

THE BRAKE PAD PARTNERSHIP

Compilation of Technical Reviewers' and Stakeholders Comments' on Air Deposition Study Draft Report

May 4, 2005

Background

The Brake Pad Partnership (BPP) is a multistakeholder effort to understand the impacts on the environment that may arise from brake pad wear debris generated in the use of passenger vehicles. Manufacturers, regulators, stormwater management agencies, and environmentalists are working together to understand the impacts that may arise from brake pad wear debris generated by passenger vehicles on the environment. BPP efforts are aimed at developing an approach for evaluating potential impacts of copper from brake pads affecting water quality in the South San Francisco Bay as an example. Brake pad manufacturers have committed to adding this evaluation approach to their existing practices for designing products that are safe for the environment while still meeting the performance requirements demanded of these important safety-related products.

The Brake Pad Partnership (BPP) is conducting a set of interlinked laboratory, environmental monitoring, and environmental modeling studies to understand the fate and transport of copper from automobile brake pad wear debris in the environment. Figure 1 illustrates the relationship among the studies. At the core of the Partnership's effort are three environmental modeling studies:

- Air Deposition Modeling—to predict how much brake pad wear debris is released and deposited in the study watershed (Castro Valley).
- Watershed Modeling—to estimate how much copper from the deposited wear debris washes into the storm drainage system and eventually reaches the waters of the South San Francisco Bay.
- Bay Modeling—to determine whether and, if so, to what extent copper from brake pad wear debris affects short- and long-term concentrations of copper in the bay.

In support of these modeling efforts, the Partnership is conducting additional studies to develop accurate input data for the models. An air deposition monitoring effort will provide data necessary for comparison of the model results with the data values as a part of the air deposition model evaluation. Stormwater monitoring data are being collected to help calibrate and validate the watershed modeling. In addition, the Partnership is conducting physical and chemical characterization analyses to determine model parameters specific to brake pad wear debris.

Air Deposition Monitoring

The San Francisco Estuary Institute (SFEI) is conducting a study under contract to the BPP to monitor the deposition of copper from the atmosphere in the Castro Valley watershed. The results of this monitoring effort will be used to evaluate the air deposition model. The air deposition monitoring effort involves the collection of dry and wet deposition samples over the course of approximately one year.

To best support the air deposition modeling effort, the modelers at Atmospheric Environmental Research, Inc., (AER) recommended placing the samplers in locations that are as different from each other as possible with respect to traffic intensity.

Finding appropriate sites proved more difficult than initially anticipated. The wet deposition monitors require an electrical power source. Because of the cost of these instruments, it is also very important to place them in secure locations where they will not be stolen or tampered with. The dry deposition samplers do not need an electrical power source however they do need to be placed in secure locations.

Wet deposition monitoring occurred on two building rooftops in Castro Valley and started in March 2004. Dry deposition monitoring occurred on a rooftop location within approximately 20 meters of a freeway (I-580) off-ramp which is heavily impacted by traffic, and at a reservoir in the upper portion of the watershed, near the ridgeline, which is not significantly impacted from vehicle traffic. Dry deposition sampling began in mid-July 2004.

In addition, based on recommendations from the air modelers at AER, SFEI measured ambient air concentrations of benzene contemporaneously with the dry deposition monitoring in November 2004. The idea was to use benzene as a tracer of vehicle traffic, with the expectation that higher benzene levels would be found at the sampling site adjacent to the freeway off-ramp, and lower levels would be found at the reservoir site that is more remote from roads. The benzene samples were taken at the same time and location as the dry deposition samples, and may provide the BPP with sufficient information to apportion the copper found in the dry deposition samples to vehicle and non vehicle sources.

SFEI completed the collection of wet, dry, bulk, and gas samples at the end of February 2005. A total of 17 wet samples, 47 dry samples, and 10 benzene (gas) samples were collected and analyzed.

The Brake Pad Partnership Steering Committee is seeking an independent expert review of the Draft Report for Air Deposition Monitoring to ensure that the approach and results of this element of the Partnership's work are technically sound and to help build in-depth understanding of and confidence in the technical studies on the part of the Steering Committee and the stakeholder communities.

Charge

With the aim of meeting these objectives, the Steering Committee has developed the following questions on which it is seeking specific comments from the reviewers:

1. What is your assessment of the quality of the methods used and resultant data?
2. In your assessment, is the sampling method and monitoring effort appropriate to the task for validating the air deposition model? If not, please explain the weaknesses that may be introduced in using this data to evaluate the model.
3. Based on your experience with similar air deposition monitoring efforts, what advice do you have regarding the interpretation and use of these data?
4. What is your opinion regarding the use of benzene as a tracer of vehicle traffic? In using benzene as a tracer, what types of uncertainty are introduced that we should be aware of?

Comments Received

Comments of Lynn Hildemann, Environmental Engineering and Science; Stanford University (April 26, 2005)

Overview

This report describes the approach used to directly measure wet and dry deposition of copper and other trace metals in the Castro Valley area, and presents the data obtained. Detailed documentation is provided regarding the sampling methods and data analyses, and the QA/QC methods appear sound. In my view, the major remaining issue is whether this report should focus solely on reporting the data, or provide additional analyses, such as section 4.4. As discussed in more detail below, if section 4.4 is to remain in the report, it needs to be substantially strengthened.

Specific Comments

- 1) Under Methodology, a little more detail on the differences between the bulk and wet deposition methods would be helpful. Specifically, it should be stated near the beginning of the report (rather than in the Conclusions) that the open funnel design of the bulk samplers means that dry deposited material will accumulate in the funnel, that it can perhaps be resuspended because the funnel is uncoated, and that this dry-deposited material will get washed into the collection unit along with the rain.
- 2) Why haven't the results reported been blank-corrected (p. 14)? With all the effort at QA/QC, I would have expected such corrections to be made.
- 3) On p.19, section 4.4 (on Sources of Copper and Other Elements) seems incomplete. Either this section should be omitted entirely, or substantially more details should be added.
 - a) If the authors wish to discuss Fe/Cu ratios, they should provide a more complete discussion. The Bradford 1996 citation does not appear in the reference list – but I wondered whether the Fe/Cu ratio reported for soil in that study can be considered to be representative of Castro Valley soil. In addition, the relevance of the NIST UPM Fe/Cu ratio to wet/dry deposition measures isn't clear to me. It would seem more relevant to cite typical Fe/Cu ratios for brake pads, and perhaps for paved road dust as well – vehicles on roadways will be resuspending road dust, and road dust is known to consist of a mixture of soil dust, vegetative detritus, tailpipe exhaust, brake wear and tire wear.
 - b) The 2nd paragraph in this section was very difficult to understand. It also seemed incongruously hypothetical – rather than imagining some source of “pure copper”, wouldn't it be more appropriate for a back-of-the-envelope exercise to ask what combination of, say, soil dust and brake dust would result in the Fe/Cu deposition ratios observed?
 - c) It seems the main purpose of the 3rd paragraph is to state that Ni was not abundant enough to provide reliable Cu/Ni ratios, so Cu/Fe was chosen instead. If this is true, then perhaps this simple statement should precede the 1st paragraph? The rest of the 3rd paragraph seems to detract from the focus of this report – ratios measured in ambient air samples will only resemble those measured in deposition samples if the particle size distributions for airborne Cu and Ni are the same, right? In addition, I'm not sure how the reported

overall “average” deposition ratio is determined from the wet, dry, and bulk measurements. If it is desirable to discuss such average values, the method used to determine them should be clearly spelled out.

- 4) Some parts of the Conclusions section read like an Executive Summary (e.g., the 1st paragraph and the 4th paragraph). Having too many secondary details in this section detracts from highlighting the major conclusions of the study.
- 5) Clearly, from Figure 7, the raw correlation between the dry deposition rate of Cu (presumably in $\mu\text{g}/\text{m}^2\text{-day}$?) and the ambient benzene levels is weak. In discussing Figure 7, the authors should note how much/little of the Cu they suspect is attributable to brake dust (rather than, say, soil dust). If more than a few percent of the Cu is coming from non-brake dust sources, it would seem important to try and estimate what fraction of the deposited copper originates from brake pads, to see whether the correlation improves when the y-axis of Figure 7 focuses just on brake pad copper. One way to take a first stab at this might be to assume that the deposited material represents a combination of soil dust (with a 1400:1 ratio??) and brake dust (with an Fe/Cu ratio like 30), and then calculate what combination of these 2 sources yields the measured ratio of deposited Fe/Cu.

Responses to Draft Charge Questions

- 1) *Quality of methods and data:* The methods used to collect the samples and the quality of analyses performed are, in my judgment, in accordance with currently-accepted research practices. The study authors have already highlighted the major areas of concern/debate regarding direct deposition measurement methods. Questions may be raised regarding whether enough data has been collected (especially geographically), but given the limited funding available for the field study, the approach adopted of trying to determine upper and lower bounds for Cu deposition seems defensible to me.
- 2) *Appropriateness of sampling method and data to model validation:* The main difficulty I see is that the data is limited geographically, and is quite variable. There will be issues regarding which deposition values are most appropriate to use in the model, and how best to represent the wide range of proximities of the various watersheds to roadways (as well as the range of traffic densities on the various roadways). Careful consideration should be given on how to come up with a “reasonable” range of assumed input values in order to obtain a realistic range of predictions from the models.
- 3) *Advice regarding interpretation and use of the data:* The data collected in this study, in conjunction with the data collected by SFEI during the last study, provide information that seems sufficient for estimating reasonable ranges of deposited material on a long term (annual) average basis. However, I would discourage any effort to try and tease out seasonal variations in the deposition fluxes, or to identify a single best-estimate value.
- 4) *Use of benzene as a vehicle traffic tracer:* It is unclear from the data collected and the analyses performed to date how well ambient benzene levels are reflecting the impact of traffic emissions at a given sampling site. But as indicated above in the previous section (item 5)) as well as below, there are a number of factors that may contribute to weakening the correlation between ambient benzene and deposited brake dust. It is not clear to me from the materials provided how benzene levels might be used in the modeling work. Nonetheless, the 2 issues below should be considered if there are plans for further utilizing ambient benzene levels in conjunction with the deposition models:

- (a) Since particle deposition is dominated by larger particles, there should be a strong gradient in deposition fluxes of brake dust with distance from a roadway – the larger brake dust particles will quickly deposit out, leaving behind smaller particles that are much slower to deposit out. However, benzene can be viewed as a fairly stable tracer – it chemically degrades on a timescale of ~10 days, and I believe it has little or no propensity for sorption by surfaces. This means that the relationship (“ratio”, if you will) between deposited brake dust and ambient benzene levels will vary strongly with distance from vehicle traffic – the further downwind of a roadway samples are collected, the higher the “ratio” of benzene to deposited brake dust.
- (b) Recent work (ES&T 39(1):331, 2005) has found that the emissions of benzene from catalyst cars can increase by as much as 2 orders of magnitude under heavy engine load conditions – thus, one could imagine certain roads (e.g., uncongested highways) with especially high benzene emissions along with low brake dust emissions, along with other highly congested roads where benzene emissions were much lower and the generation of brake wear dust was much higher.

Comments of Betty Pun, AER, Air Modeler (April 28, 2005)

Thank you for a very thorough job on the report. I have just a few minor comments, mostly regarding how best to use the data.

In Table A-1, ppb units are used for concentrations. Is that mass/mass, volume/volume, or mole/mole units? Would you consider providing the data in microgram/liter liquid or some other mass/liquid volume units? Thanks.

On Figure 5 and in Table A-1, there are some negative wet deposition values. It is not obvious from Equation 1 how negative numbers are obtained. Should we interpret them as zero values?

If we assume benzene is a tracer for automobile emissions, Figure 7 seems to indicate that the zeroth order assumption that that all measured copper dep deposition fluxes originate from traffic is not a bad one. Can you provide the uncertainty estimates on the fitted line so that we can get an idea of what the bounds are for the fraction of copper coming from traffic.

We would appreciate some guidance as to how meaningful it is to use individual measurements vs. seasonal / annual averages for the evaluation of the air deposition model, given the variability in the data.

Comments of Kelly Moran, representing Bay Area Storm water Management Agencies (April 28, 2005)

Thank you for the opportunity to review the Castro Valley Atmospheric Deposition Study draft report. Overall, I found it to be a good report--well written and clearly describing the study methods and results. I appreciate the care that went into this work, which was conducted under significant time constraints and financial limitations. I believe this study will serve the Brake Pad Partnership well as input data into our air deposition and watershed modeling.

The report findings of significant differences between the near-highway site and the upper watershed site reinforce the basic premises of our conceptual model. This feedback is nice to get, as it adds to the evidence supporting the validity of the conceptual model that we've used as the basis for our overall project design. I'm glad that we added these sites to our monitoring.

In the discussion of comparisons to other deposition studies, I suggest that the author consider including another factor in his discussion of possible reasons for the higher deposition rate measures in Castro Valley. I note that the other data are several years old (and some probably a decade old). In this last few years, copper use in brake pads may have increased, given the increase in OE pads reported in the copper use monitoring data collected by the BPP. Thus it is possible that the potential that changes in copper use in brake pads could be a factor in the higher copper deposition values measured in this study.

Section 4.5 is a bit awkward. I think its title really ought to be something like "considerations in use of these data in BPP modeling". The points made in this section are appropriate considerations for our modeling--as such, I'm glad they are in the report. However, I found Table 11 and the last half sentence in the third paragraph in this section to be out of place. These come across as speculation about the outcomes of future studies. Comparisons of this sort should be done in future BPP studies that provide Bay loading data. I don't feel they are appropriate here.

Finally, I found some minor typos that the author will want to correct: Section 4.5 first sentence (quantify and contribution), third paragraph second sentence (those), and Table 8 headers (Ni became "Nil").

Comments of Peter Kozelka, EPA Region IX, Water Division (April 29, 2005).

Responses to Draft Charge Questions

1. What is your assessment of the quality of the methods used and resultant data?

The BPP Castro Valley Air Dep. study incorporated high quality sampling methods and analytical techniques to produce the results. As described in the study, the procedures for wet deposition are straightforward, whereas those for dry deposition are operationally defined and therefore results recognize the appropriate limitations. This study chose to continue with sampling methods similar to those used in the past for collecting air deposition data in SF Bay area for evaluating potential impacts to water quality. I concur with this decision.

2. In your assessment, is the sampling method and monitoring effort appropriate to the task for validating the air deposition model? If not, explain weaknesses that may be introduced in using data to evaluate the model.

This study utilized sampling sites with divergent characteristics based on traffic patterns. The sampling sites were selected to represent several different types of input required for the model. While the resultant data may be appropriate for *calibrating* the model, I am uncertain if it will be feasible to *validate* it. That is, the available data will be used to set up and calibrate the model; i.e., determine if model is reasonably accurate in comparison to ambient conditions. However, model validation relies on significantly more robust data sets, which accommodate comparison *after* calibration has occurred. For example, a ten-year data set could provide five years of data for calibration while the other five years

could provide validation. This subtle distinction cannot be overlooked, along with expectations regarding maximal use of the current data set.

Small concerns:

Was a meteorological station operating next to these samplers during the study? If not, what is the approximate distance from each sampling site to the neighboring met. station. What level of error is produced from a sampling site that is potentially in another microclimate from the met station?

During my review of the TableA-1 data, I noticed that replicate samples were collected for large volumes (> 400 g water) but not for smaller ones. It is difficult to estimate sampling precision for these smaller volume (<200 g) samples which are approximately 30% of total n.

3. Based on experience with similar air dep. monitoring efforts, what advice do you have regarding the interpretation of these data?

This BPP air dep study and the previous SFEI air dep study have produced valuable data for interpretation of annual air dep rates associated with fairly different site characteristics. This is a critical first step toward approximating the rates based on local conditions. Yet both of these studies collected data over a short time frame—1 year or less, so it is difficult to evaluate if these data adequately represent the typical conditions or merely a snapshot under extreme conditions. That is, were the wet dep sampling events associated with typical storm conditions (rain washout followed by dry conditions) or atypical wet weather (lingering rainfall with little dry periods in between)? Has this study adequately accounted for these variable antecedent conditions? TMDL practitioners will grab the wet dep rate from this study and utilize annual precipitation information to approximate indirect Cu loads. Can the rate results from this study adequately support the practitioners use or are some qualifications required? (If so they should be included in the abstract.)

Have other studies shown there to linear correlation for wet dep and precip? What sort of relationship applies to dry dep of copper?

I believe, one can proceed to utilize this data although prudence will advocate more air dep monitoring (over several years) to evaluate if assumptions are valid for these parameters correlated to ambient air conditions.

This BPP study estimates $40 \text{ ug m}^{-2} \text{ d}^{-1}$ total Cu dep rate. Can we provide some error value to go along with this estimate?

4. What is your opinion regarding the use of benzene as a tracer of vehicle traffic? In using benzene as a tracer, what types of uncertainty are introduced that we should be aware of?

As I understand it, this study incorporated benzene as tracer of traffic based on results from another study showing that total traffic volume is correlated to benzene concentrations/flux. While it seems like an idea with merit and precedence, I am not familiar with this research area as to comment on the types of uncertainty to be considered.

Comments of Mike Bergin, School of Civil and Environmental Engineering, Georgia Institute of Technology (May 2, 2005)

General Comments

The PI's present dry, wet and bulk deposition measurements for a few trace elements at four sites in the Castro Valley. The data is particularly interesting given that the fluxes actually do not show a great deal of variability (for example mean Cu bulk fluxes are within roughly a factor of 2 at all sites). In addition, the standard deviations for Cu bulk deposition are ~ 30% of mean values (making a coefficient of variation of 0.3) suggesting modest temporal variability. The conclusion I draw from the study is that there is not a great deal of temporal and spatial variability across the monitoring sites. This is good news in that it suggests perhaps only a few monitoring sites represent regional deposition.

On a more negative note I do not think the report clearly presented and written. There are also several issues that should be discussed including the relationship between the current and past study in the Valley, the environmental importance of Cu deposition, and the lack of atmospheric particulate matter sampling during the study to name a few. Also, the objectives have not been met and as I suggest below should very likely be restated.

Overall, I believe the data are potentially interesting and of use for model comparisons but I do not believe the report in the current form will be of use to scientists, policy makers, and the general public. I suggest significant revisions. Some specific comments/suggestions are given below.

Specific Comments

1. Introduction, page 6. It would be helpful to more clearly summarize the results and conclusions of the previous study by Tsai (2000) and to discuss why the current study is needed and how it complements and adds to the prior study.
2. Introduction. I suggest including a paragraph or two on the impacts of trace elements (in particular Cu) on the environment. I assume that a wide range of people may be reading the report and it is important to highlight the motivation of the study.
3. Introduction. It is also suggested that all of the elements/compounds presented in the paper be briefly introduced and discussed. It would be helpful to mention the sources of each, and the motivation for presenting the results.
4. Objectives, Page 7. The objectives of the study should probably be rethought. I do not believe that an objective was 'to measure atmospheric deposition of copper to watershed surfaces' but rather to roughly estimate the deposition to the watershed using surrogate surfaces. Also, there clearly were not enough sampling sites as well as sampling to 'determine the spatial and temporal variability of deposition'. In addition, the techniques used are not adequate to 'estimate or bound' vehicle sources of copper. I believe anyone carefully reading the proposal would come to the conclusion that all of the objectives are in some way not met.
5. Methodology, page 8, paragraph 1. Technically speaking atmospheric deposition consists of only 2 processes, dry and wet deposition. The discussion in the report is confusing and should be reworded.

6. Methodology. I am a bit confused why atmospheric sampling of particulate elements wasn't conducted. This would have been extremely helpful for model comparisons as well as for comparing with benzene to determine the mobile source contribution. Perhaps the funding was such that it was not possible. I think that this should somehow be addressed given that others who read the report will have a similar question.

7. Page 8, paragraph 4. It seems as if there must be other trace elements in addition Cu in brake wear debris. At least the ratios of specific elements must be unique to brake wear. Are there source profiles for brake wear available that can be used to determine traces and/or tracer ratios of importance?

8. Page 9. Benzene is a gas-phase pollutant that likely has significantly different deposition characteristics compared to particulate Cu. Why should it be expected that the atmospheric concentration of benzene and the deposition of Cu are adequately correlated to link their sources?

9. Page 10. It would be helpful to briefly summarize the NADP site selection criteria.

10. Page 15. Statistics (means, standard deviations, and ranges) should be cited and clearly discussed.

11. Page 16. The flux equations should be contained in the methodology section.

12. Results and discussion. As a general comment, the results should be used to estimate (with uncertainties) the annual deposition to the valley due to both wet and dry deposition. It would appear that dry deposition may be the main processes depositing Cu and trace elements to the valley. Although, dry deposition is a continuous process and wet deposition an event process. It is possible that the environmental impact is sensitive to the time frame of deposition.

13. Page 19. It is suggested that the authors estimate enrichment factors to determine the influence wind blown dust/soil has on elemental concentrations.

14. Table 6. Pb concentrations appear to be nearly as high as Cu fluxes. What is the significance of this? Is there a correlation between Pb and Cu fluxes. Presumably lead is from mobile sources?

15. General comment. Is there an emission inventory available for Cu? If so what is the relationship between the estimated emission and deposition in the valley region?

Comments of John Ondov, Dept of Chemistry and Biochemistry, University of Maryland (May 2, 2005)

My feeling is that the study goals are too limited to answer what ought to be the most important questions. I'm curious also, that there is no summary of the literature on why brake and tire wear particles is of issue and what is known about their emission, composition, and so on. Having said this, I imagine that the work was probably a reasonable level of effort if the purpose was to detect a potential problem.

Responses to Draft Charge Questions:

1. What is your assessment of the quality of the methods used and resultant data?

Standard low-cost methods were used. Wet deposition measurements are generally more accurate than those for dry deposition. Both appear to have had adequate sensitivity. However, I don't see size distribution data, without which estimation of dry deposition fluxes are precarious. However, these are probably reasonably bounded by the dry deposition plates. It would be nice to see eddy accumulation measurements applied to the problem of dry deposition. These are difficult, but might provide better results than calculations based on estimates of deposition using models and measured atmospheric concentrations, especially, if concentration vs particle size distributions are not being determined.

2. In your assessment, is the sampling method and monitoring effort appropriate to the task for validating the air deposition model? If not, please explain the weaknesses that may be introduced in using this data to evaluate the model.

According to what I read above, the purpose of the Air deposition model is "to predict how much brake pad wear debris is released and deposited in the study watershed (Castro Valley)." The model at best can predict how much Cu, Zn, etc. deposits in the watershed, but it isn't at all constructed so as to predict how much brake pad debris is released, nor even how much of that is deposited. The latter, would require source apportionment not considered anywhere in the report. Copper and Zn aren't the same as brake wear particles. So one might only predict how much brake/tire debris is deposited, if one assumes that all of the Cu, Zn, etc. has but two sources, i.e., brake pads and tires, and that the abundance of Cu, Zn, etc., in particles emitted upon wearing (not necessarily the parent material) is known. Some or all of this might be known, but none of this was discussed. I would like to have seen application of a micro-orifice impactor (this is a good one!), Tom Cahill's drum impactor (better because one could develop time resolved measurements of metals by particle size (~3-hr resolution, maybe better for Cu, and or SEAS - which gives 30 min time resolution for metals. Then there would be a better chance to apportion the sources and emission mechanisms of Cu, Zn, ...

Dry deposition is known to be highly dependent on turbulence, and hence horizontal wind velocity. This can be a highly non-linear effect. Most of the deposition could easily occur during a relatively few higher wind events. I would like to have seen some evaluation of meteorology and particle size. What was the deposition-mean particle diameter? What is the source of the particles containing Cu and Zn? Traffic dispersed surface dust contaminated with brake and tire wear particles and or particles directly emitted from the brakes and tires? Some electron microprobe work, but at least some presentation of what's known about this from the literature would be highly useful.

Most importantly, why should we care about deposition of Cu-containing particles? Is Cu in these particles known to be soluble or biologically available? Are concentrations in Lake Chabot (or elsewhere) increasing, either in the lake water or sediments? Do fish have high levels of Cu? Is there a problem with drinking water? I could easily imagine these things might be so, but one shouldn't base action on imagination!

Why not normalize Zn, Cu, and Fe concentrations to Si or Al. Fe in urban dust is surely elevated relative to its average crustal abundance. Fe is probably not a great choice for calculations made herein.

3. Based on your experience with similar air deposition monitoring efforts, what advice do you have regarding the interpretation and use of these data?

Make short-term measurements of pollutants to be used as tracers of vehicle emissions. CO and NO_x would likely be useful and can be done on a time scale of minutes! Ultrafine particle spectra could also be very useful in this regard. These would all be good tracers of particle traffic! For dust related sources, it would be nice to have measurements of particles in the 1 to >20 μm size range.

Measure particle size distributions and employ a 3-D sonic anemometer to develop turbulence parameters. Note that below, it's indicated that a tracer of "traffic" was desired.

I wonder if you meant to use the words: "tracer of traffic emitted pollutants," i.e., rather than "tracer of traffic." A tracer of traffic would seem to indicate that maybe you really want a measure of traffic, e.g., traffic counts/unit.

Also, See comments above and below.

4. What is your opinion regarding the use of benzene as a tracer of vehicle traffic? In using benzene as a tracer, what types of uncertainty are introduced that we should be aware of?

Benzene wasn't shown to be a tracer of particle traffic in this study nor was evidence that this is true presented. If there are no big non-automotive sources (e.g., fuel storage, chemical industry, etc.) then it probably is a tracer of traffic emissions, as noted below, not the ones sought in this study. Zn and Pb didn't seem to correlate well with Benzene, which doesn't necessarily say much about its effectiveness as a tracer of motor vehicle emissions. Emission of Benzene, a fuel constituent, is governed by processes different than emission of Cu and Zn from brake (and Tire) wear. In fact, these might be expected to be anticorrelated because Brake wear particles will be emitted when vehicles slow down, while fuel-derived emissions will either be constant (e.g., evaporative losses) or reduced when vehicles slow down. Why not use traffic counts as a measure of particle traffic? and CO and NO_x as a tracer of traffic emitted pollutants. You could get these easily at a few minutes time resolution.

Comments of Geoff Brosseau, Bay Area Stormwater Management Agencies Association (May 2, 2005)

I don't have time to get into the details of the data but my read of the abstract and conclusions re: the higher deposition rate made me wonder about the comparability of the older data to the newer data. I'm assuming that IF (I don't know enough to know if they have) sampling and analysis techniques have improved (e.g., lower detection limits, more complete samples) between the older data collections and this recent effort such that the recent effort might indicate higher deposition rates, that that experimental difference has been corrected for? Thanks!

Comments of Ken Schiff, Southern California Coastal Water Research Project (May 3, 2005)

Responses to Draft Charge Questions:

1) What is your assessment of the quality of the methods used and resultant data?

In general, the methods used were sound. The use of surrogate surfaces, wet deposition, and bulk collectors have been developed previously and published in the literature. The resultant data appear to have achieved a quantifiable level of sensitivity and accuracy based on blanks and standard reference materials.

- 2) In your assessment, is the sampling method and monitoring effort appropriate to the task for validating the air deposition model? If not, please explain the weaknesses that may be introduced using this data to evaluate the model.

The sampling methods and monitoring effort are an improvement over existing data. Existing data focused on regional air quality and resulting deposition (Tsai et al 2001), so obtaining watershed specific information will be extremely helpful to the modelers. This is demonstrated in the substantially higher deposition estimates in Castro Valley compared to Tsai, et al (2001). Spatially dispersed data (at four sites throughout the watershed) also lends itself to model calibration validation. Finally, temporally distributed data also enhances the ability to model deposition because it assesses the variability in differing atmospheric conditions.

Despite its improvement over existing data, the study could have been designed better for model development purposes. Based on my experience, I see three categories of design issues from the draft report. The first issue focuses on data that will be needed by the modelers, but was not collected including; dry weather meteorology, wet weather meteorology, dry deposition particle size information, source emissions, and data on small-scale spatial gradients. Dry weather meteorology will be one of the main forcing functions in the dry weather transport and deposition model. These data are best collected synoptically with the deposition data, but data from a nearby long-term monitoring gage may suffice. Similarly, the precipitation concentration and wet deposition data are significantly influenced by the timing and quantity of localized rainfall. Once again, a nearby rain gage may do the trick. Although a surrogate surface was used to measure deposition, the modelers have to rely on atmospheric concentrations and particle size distributions for deposition estimates. Perhaps there are other data available so that this component of the monitoring design was not needed? When we have conducted atmospheric modeling, one of our main issues was ensuring we had adequate estimates for all atmospheric sources of copper (not just brake pad wear debris). I saw no information in this report on copper source emissions, which will be critical for calibrating and validating the modeling effort. Finally, it is apparent from this study that there is some small scale gradients near freeways that will be of localized importance. We have observed similar results in Los Angeles with enhanced atmospheric concentrations and deposition of copper within 100m of freeways. The importance of this phenomenon to the atmospheric modeling is a function of model grid spacing. If the modeling grid is relatively fine, then this information will be important and would warrant additional gradient sampling to further calibrate and validate the model. If the grid is coarser, then the need for these small-scale interactions is less important.

The second area of design issues was underdeveloped data analysis for the information that was collected. One good example is the wet deposition results. Since a storm summary was not available, it is not possible to evaluate the variability in precipitation concentrations or wet deposition flux. Specifically, we have observed two features that would be important for modeling validation. The first is rain-weighting the precipitation concentration information. This is common practice in the literature and helps to reduce bias, particularly in especially wet or dry years. The second element would be to evaluate pollutant build-up in the atmosphere. We have found that atmospheric concentrations take at least five days to build-up in urban Los Angeles coastal watersheds. Therefore, dry deposition flux measurements are reduced following significantly sized rainfall events. This assumption could be used to validate atmospheric concentration/deposition modeled estimates if timing of the dry deposition measurements were sufficient.

The last category of design issues was data that may not be useful to the modelers. The bulk data appears to have limited value because it does not measure wet or dry deposition (measures a combination). Moreover, it does not represent wet deposition plus surrogate surface deposition. The value to me, therefore, seems limited.

- 3) Based on your experience with similar air deposition monitoring efforts, what advice do you have regarding the interpretation and use of the data?

Based on my experience, the results from this study were not unexpected. The assessment that atmospheric deposition was generally high and variable in urban areas was clearly evident in our studies. What should be of greater interest to managers and modelers, is the uniformity of copper flux estimates regardless of location in the urban section of the watershed. Even at the site near the freeway, the average concentrations were not dramatically higher (I'm surprised they reached the level of statistical significance given that the SD overlapped the mean of other sites in Table 6). This assessment is only further supported by the similarities in deposition flux observed in other urban airsheds (i.e. Chicago), but not at the sites distant from urban centers in Table 8 (these were more similar to the Madison site).

My advice for additional interpretation would be to collect some of the ancillary information (i.e. met data) in an attempt understand the variability in dry and wet deposition. This will not only improve the interpretation of the results, but will provide extremely useful information to the modelers. If specific ideas are needed, I'd be glad to point the investigators in the right direction.

- 4) What is your opinion regarding the use of benzene as a tracer of vehicular traffic? In using benzene as a tracer, what types of uncertainty are introduced that we should be aware of?

The use of a tracer for brake pad wear debris is an excellent idea. This seems like the best choice for tracking the fate and transport through the airshed and quantitatively validating cross-media transport. Other tracers have been used in the past including

crustal element ratios (attempted weakly in this report), radioisotopes, artificial particles, multi-variate analysis, amongst others.

Although benzene may be a good tracer of traffic because of its tailpipe emissions, it may not be the best tracer for copper. Because benzene is volatile gas phase and copper is almost entirely aerosol phase, I don't intuitively expect them to behave similarly and this will limit benzene's utility as a tracer for copper.

General Comment:

My impression is that we are seeing a very early draft of this study. While it's not necessarily a bad thing to see early drafts as a review committee, I have many concerns about the construction of the document. Reorganization of the manuscript will be mandatory in making the document a better resource. For example, the introduction was almost completely bureaucratic and did not provide sufficient technical background for establishing the need for the study. The objectives section did not satiate my appetite for understanding what the investigators specifically were trying to accomplish. I have several more organizational hurdles, but when the time comes to accomplish that task, I will be available for suggestions for improvement.