAR = Los Angeles River; SGR = San Gabriel River; SAR = Santa Ana River; and NB = Newport Bay.

These two synoptic examples of plume salinity and turbidity (Figures 5 and 6) reveal another pattern consistent with all of the remaining sampling dates: although the sampling grids extended many kilometers along- and across-shore, low salinity plumes always extended beyond the geographical limits of the surveys. Thus, none of the surveys captured the "entire" extent of the river plume, as was anticipated.

Plume Freshwater Volume

Results of the volumetric calculations reveal that 10's of millions of cubic meters of freshwater could be accounted for within the survey limits (Tables 1 and 2). The greatest amounts of freshwater were consistently observed along the San Pedro Shelf portion of the study, which not only had the largest river discharge inputs (Figures 2 and 3) but also had a sampling area 2 - 20 times larger than the other sites (Tables 1 and 2). The volume of freshwater observed within the survey areas generally decreased with sample date, which suggests that plume waters moved outside of the sampling grids, rather than simply mixing down into the water column.

A couple of exceptions to this multiple-day pattern exist, and they can largely be accounted for by changes in the sampling grids. For example, only a limited sampling effort was possible on the San Pedro Shelf on March 24, 2005 (31.4 km^2 versus the typical ~230 km^2), which resulted in much less freshwater observed (Table 2). The 2005 data from the Tijuana River plume suggested that freshwater volume in the plume doubled on the last day of sampling (Table 2), however the sampling grid was sig-

Table 1. Integrated CTD survey results for the 2004 surveys.

	Santa Clara River	Ballona Creek	San Pedro Shelf	San Diego River	Tijuana River
Area Surveyed (km^2)					
24-Feb-04	--	--	--	10.2	35.9
27-Feb-04	--	*(1)*	155.9	--	--
28-Feb-04	--	35.2	291	--	114.5
29-Feb-04	76.8	--	--	--	114.5
1-Mar-04	--	35.2	291	--	--
Integrated Fresh Water (m^3)					
24-Feb-04	--	--	--	79,501	1,362,000
27-Feb-04	--	*(1)*	27,512,000	--	--
28-Feb-04	--	1,264,700	21,003,000	--	411,680
29-Feb-04	34,570		--	--	88,899
1-Mar-04	--	321,870	16,503,000	--	--
Surface Plume Sediment Mass (t)					
24-Feb-04	--	--	--	42	1,577
27-Feb-04	--	*(1)*	31,709	--	--
28-Feb-04	--	1,027	4,744	--	1,076
29-Feb-04	1,740	--	--	--	1,171
1-Mar-04	--	864	2,114	--	--
Ratio of Fresh Water to Sediment ($kg\ m^{-3}$)					
24-Feb-04	--	--	--	0.53	1.16
27-Feb-04	--	*(1)*	1.15	--	--
28-Feb-04	--	0.81	0.23	--	2.61
29-Feb-04	50.33	--	--	--	13.17
1-Mar-04	--	2.68	0.13	--	--

Notes: *(1)* data collection not adequate to spatially integrate.

nificantly altered on this date in an attempt to capture the presumably northward transporting plume. This modified sampling plan also resulted in capturing another reduced salinity plume from Mission Bay. Lastly, sampling of the Santa Clara River suggested increases in the freshwater plume volume with time (Table 2). Although this is correct, we note below that the portion of the river discharge flux actually observed in this plume was insignificant on all days.

The ratios between the observed plume freshwater volume and the river discharge volume were computed and are shown in Figure 7. We included an additional amount of river discharge for the third day of the 2005 Tijuana River observations equal to the San Diego River discharge because the ungauged watershed area discharging into San Diego Bay is approximately equivalent to the watershed area of the San Diego River.

A substantial portion of the river discharge volume was observed during most cruise dates, although these values typically decrease with sample date (Figure 7). Significant variability also exists across the study regions. As alluded to above, there was consistently negligible river water observed offshore of the Santa Clara River mouth (Figure 7). We suggest below that this river water was transported to the south of the sampling grid due to wind-dominated alongshore currents as discussed below. For Ballona Creek, San Pedro Shelf and Tijuana River, between 35 and 65% of the river water could be accounted for during the first day following a peak discharge date (Figure 7). Although these ratios appear relatively high compared to the remaining observations, they also suggest that roughly half of the river water had advected away from the sampling grids in the first day of plume formation. The rate of removal of freshwater from the sampling grids on subsequent days ranged 12% of the remaining water per day (San Pedro Shelf) to 80% per day (Tijuana River) for these three sites (mean ±std. dev. = 37 ±23% per day).

Table 2. Integrated CTD survey results for the 2005 surveys.

	Santa Clara River	Ballona Creek	San Pedro Shelf	Tijuana River
Area Surveyed (km^2)				
13-Feb-05	--	--	--	81
14-Feb-05	--	--	--	81
15-Feb-05	--	--	--	83.1
23-Mar-05	--	--	226.5	--
24-Mar-05	28.9	35.2	31.4	--
25-Mar-05	28.9	--	228.5	--
26-Mar-05	28.9	35.2	--	--
Integrated Fresh Water (m^3)				
13-Feb-05	--	--	--	1,918,000
14-Feb-05	--	--	--	1,645,400
15-Feb-05	--	--	--	3,536,000
23-Mar-05	--	--	23,270,000	--
24-Mar-05	21,800	2,805,000	1,322,000	--
25-Mar-05	35,190	--	11,754,000	--
26-Mar-05	51,440	1,661,000	--	--
Surface Plume Sediment Mass (t)				
13-Feb-05	--	--	--	960
14-Feb-05	--	--	--	602
15-Feb-05	--	--	--	1,539
23-Mar-05	--	--	5,894	--
24-Mar-05	4,133	273	575	--
25-Mar-05	1,014	--	2,207	--
26-Mar-05	939	60	--	--
Ratio of Fresh Water to Sediment ($kg\ m^{-3}$)				
13-Feb-05	--	--	--	0.5
14-Feb-05	--	--	--	0.37
15-Feb-05	--	--	--	0.44
23-Mar-05	--	--	0.25	--
24-Mar-05	189.59	0.1	0.43	--
25-Mar-05	28.82	--	0.19	--
26-Mar-05	18.25	0.04	--	--

Plume Sediment and CDOM Relationships

As noted above, patterns of salinity and sediment generally did not correlate well. A compilation of all total suspended-solids (TSS) and salinity samples shows that salinity explained very little of the variance in the TSS data across the region during the surveys ($R^2 = 0.02$; data not shown). In fact, the three highest measured concentrations of TSS (45 - 80 mg L^{-1}) occurred in waters with negligible freshwater. Salinity and beam-c also correlated poorly, and very little of the beam-c variance could be explained by salinity ($R^2 = 0.15$; data not shown). These poor relationships did not exist only for the data when considered in bulk, but also existed when individual sample days were considered for each river system (Figure 8). Although one sample date had excellent salinity-TSS correlation ($R^2 = 0.94$; Figure 8), we note that this was for the Santa Clara River during the 2004 sample date when little of the river water was observed (*cf.* Figure 7).

The fluorometer CDOM concentrations correlated much better with salinity than did either TSS or beam-c (overall $R^2 = 0.58$; mean of individual $R^2 = 0.56$; Figure 8). No significant ($p < 0.05$) relationships between sample date and CDOM correlation coefficients were found, although slight decreases in linear regression slope with sample date was observed in most data. The CDOM correlations were consistently poor for the Santa Clara River data ($R^2 = 0.32 \pm 0.14$), and this may be due to either the limited river water observed or actual variability in the river water characteristics. Much better CDOM correlations existed for Ballona Creek ($R^2 = 0.65 \pm 0.28$) and the San Pedro Shelf ($R^2 = 0.54 \pm 0.28$), while

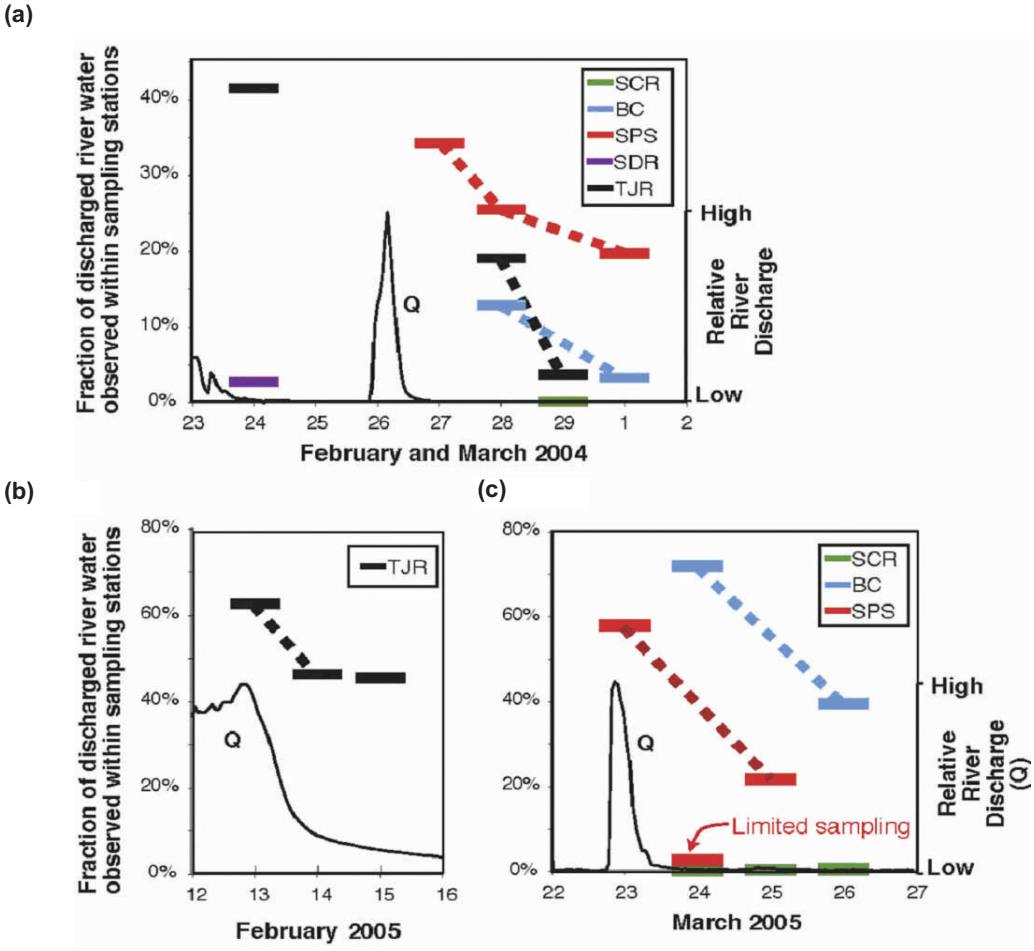

Figure 7. Integrated plume fresh water observed during the surveys as a proportion of the total event river discharge. Sites include: Santa Clara River (SCR), Ballona Creek (BC), San Pedro Shelf (SPS), San Diego River (SDR), Tijuana River (TJR). A discharge (Q) curve is also presented based upon the mean discharge shown in Figures 2 and 3. Note differences in scale between (a), (b), and (c).

CDOM fluorescence was not measured for the Tijuana River system. We discuss the implications of these observations to remote sensing of these river plumes in the Discussion section below.

Observations of Plume Transport

Results presented above suggest that plume freshwater was transported significantly beyond the sampled stations. Here we examine measurements of this transport from drifters, HF radar and satellite remote sensing. Ten drifter deployments within plumes revealed many different patterns of plume movement. For example, two contrasting observations from the Santa Ana River plume are shown in Figure 9. The majority of drifter observations were dominated by alongshore transport, which could exceed 30 cm s^{-1} (Figure 10). Across-shore currents were strongly correlated with alongshore currents but

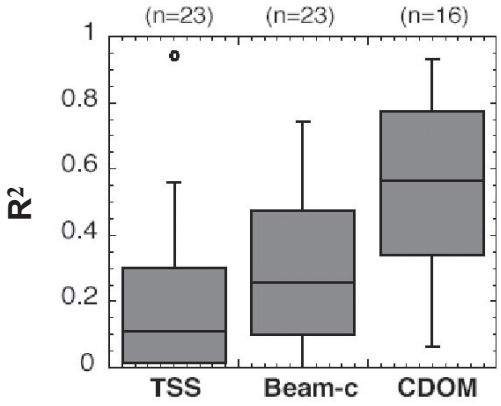

Figure 8. Box-plots of the correlation coefficients from site-specific linear regressions of TSS, beam-c and CDOM with salinity during each sampling date. Total number of regressions (n) differ because the Tijuana River plume was not sampled for CDOM. Boxes are defined by quartiles; lines show the limits of the data within 1.5 times the interquartile distance from the quartiles; and outliers are shown with circles.

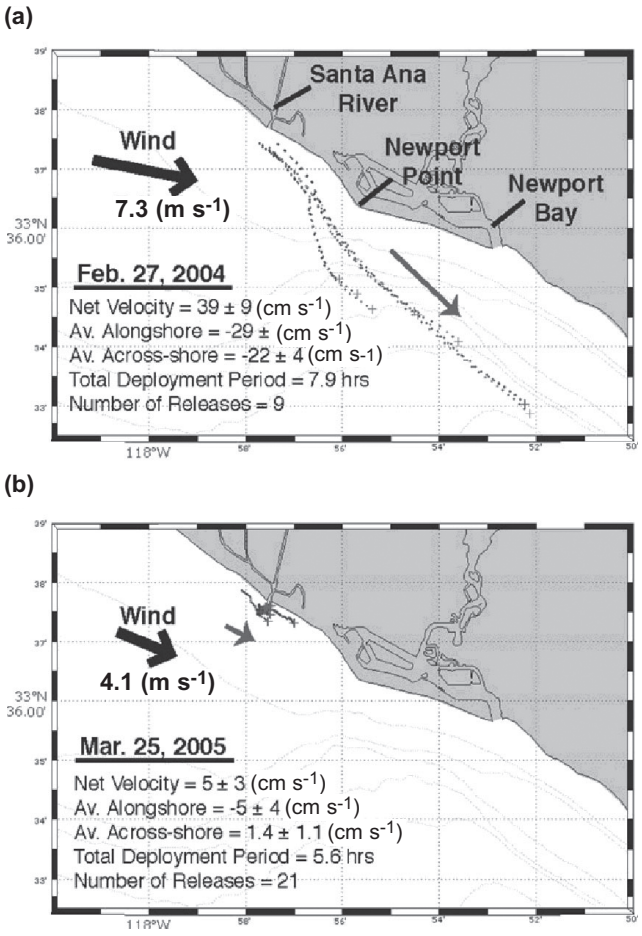

Figure 9. Drifter results from the Santa Ana River plume during contrasting advection conditions. Positions of each drifter are shown at 10-minute increments. Summary statistics for the releases shown in the lower left of each subfigure. Mean wind speed vectors shown for a 6-hour period of time prior to the middle of the observations from NDBC 46025.

were consistently smaller in magnitude (Figure 10). Rivers did not appear to influence the across-shore velocity as drifter trajectories were not deflected offshore immediately seaward of the river mouths, which was likely related to low river discharge rates on the drifter deployment days (*cf.* Figures 2 and 3).

Surface currents were also measured by HF radar arrays in two of the study regions. We spatially subsampled the surface current data into areas relevant to plume movement (Figure 11). For the Santa Clara River only a region immediately offshore of the river was sampled, while four regions were subsampled for the Tijuana River to evaluate the expected variability of circulation of this region (Figure 11). The variance of the hourly current measurements within each subsampled region was generally low, and mean hourly standard deviations were 12 cm s^{-1} for the Santa Clara, <6 cm s^{-1} for all nearshore Tijuana (I - III) and 9 cm s^{-1} for offshore Tijuana (IV). For all subregions, we calculated mean daily currents centered on local midnight to best represent total circulation between satellite imagery (obtained approximately at local noon) and to approximate the subtidal portions of the currents.

Compilations of some of the available HF radar, drifters and satellite imagery are shown in Figures 12 to 14. During and following the 2004 event, strong equatorward currents (>30 cm s^{-1}) were measured in both the Santa Clara River plume and the San Pedro Shelf regions (Figure 12). Satellite imagery obtained during this period revealed plume fronts from the Santa Clara River and San Pedro Shelf regions moving offshore and equatorward at rates (>30 km d^{-1}) consistent with the measured current directions (Figure 12).

During 2005 similar equatorward currents existed and persisted near the Santa Clara River mouth for at least 10 days as shown by HF radar data (Figure 13). For both events mean currents on the Santa Pedro Shelf were strongest (>30 cm s^{-1}) during the first day following river discharge (Figures 12 and 13). The equatorward currents offshore of the Santa Clara River mouth were clearly responsible for transporting the Santa Clara River plume toward the Santa Monica Bay for a period of at least a week (Figure 13). During this time long (~50 km) filaments of turbidity, CDOM and perhaps phytoplankton were observed originating near the Santa Clara River and extending into the outside of both Santa Monica and San Pedro Bays (Figure 13). Both HF

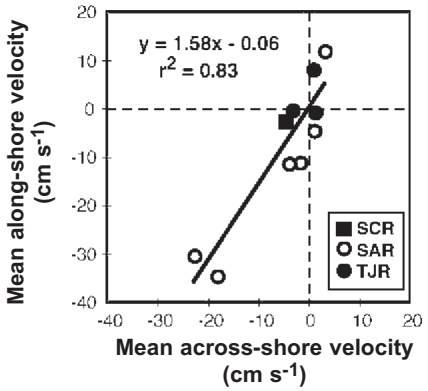

Figure 10. Mean alongshore and across-shore current velocities from river plume drifter deployments. Alongshore defined as poleward (positive) and equatorward (negative), and across-shore defined as onshore (positive) and offshore (negative). SCR = Santa Clara River; SAR = Santa Ana River; and TJR = Tijuana River.

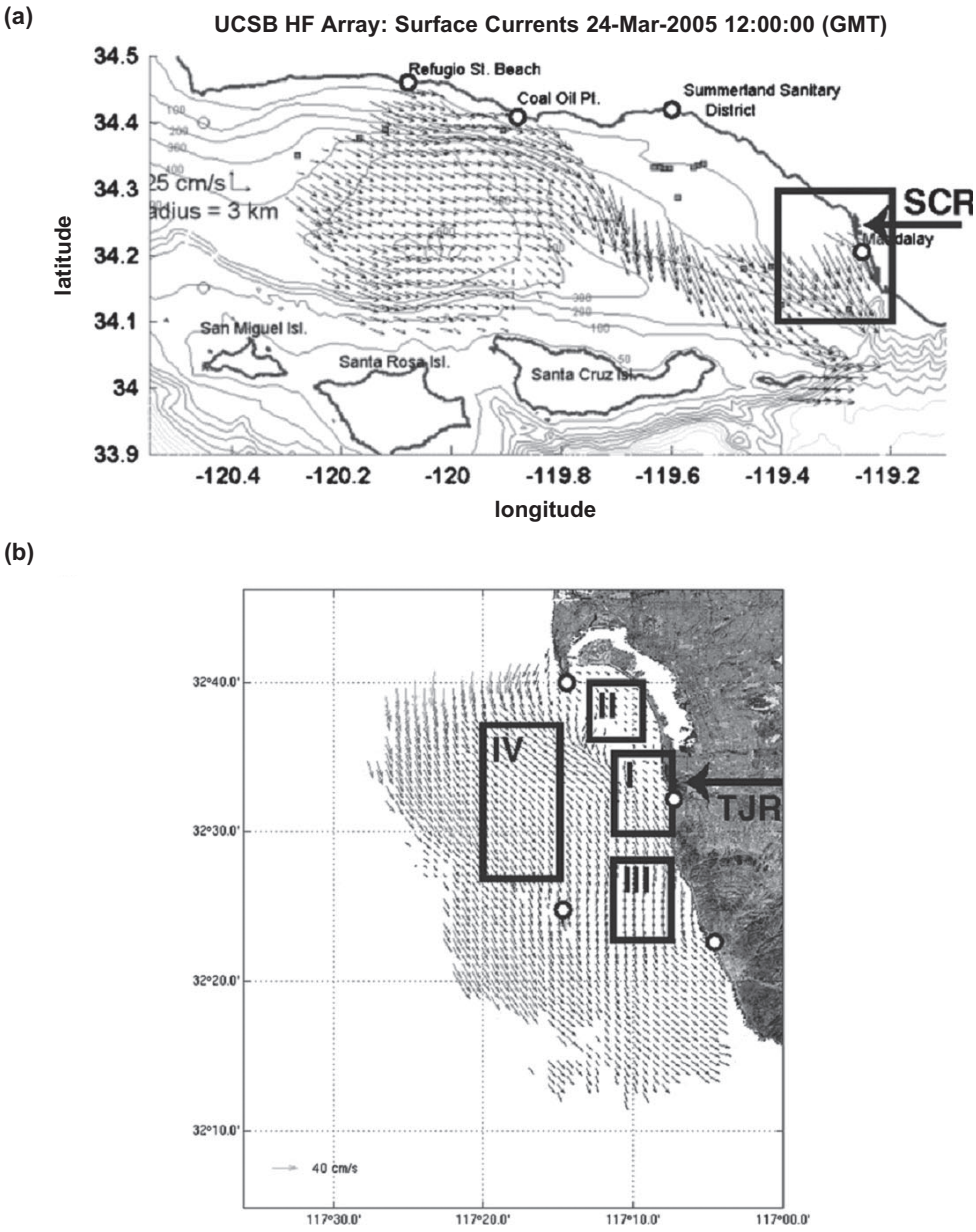

Figure 11. Example mean daily surface currents from the two HF Radar surface current arrays. Inset boxes show the regions directly offshore of the river mouths for which mean currents were calculated (see text). Surface currents near the Santa Clara River mouth (SCR) from the UCSB HF Radar array (a). Surface currents near the Tijuana River mouth (TJR) from the SIO HF Radar array (b).

radar and satellite data suggest that advection of this plume averaged 15 - 45 cm s^{-1} each day (mean = 26 cm s^{-1}), which is fast enough to transport Santa Clara River water into the center of Santa Monica Bay in two to six days (mean = 3.5 days).

We note that plumes from Ballona Creek during both events were much more difficult to identify with the satellite imagery than from either the Santa Clara River or San Pedro Bay regions (Figures 12 and 13), which may be due to the small size and/or quick dispersal of this plume.

Satellite and HF radar observations for the Tijuana River plume show that circulation in the Tijuana River plume region was complex during the events (Figure 14). A counterclockwise eddy was observed south of Point Loma during February 23 - 26, 2004, which changed to southerly flow conditions on February 27 - 29, 2004. We note that the mean daily alongshore currents furthest offshore of the Tijuana River (region IV, Figure 11b) explained 60%, 51% and 76% of the alongshore mean current variance in three inshore regions (I – river mouth,

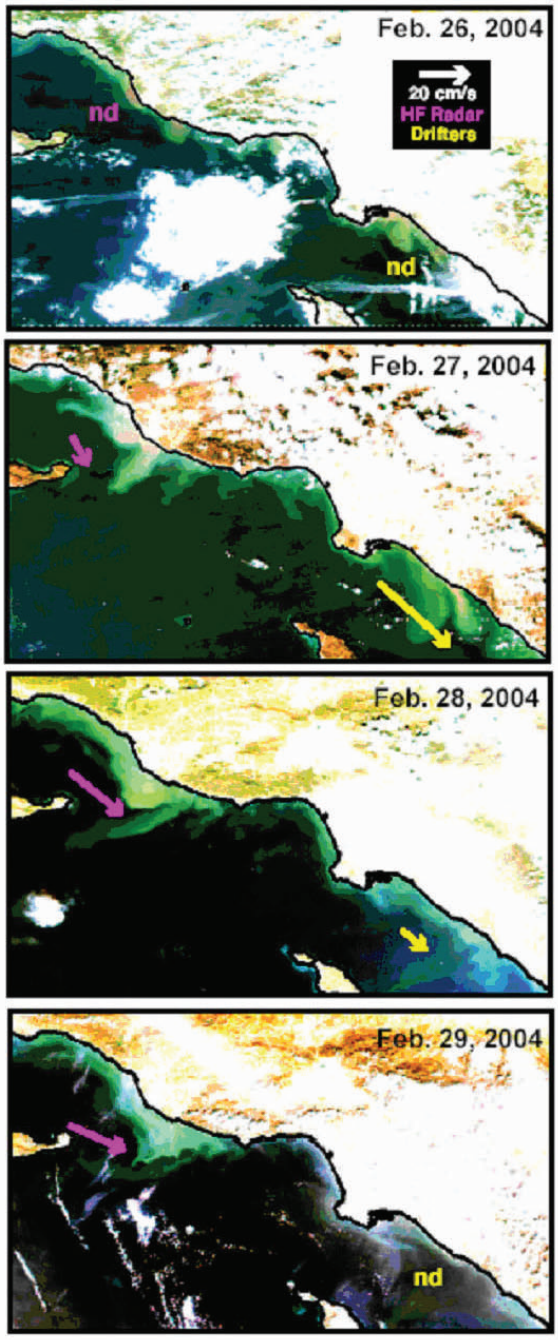

Figure 12. Four-day time series of true-color satellite imagery from MODIS Aqua and Terra of the northern portion of the study area during the 2004 sampling period. Velocity vectors are shown from the HF Radar observations of the Santa Clara River plume area (pink) and drifter releases offshore of the Santa Ana River (yellow). Days without velocity observations are denoted with "nd".

II – north of mouth, III – south of mouth), respectively during the 2004 and 2005 events. Thus, although there is spatial variability in the currents, there was relatively strong coherence in the current patterns during the events sampled.

Discussion

Plume Sediment and CDOM Relationships

Although the relations between salinity and sediment concentrations were poor, the TSS and beam-c data were adequate to estimate the mass of sediment in the buoyant river plumes. To estimate sediment mass we used a similar spatial integration method as used in the freshwater volume calculations above. For each CTD+ station we computed the plume sediment mass (*Sed*, in g m^{-2}) by:

$$Sed = \int_z \alpha \, [C_p(z) - C_O] \, dz \qquad (2)$$

where C_p is the measured beam-c profile (in m^{-1}) with respect to depth (z, in m) within the buoyant plume, C_O is the ambient ocean water beam-c defined from our data to be one m^{-1} (*cf.* Figures 4 - 6), and α is a coefficient (in mg-m L^{-1}) converting beam-c to suspended-sediment concentration. As noted, calculations were limited to the surface buoyant plume by limiting the *Sed* calculations to portions of the profiles with salinities less than the plume thresholds discussed above (33.0 and 33.1 psu). Further, if $C_p(z)$ was less than C_O we set $[C_p(z) - C_O]$ equal to zero.

To calculate α we compared the TSS and beam-c data from the surface water samples. A significant linear relationship forced through the origin was found between these variables, and beam-c explained almost half the variability in TSS. This relationship was much better during 2004 than 2005 (R^2 of 0.61 and 0.39, respectively), although the slopes during these two periods were not significantly different ($p < 0.05$). The correlation differences between TSS and beam-c may be a result of: (1) differences in sampling technique – bottle samples versus *in situ* optical samples, and/or (2) grain-size variability in the sediment, which is known to induce significant variability in α (Baker and Lavelle 1984). Although it is difficult to assess the causes of the variability in the data, we note that the value of α derived from this data (1.65 mg-m L^{-1}) is both near the suggested value of 1.4 mg-m L^{-1} for clay and fine silt particles by Baker and Lavelle (1984) and consistent with data from the Santa Clara River plume reported by Warrick *et al.* (2004a). Lastly, we note that relationship between F_{fw} and *Sed* was also very poor ($R^2 = 0.01$; data not shown), which is consistent with other results discussed above.

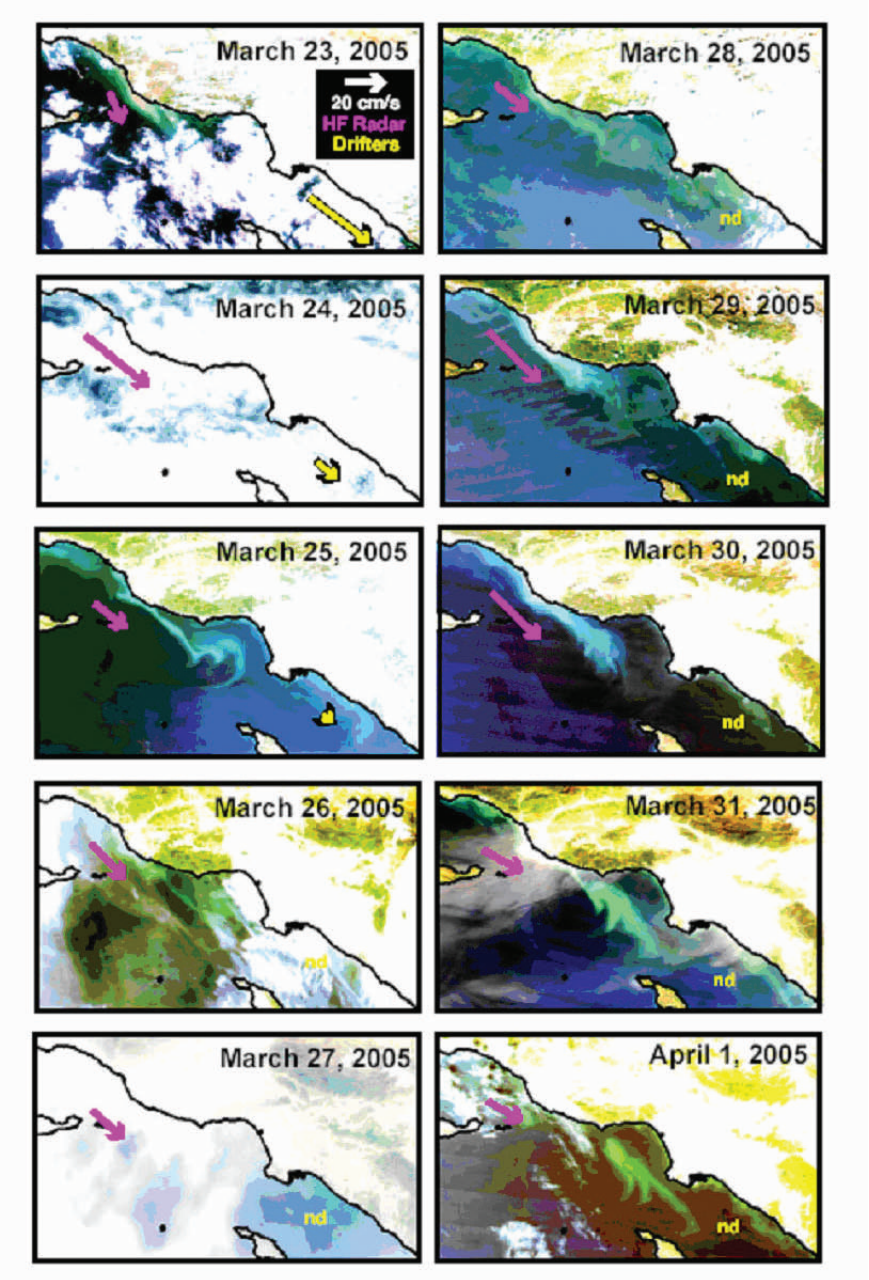

Figure 13. Ten-day time series of true-color satellite imagery from MODIS Aqua and Terra of the northern portion of the study area during the 2005 sampling period. Velocity vectors are also shown from the HF Radar observations of the Santa Clara River plume area (pink) and drifter releases offshore of the Santa Ana River (yellow). Days without velocity observations are denoted with "nd".

The calculated mass of sediment contained within the buoyant plumes ranged from O(10) to O(10,000) t on the various sampled dates, and sediment mass within each sampled plume generally decreased with sampling date (Tables 1 and 2). The river suspended-sediment concentration, if sediment mixed conservatively, was estimated by the ratio of observed plume sediment to plume fresh water (Tables 1 and 2). This sediment:water ratio was 0.1 to 1.2 kg m^{-3} for the first day of sampling from all of the systems but the Santa Clara (the Santa Clara had very little water sampled and the first day ratios in excess of 50 kg m^{-3}). We note that actual river suspended-sediment concentrations during these events were likely ~10 times higher than these ratios (Brownlie and Taylor 1981, Warrick and Milliman 2003). Further, although thousands of tonnes of sediment were estimated in the plumes (Tables 1 and 2), these amounts were consistent to other measurements of southern California river plumes (Mertes and Warrick 2001) and were considerably less than the hypothetical amounts of sediment flux from such

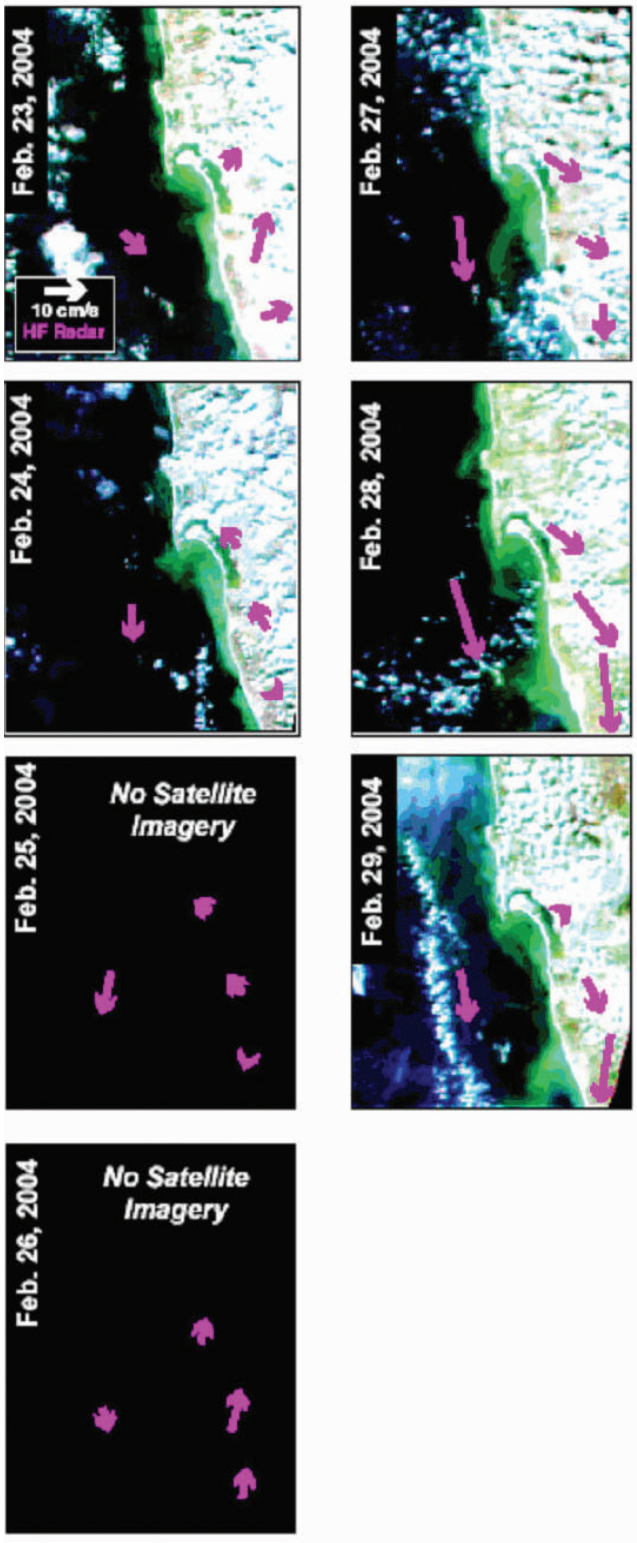

Figure 14. True-color satellite imagery from MODIS Aqua and Terra of the southern portion of the study area during the 2004 sampling period. Mean daily velocity vectors are also shown from the HF radar observations of the Tijuana River plume area (pink). Vectors have been placed on land immediately adjacent to the sampled regions so that the coastal plumes are not obscured.

events on the rivers (Brownlie and Taylor 1981). Thus, we suggest that at least 90% of the river suspended-sediment was not observed on the first day of sampling, likely due to high rates of particle settling (*cf.* Warrick *et al.* 2004a).

During the subsequent days, both increases and decreases were observed in the sediment:water ratios (Tables 1 and 2), which suggests that both losses and gains of sediment occurred in the sampled plumes. Gains were especially apparent in the Tijuana River system (Table 1).

Transport Forcing

In this section we examined a number of plume transport forcing parameters to evaluate why the plumes transported in they manner they did. Our techniques closely follow those of Garvine (1995), Geyer *et al.* (2000), Fong and Geyer (2002), and Whitney and Garvine (2005).

First, the baroclinic height anomaly (h_f) was calculated assuming hydrostatic pressure with the baroclinic pressure anomaly (P_f), such that,

$$h_f = P_f / g \rho_0 \qquad (3a)$$

where

$$P_f = g \int_h [\rho_0 - \rho(z)] \, dz \qquad (3b)$$

and g is the gravitational constant, ρ_0 is the ambient seawater density, $\rho(z)$ is the density at depth z, and h is the total water depth. The maximum hf for each cruise was consistently measured on the first day of sampling and ranged between 0.0 and 1.7 cm across the sites (Table 3). Values of h_f were consistently lower for the Santa Clara River plume than for the remaining sites.

Second, the baroclinic velocity anomaly (u_f) provides an estimate for the initial plume velocity associated with buoyancy forcing at the river mouth and was computed using Bernoulli's equation and h_f ,

$$u_f = (2 \, g \, h_f)^{0.5} \qquad (4)$$

The maximum values of this baroclinic velocity were generally 20 - 55 cm s^{-1} during each cruise (Table 3).

Table 3. Plume forcing statistics from the CTD+ casts during 2004 and 2005.

	Santa Clara River	Ballona Creek	San Pedro Shelf	San Diego River	Tijuana River
Maximum salinity anomaly (cm)					
2004 cruise	1	26	58	5	7
2005 cruise	7	27	32	n.d.	14
Maximum baroclinic height anomaly (cm)					
2004 cruise	0.01	0.73	1.67	0.25	0.27
2005 cruise	0.18	1.16	1.22	n.d.	1.57
Maximum baroclinic velocity anomaly (cm s^{-1})					
2004 cruise	4.8	37.9	57.3	21.9	23.1
2005 cruise	18.6	47.6	48.8	n.d.	55.5
Geostrophic Velocity (cm s^{-1})					
2004 cruise	0.1	5.7	13.1	1.9	2.1
2005 cruise	1.4	9	9.5	n.d.	12.3
Wind stress index (|Ws|)					
Peak discharge	0.3–0.8	0.4–0.6	0.4–0.5	0.4–0.6	0.4–0.6
Peak wind	1.8	>2	1.5	1.6	1.6
Linear slope of wind– current correlation					
Mean	0.039	n.d.	0.033	n.d.	0.027
95% confidence interval	0.013	n.d.	0.016	n.d.	0.006

If the plumes resulted in geostrophic momentum balances, Fong and Geyer (2002) suggest that the alongshore velocity of this transport can be approximated by:

$$v = g' h_0 / f L \quad (5)$$

where g' is the reduced gravitational constant resulting from the plume (equivalent to $g\Delta\rho/\rho_0$), h_0 is the thickness of the plume nearest the coast, f is the Coriolis parameter (~8.2 x 10^{-5} s^{-1}) and L is the plume width offshore of the coastline. Using maximum values for g' and h_0 for each cruise and assuming L was O(10) km, geostophic velocities were computed to be O(10) cm s^{-1} (Table 3). We note that these velocities would be directed poleward, which is both smaller and in the opposite direction of the majority of observations presented here (Figures 12 - 14).

We next looked into the effects of winds on the buoyant river following a number of previous studies (e.g., Chao 1988, Munchow and Garvine 1993, Kourafalou *et al.* 1996, Geyer *et al.* 2000, Whitney and Garvine 2005). We examined both wind speed and wind stress, and wind speed provided the best correlations with plume velocity observations, consistent with the theory and observations presented by Garvine (1991) and Whitney and Garvine (2005). Mean alongshore currents measured by the drifters were significantly correlated to local alongshore wind speed (R^2 = 0.66, p <0.01; Figure 15). Maximum correlation was found for the mean winds occurring during the 6-hour prior to the middle of the drifter release period.

Stronger correlations were found between mean daily wind stress and mean daily plume velocity immediately offshore of the river mouths from the HF radar data (Figure 16). High correlations were found at zero lag for 24-hour averages (R^2 = 0.68 - 0.71), but peak correlations occurred for mean 24-hour winds that were lagged by three hours compared to

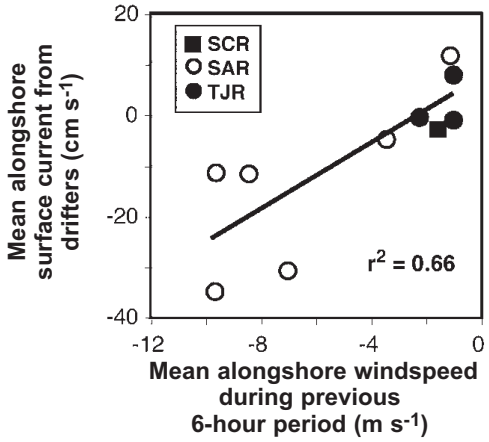

Figure 15. The relation between alongshore wind speed and mean alongshore surface currents measured for drifters. Maximum correlation occurs for the mean wind stress during the six hours prior to the deployment. Alongshore defined as poleward (positive) and equatorward (negative). Rivers plumes monitored include the Santa Clara River (SCR), Santa Ana River (SAR) and Tijuana River (TJR).

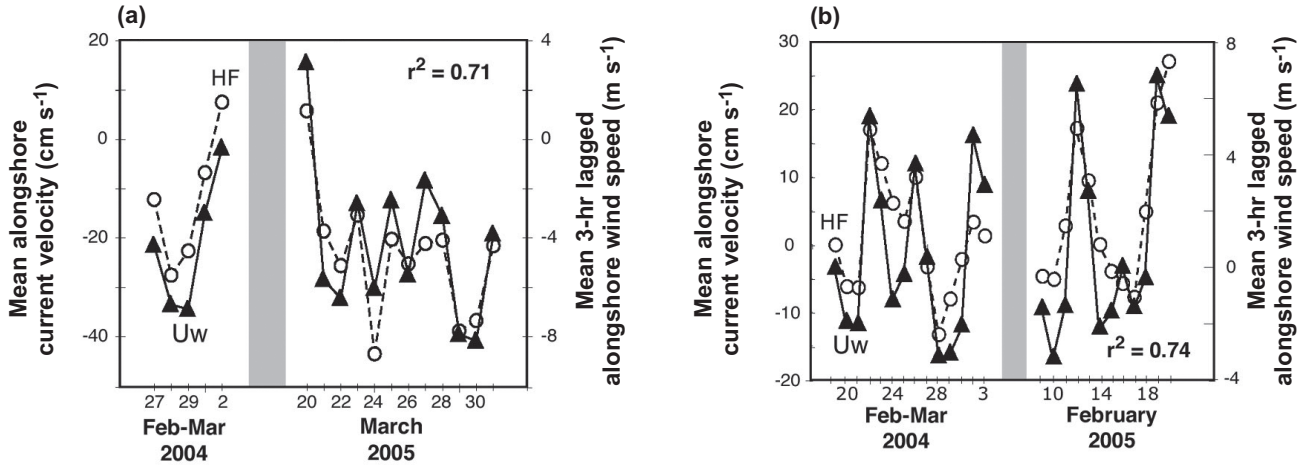

Figure 16. The relation between mean daily alongshore wind speed (▲) and mean daily surface currents of river plumes from HF radar (○) during sampled events. Santa Clara River plume with 24-hour mean wind speed from the NDBC East Santa Barbara Channel buoy (46053) lagged by a 3-hour preceding period (a). Tijuana River plume with 24-hour mean wind speed from the NDBC San Clemente Basin buoy (46086) lagged by 3 hours (b). Correlation coefficients given for the linear regression between currents and winds. Alongshore defined as poleward (positive) and equatorward (negative).

currents (R^2 = 0.71 - 0.74; Figure 16). This observation is consistent with a multiple hour lag for maximum correlation in wind-plume response by Munchow and Garvine (1993) and Geyer *et al.* (2000). For the regions immediately offshore of the Santa Clara and Tijuana river mouths, mean daily wind stress explained 71 - 74% of the alongshore surface current variance and captured most of the temporal shifts in these currents (Figure 16). Across-shore surface currents were somewhat poorly correlated with wind speed (maximum R^2 = 0.28 - 0.44, data not shown).

Further evaluation of the influence of wind can be provided by a framework suggested by Whitney and Garvine (2005). They propose that the wind stress index (W_s) can determine whether a plume's along-shelf flow is wind- or buoyancy-driven, where W_s is the ratio of buoyancy-driven velocity (u_{dis}) and the wind-driven alongshore velocity (u_{wind}). The first variable can be evaluated by either considering a two-layer system in geostrophic balance, which may be reduced to:

$$u_{dis} = K^{-1} (2\, g'_r\, Q\, f)^{1/4} \qquad (6)$$

where K is the dimensionless current width (or Kelvin number), which is ~1 for southern California plumes (Warrick *et al.* 2004b), g'_r is the reduced gravity of the river water (~0.24 m s^{-2} assuming 32 psu ambient seawater and 0 psu river water both at 10ºC), Q is the volumetric river discharge rate, and f is the Coriolis parameter, or by using Equation 4 to solve for u_f if the plume is not geostrophic. Assuming a barotropic wind response, a steady state momentum balance between wind stress and bottom stress, and quadratic drag laws, Whitney and Garvine (2005) suggest that u_{wind} can be estimated by:

$$u_{wind} = \{(\rho_{air}/\rho)\,(C_{10}/C_{Da})\}^{1/2}\; U \qquad (7)$$

where ρ_{air} and ρ are the density of air and seawater, C_{10} and C_{Da} are the drag coefficients for the air-sea boundary and the seabed, and U is the alongshore component of the wind speed. It can be shown that u_{wind} is equal to ~0.0265U under the assumptions given above (Whitney and Garvine 2005). When the absolute value of W_s is less than one, a river-induced buoyancy current should dominate. However when W_s is greater than one, the plume should be dominated by wind-driven flow. Upwelling-favorable winds will arrest or, perhaps, reverse a buoyant geostrophic coastal current, whereas downwelling-favorable winds will enhance the current.

Using this framework, we computed W_s for the time series of daily mean discharge and wind records surround the sampled events. On peak days of river discharge $|W_s|$ ranged between 0.3 and 0.8 (Table 3).

Peak winds often occurred within 1 - 3 days after the peak discharge, during which $|W_s|$ ranged from 1.5 to over 2, suggesting wind-driven flow (Whitney and Garvine 2005). If the assumptions made above hold, then the linear slope between U and u_{wind} should be approximately 0.0265. Using data presented in Figures 15 and 16, we computed linear slopes between winds and currents that were somewhat higher but statistically indistinguishable from this theoretical value (Table 3).

Finally, we computed the wind strain timescale (t_{tilt}), which is defined by the time is takes for Ekman transport to either compress a plume toward the shoreline during downwelling winds or expand a plume offshore by upwelling winds by a scale of 2 (Whitney and Garvine 2005), and can be approximated by:

$$t_{tilt} = (K\ R\ h_1\ \rho f) / (16\ |\tau_{sx}|) \qquad (8)$$

where K is approximately 1 (Warrick *et al.* 2004b), the internal Rossby radius (R) is approximately 104, the plume thickness (h_1) is ~3 m, ρ is ~1024 kg m^{-3}, and the alongshore wind stress (τ_{sx}) is calculated with the quadratic drag laws described above. Using Equation 8, t_{tilt} values for wind speeds of 2, 4 and 8 m s^{-1} were computed to be 8, 2 and 0.5 hours, respectively. Thus, for the wind speeds typically observed during and immediately following river discharge events (*cf.* Figures 16 and 17), the effect of wind occurs on time-scales much shorter than a day.

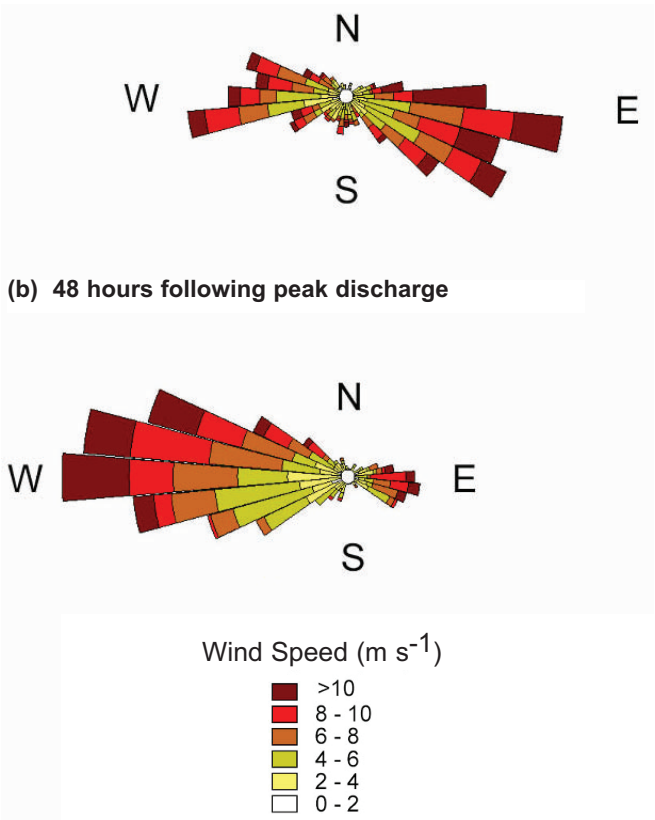

Figure 17. Wind rosettes from the East Santa Barbara Channel (NDBC 46053) during the 48 hours prior to and following peak discharge in the Santa Clara River from 15-minute discharge data. Wind is oriented to the direction from which the wind originated and was compiled for the 18 events in excess of 25 m^3 s^{-1} during the period overlapping records (1994 - 2004).

General Plume Patterns

Previous studies have established, primarily through the use of satellite imagery, that southern California river plumes are transported 10s of kilometers offshore. Our study indicates that alongshore movement of these plumes can be more prevalent than across-shore movement. Mean daily alongshore plume advection, as measured by drifters, HF radar and satellite was as high as 50 cm s^{-1}, suggesting that contaminants discharged from a river system can be quickly transported to coastal waters offshore of adjacent basins. This was especially apparent for the Santa Clara River plume, which was observed to extend toward Santa Monica Bay during all of our observations.

The plumes were also found to retain their integrity as they advected along the coast. While the salinity signature of the river discharge changed dramatically within the first kilometer of mixing with ocean water (i.e., inshore of our ship measurements), the plumes were clearly distinguishable as a water mass for at least five days following a storm. This distinction was apparent in both lateral and vertical dimensions, extending 10s of kilometers and several meters, respectively. Unfortunately we could not calculate rates of vertical mixing with the CTD+ data, largely because of the strong lateral movements that prevented resampling of water masses.

Although there is widespread consensus that local wind stress explains little of the current variability within the Southern California Bight (e.g., Lentz and Winant 1986, Noble *et al.* 2002, Hickey *et al.* 2003), we found that wind was an important, and often the dominant, forcing function for transport of the river plumes. We note that although wind

explained only 66% of the alongshore current variability as measured by the drifters, we did not attempt to remove tidal effects from these data, which would likely improve correlations.

Because winter storms are related to broad atmospheric low-pressure systems moving across southern California, wind patterns are commonly poleward (downwelling) prior to river discharge and equatorward (upwelling) following discharge (Winant and Dorman 1997, Nezlin and Stein 2005). An example of this can be seen in the winds of the Santa Barbara Channel during the 48 hours before and after river discharge events (Figure 17). During the 48 hours following a discharge event, winds are four times more likely to be upwelling (from the west) than downwelling, and ~80% of these winds are greater than 4 m s^{-1}. Post-storm variability in wind stress will be related to broad atmospheric conditions across the eastern Pacific and western North America. The 11-day period of upwelling winds following the March 2005 event (Figure 16a) was related to a transition to spring conditions of upwelling-dominated wind and appears to be uncommonly long. Post-storm upwelling winds appear to more commonly last only one to five days following an event.

We note here that wind explained more of the surface current variance immediately offshore of the Tijuana River mouth than for any of the adjacent coastal subregions measured with HF radar (Figure 18). Hydrographic surveys of this broad region show that freshwater-induced stratification was consistently strongest immediately offshore of the river during the time considered. These combined results are consistent with observations that shallow stratification increases the response of surface currents to wind stress (e.g., Chao 1988, Kourafalou *et al.* 1996). The poor-relationship ($R^2 = 0.36$) in the offshore region was consistent both with lower measured levels of stratification in this region and with the observation by Lentz and Winant (1986) that wind stress becomes less important in the momentum balance with depth on the southern California shelf.

Thus, wind explained a majority of the plume transport variance over temporal scales of days. Due to the temporal coherence of winds and river discharge (e.g., Figure 17), river plumes are commonly observed to flow to the left after leaving the river mouths, which is opposite of the expected direction due to Coriolis (Yankovsky and Chapman 1997). Although wind-dominance is observed in a number of river plume systems throughout the world (e.g.,

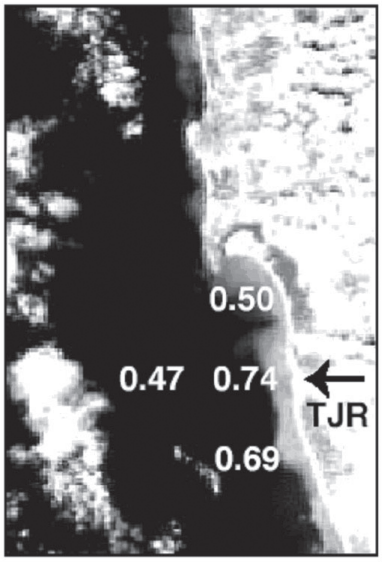

Figure 18. Maximum correlation coefficient (R^2) for linear regression between lagged mean daily alongshore wind speed at NDBC 46086 and mean daily alongshore HF radar surface currents within the four regions identified in Figure 11b.

Hickey *et al.* 2005, Pinones *et al.* 2005, Whitney and Garvine 2005), we note that the southern California plumes are distinctive in that the discharge events occur over time scales of hours and the winds are temporally coherent with discharge and have time scales of days. Thus, the upwelling wind-dominance of southern California river plumes is a common condition. Other river plumes have much longer discharge events, which may or may not be coherent with winds, resulting in less regular wind-dominance or alternating direction of wind-dominance (Hickey *et al.* 2005, Pinones *et al.* 2005, Whitney and Garvine 2005).

We fully expect that other factors, such as river discharge inertia, buoyancy-related currents, tidal currents, and non-wind generated subtidal currents, also have significant effects on plume advection within specific scales of space and time. For example, tidal currents were observed in the hourly HF radar data with magnitudes of 5 - 15 cm s^{-1}, and although these currents are important to instantaneous plume advection, they generally induced no net current over daily time scales. Further, we computed values of plume-induced baroclinic velocities of up to 20 - 55 cm s^{-1} (Table 3), which suggests that initial advection of the plumes from the river mouths was quite rapid in response to this buoyancy. The initial advection was also likely influenced by river discharge inertia from the velocity of the river flux

(~50 cm s^{-1}; *cf.* Warrick *et al.* 2004b). The jet-like plume shapes observed by satellite on February 26, 2004 (Figure 12) likely result from these high initial velocities (*cf.* Garvine 1995). We calculate that the four visible plume fronts in this image advected ~20 km from the river mouths, which is equivalent to a mean velocity of ~45 cm s^{-1} since the peak discharge of the rivers (*cf.* Figure 2). We note that these initial (i.e., 12-hour) velocities appear to be strongly across-shore in direction, which differs from the alongshore-dominated transport measured later during the events. Lastly, geostrophic velocities were computed to be small compared to actual observed velocities and also directed in the opposite direction of the majority of observations. Thus, we suggest that geostrophic flows were generally much weaker than wind-induced flows, which is consistent with calculations of W_s and t_{tilt} above and Santa Monica Bay observations of Washburn *et al.* (2003). Summarizing, plume advection appears to be dominated by river discharge inertia and buoyancy within a few hours and kilometers of the river mouth, while winds dominate plume advection during the following days.

Accurately describing these storm-induced river plumes required a combination of assessment tools. Ships provided the best information, but the rapidity of plume evolution outpaced ship movement while sampling. Even with the large number of ships that were mustered for this study, we found that almost half of the plume water volume occurred outside of the area able to be sampled within the first study day. In addition we found that ships were unable to sample on several of the days most critical to plume evolution, as the high winds that typically follow a storm event led to an unsafe sea state (*cf.* Nezlin *et al.* 2007b).

Satellites provided a valuable synoptic view, but once or twice per day (at best) frequency of the moderate-resolution polar orbiting satellites is temporally insufficient to describe the rapidly evolving plume. Moreover, these images are often obscured by cloud cover (Nezlin *et al.* 2007b), further reducing their temporal resolution. High frequency radar provided a continuous synoptic view but only provided surface currents, without definition of plume edge. Drifters provided a Lagrangian perspective of surface currents that could be utilized real-time to track plume advection or in retrospective analyses of current forcing. Although not utilized here, we suggest that autonomous underwater vehicles (AUVs) would fill important information gaps on the movement and mixing of water properties when ships are not able to sail and cloud-cover prevents satellite observations. When combined altogether we found that these techniques provided essential information to track plumes and better understand the transport of watershed-derived pollutants and pathogens in the coastal ocean.

Future identification of discharged river water and its water quality impacts throughout the Southern California Bight will require tracers of the discharged water and pollutants. Although salinity is surely the best plume tracer, it can only be readily measured *in situ* with conductivity/temperature sensors, which limits the timing and locations of observations. Measurements of salinity from remote platforms have great potential and would provide a valuable synoptic overview, but these observations are presently limited to an experimental basis using airborne sensors. Further, it is not clear how well these emerging capabilities will be able to adequately resolve and characterize the small-scale variability and narrow ranges of salinity often observed in these coastal regions. Our results suggest that the optical properties of CDOM may be effectively exploited to track plumes in southern California and could serve as better tracers than suspended sediment or turbidity observations. This is especially relevant for future identification and tracking of plumes with remotely sensed imagery (e.g., Mertes and Warrick 2001, Nezlin *et al.* 2005), and we suggest further investigation of the use of CDOM absorption and other satellite ocean-color derived products to monitor the distribution of plumes and assess their ecological impacts.

The combined use of ship-based sampling and remotely sensed ocean imagery provided new insights into the patterns and dynamics of river plumes offshore of the largest southern California watersheds. Plumes were observed to quickly move from the river mouths and to respond strongly and quickly to winds. The combined measurements clearly show how plume waters were transported to adjacent portions of the Southern California Bight within days of discharge. This suggests that water quality and ecological impacts from outflow of a watershed may be exhibited in portions of the coastal ocean far from this source watershed. Considering that these plumes are important vectors for land-based pollutants, pathogens and nutrients, better understanding is needed of the water quality and ecological implications and impacts of these plumes.

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Environmental Monitoring Division (CLAEMD), City of San Diego (CSD) Ocean Operations/Toxicology Group, Aquatic Bioassay and Consulting (ABC) Laboratories, McGuire Environmental Consultants (MEC), and the Universidad Autonoma de Baja California (UABC). We would like to thank the crews of the following research and monitoring vessels for their dedication and hard work during challenging conditions: Hey Jude (ABC), La Mer (CLAEMD), Monitor III (CSD), Ocean Sentinel (LACSD), JOHN-B (MEC), ZEUS (MEC), Westwind (OCSD), Nerissa (OCSD), and Alguita (UABC). A number of individuals were instrumental to the development and data processing of the study, including Dario Diehl, Larry Cooper, Brian Emery and Mark Otero. This work was supported with funding from the participating agencies, USGS CMG Program Funds, and a NASA Oceans & Ice Research Project Award (NRA-04-OES-02). We appreciate the careful reviews and comments from Rich Garvine and an anonymous reviewer that improved the final edition of this paper. The contents of this article are solely the opinions of the authors and do not constitute a statement of policy, decision, or position on behalf of the United States Geological Survey (USGS), the National Oceanic and Atmospheric Administration (NOAA) or the United States Government.

Exhibit I

Environmental Defense Sciences

723 East Green Street, Pasadena, CA 91101 Tel: 626-744-1766 Fax: 626-744-1734

February 3, 2012

Jeanine Townsend
Clerk to the Board
State Water Resources Control Board
1001 I St., 24th Floor
Sacramento, CAA 95814

Submitted via email

Subject: **TMDL for DDT**

Dear Ms. Townsend and State Board members:

The purpose of this letter is to express my professional opinion that the proposed Total Maximum Daily Load for Toxic Pollutants in Dominguez Channel and Greater Los Angeles and Long Beach Harbor Waters (TMDL), as it applies to DDT, has no reasonable scientific basis, based upon a review of specific statements in the TMDL that are related to DDT. In addition, the actuality that the TMDL has no reasonable scientific basis is also demonstrated by the fact that "special studies," like those referenced in Paragraph 8 of the Preamble to the State Board's proposed adopting resolution released on January 25, 2012, are deemed necessary by the water boards to provide a reasonable scientific basis for the TMDL at some point in the future.

First and foremost, the numbers for DDT flux into the Harbor system that are presented in Tables B-1 through B-8 of Appendix II are in fact made up out of whole cloth by the TMDL modelers because the modelers had no measured DDT concentrations for the inflows. They simply ascribed a DDT concentration to the sediment flowing into the Harbor. Excerpting from Appendix B to Appendix II:

More-detailed study and collection of stormwater concentrations of DDT, PCBs, and chlordane (at lower detection limits) may provide necessary information for development of a detailed regional modeling approach similar to the metals or land use specific EMCs similar to the PAHs. In the absence of such datasets to characterize wet-weather loads from the watersheds, sediment concentrations were used to model these pollutants in the Harbor watersheds. Similar to methods used in prediction of existing DDT, PCBs, and chlordane loads to

Watershed Model Development for the LA/LB Harbors – Final

support development of the Newport Bay Toxics TMDL (SARWQCB, 2000), loads can be predicted as a sediment concentration assigned to all sediment loads transported from watersheds to the receiving waters. For the current study, sediment loads to the Harbors and SPB are predicted based on LSPC models of SGR, LAR, and nearshore areas.

Additional assumptions for sediment concentrations of DDT, PCBs, and chlordane, expressed as constant values for all sediment transported from each watershed, are required. Sediment concentrations for the Harbor region have been calculated for the Bight 03 sediment stations. Bight 03 data were collected during summer 2003 at various stations throughout the southern California Bight, including the harbor region. In general, a single sample was collected at each location (see Bight 03 documentation available from SCCWRP regarding the detection limits and other details on the data). Figure 23 through Figure 25 illustrate the range of sediment concentrations found at these stations for DDT, PCBs, and chlordane. These figures show that, for the LAR estuary, DDT, PCBs, and chlordane concentrations are all higher near the mouth of the river than throughout the rest of the estuary. This trend does not persist in the SGR estuary, which tends to have lower concentrations of all three organics compared to the rest of the Harbor and SPB, where, as expected, higher concentrations are generally seen in areas with reduced circulation and flushing.

In other words, there were no sediment concentration data in the stream flows so it was assumed that the inflowing sediment had DDT concentrations similar to Harbor sediments, despite the acknowledgement that DDT is a “legacy” pollutant. Thus the estimated fluxes of DDT into the Harbor have no reasonable scientific basis and the numbers for DDT in Tables B-1 through B-8 are just unsupported conjecture at best.

This conclusion is further supported by the statements in the TMDL on page 45 of Appendix II:

the pollutant do not exist. However, because of the persistence of DDT in the environment, reservoirs of the pollutant are often present in the watershed and in the receiving waters. Few detectable levels of DDT have been observed at mass emissions stations in the Los Angeles Region (4,4'-DDD, 4,4'-DDE, and 4,4'-DDT were measured, each with a detection limit of 0.1 µg/L) (LADPW, 2006). Ackerman and Schiff (2003) report EMCs for DDT for land use monitoring performed by San Diego, Ventura, and Los Angeles municipalities as part of their NPDES permit programs. These EMCs resulted from flow-weighted composite samples collected throughout the duration of storm events. Of the five land uses analyzed (agriculture, commercial, industrial, open, and residential), only agricultural land use was shown to have detectable levels of DDT in runoff. PCBs and chlordane are also referred to as legacy pollutants, and similar to

In other words, what data were available showed few detectable levels of DDT in the storm waters entering the Harbor system. Despite this seeming lack of detectable DDT in the inflows the TMDL claims that 8,912 gram/yr of DDT is entering the Harbor system (sum of DDT fluxes to the Harbor in Tables B-1 through B-8). However, even if this were the case, the TMDL analysis shows that the impact of this on the Harbor sediments is essentially negligible.

Here is what the TMDL states about the Harbor sediments and DDT inflow flux in Appendix III (page III-74):

DDT

The maximum and average DDT sediment concentration exceeded criteria in all zones for both the base and no upland sources scenarios (Table 6). The percent difference in concentrations between the two scenarios shows that there appears to be minimal influence of loadings from upland sources. All waterbodies show approximately the same concentrations for the base and no upland sources scenarios. This indicates that DDT bed sediment contamination is predominantly a legacy issue and upland sources appear to be contributing loads of sediment that are cleaner than what is currently in bed sediments. Essentially, bed concentrations are well above the standards in each zone (for both scenarios), suggesting that sediment remediation is required in each zone to achieve sediment targets. The model shows that the combination of clean sediment deposition and the diffusion of legacy DDT contamination are causing bed sediment concentrations to gradually decrease over time. DDT is the most sensitive pollutant evaluated – ultimately, achieving sediment targets for DDT results in all other pollutants meeting their respective targets.

Table 6. Sediment DDT concentrations for the base and no upland sources scenarios

Zone	Waterbody Name	DDT (total) in top 5 cm of sediment (ug/kg)					
		Criteria: 1.58 ug/kg					
		Base Scenario Avg	Base Scenario Max	No Upland Sources Scenario Avg	No Upland Sources Scenario Max	% Diff Avg	% Diff Max
01	Dominguez Channel Estuary	21.85	66.16	20.38	66.16	6.70	0.00
02	Consolidated Slip	137.74	472.59	135.59	472.59	1.56	0.00
03	Inner Harbor – POLA	10.62	31.27	10.32	31.27	2.84	0.00
04	Fish Harbor	5.49	16.87	5.45	16.87	0.63	0.00
05	Cabrillo Marina	42.70	160.14	42.72	160.14	-0.05	0.00
06	Inner Cabrillo Beach Area	36.19	107.98	36.13	107.98	0.17	0.00
07	Outer Harbor – POLA	18.66	59.93	18.64	59.93	0.11	0.00
08	Inner Harbor – POLB	7.23	20.98	7.17	20.98	0.86	0.00
09	Outer Harbor – POLB	11.02	33.82	10.98	33.82	0.34	0.00
10	Los Angeles River Estuary	10.72	35.41	10.34	35.41	3.46	0.00
11	San Pedro Bay	10.77	34.30	10.62	34.30	1.36	0.00

Orange color indicates average zone concentration exceeds contaminant sediment criteria

In other words, the TMDL states that the modeling indicates that there is minimal influence of upland sources and that the concentrations of DDT in the Harbor sediments are in fact reducing, as is also the case for PAHs (see Figures 8 and 9 of Appendix III). Although similar graphs to Figures 8 and 9 are not provided for DDT in the TMDL, the modeling results given in Table 6 above mirror those for PAH. It can be seen that the average concentration of DDT over the four year modeling period is much less than the starting maximum, which implies that the sediment DDT concentrations are actually going down significantly over the four year modeling period. So despite the large influx of DDT postulated to exist in the storm waters, the Harbor sediment DDT concentrations decayed.

Furthermore, the difference between having these hypothetical upland sources and not having them made little difference to the model results; the concentration of DDT in the Harbor sediments decayed in both cases, as is acknowledged above in the TMDL.

Similarly, the "current" loads of DDT to the Harbor sediments presented in pages 19-21 of the Final Staff Report are invented numbers that are arrived at by using the computed sediment mass flux to the Harbor bed multiplied by the existing sediment concentration in each section of the Harbor and, as such, the numbers bear no relationship to any actual deposition of DDT into the Harbor sediments. As is acknowledged elsewhere in the TMDL (see quotation above), the concentration of DDT in the Harbor sediments is decaying in part because of the deposition of cleaner sediments.

In summary, the TMDL analysis of DDT has no reasonable scientific basis. The proper technical conditions for a DDT TMDL are not present, and the technical TMDL provides no rational basis upon which the Regional Board can make sound management and implementation decisions with regard to DDT.

Sincerely,

E. John List, Ph.D., P.E.
Principal Consultant

Exhibit J

TMDLs for legacy chemicals (PCBs and DDT) are not based on reliable technical information

Comments to State Water Board on behalf of Montrose Chemical February 7, 2012

Charles A. Menzie, Ph.D.
camenzie@exponent.com

Bio for Charles Menzie Ph.D.

- Director of Ecological and Biological Sciences Practice
- 40 years experience
- Nationally recognized for work on environmental risk assessment and fate and effects of chemicals
- Member of the California Sediment Quality Objective (SQO) Scientific Steering Committee

The TMDLs for legacy chemicals are not based on reliable technical information or analysis

- Technical problems:
  - Incomplete and likely incorrect conceptual model
  - Loads have not been properly accounted for or modeled
  - TMDLs are based only on an estimated deposition pattern
  - TMDLs are “sediment-only”, ignore the system, and will be difficult to implement
- Management consequences
  - Decisions will not be supported by sound science
  - Correcting the above problems will become increasingly difficult as management actions are set into motion

Major technical issues

- TMDLs are based on a belief (not data or modeling) that sediments are *the* source and will remain constant
- TMDLs based only on estimated solids deposition and ignore the system including solids inputs and by-pass
- Atmospheric loads were incorrectly assigned to sediments
- Extremely low target levels have been chosen despite the known uncertainties associated with their use
- The derivation process has not relied on the state's own SQO guidance
- The TMDL derivation method and proposed implementation are unique to the LA Region

Assimilative capacity has been ignored

- Because sediments are treated only as the source, their important role for assimilative capacity has been missed
- The inputs of solids into and out of the system are critical aspects for assimilative capacity
- Because these are critical aspects, the TMDL's failure to account for them renders it unsound and unreliable