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Title: Atmospheric deposition as a source of carbon and nutrients to barren, alpine soils of the Colorado Rocky Mountains

Author(s): N. Mladenov et al.

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Anonymous Referee #1

This is an interesting paper that quantifies the input of Aeolian organic matter and other biogeochemicals to alpine environment in central Colorado. The authors make a solid case that these environments are experiencing rapid environmental change. A well-developed rationale presented is an increase in N export in streamflow and how these changes will affect nutrient loss from terrestrial systems and nutrient content in aquatic ecosystems.

Comment: In this study the authors propose that deposition may be a source of nutrients or a source of carbon, which limits microbial activity in newly exposed/ developing soils and quite possibly (although specified in the text) drives soil weathering – this would be an important area to build upon. This is especially true given the net efflux on Ca from the watershed – does it come from newly exposed mineral surfaces or powered by organic C in deposition.

NM: This is an area of ongoing research for our group. The high efflux of Ca from the watershed may be mainly related to the newly exposed rock surfaces in such areas as the rock glaciers, where the dissolved Ca concentrations in the rock glacier outflow reach 4000 ueq/L. We have added this information from Williams et al. (2006) to the discussion, end of Section 5.1. We have also referred to the study of Clow et al (1997), who performed Ca budget calculations in a nearby alpine site Loch Vale (Rocky Mountains, Colorado) and used Sr isotopes to determine that about 25% of the Ca export from the watershed was Ca from long range aeolian transport.

Comment: Vegetation productivity and respiration estimates are available for nearby Niwot ridge and should be added on or about page 2398 line 20 where you assume that these areas are carbon neutral. This does not negate your story and the importance of deposition to the remainder of the watershed; especially those non-vegetated areas

NM: We agree with the reviewer that this is important information that was lacking. Using values from the Bowman and Seastedt (2001, p 180), we are able to better constrain the alpine aboveground productivity rates to 150 g/m²/yr for the commonly observed fellfield, dry meadow, wet meadow, tundra, and snow bed vegetation. However, aboveground respiration in the alpine zone of Niwot Ridge is not as well studied. In the revised manuscript, we have cited the best estimate for respiration from Blanken et al. (2009) measuring NEE in an alpine fellfield at Niwot Ridge with eddy covariance methods. Blanken et al. (2009) showed that “the alpine site was a net source of C when integrated over two summers and one winter.” Blanken’s study suggests that the fellfield site has transitioned from a C sink to a C source. More recent findings from Knowles et al. (2012) support the increase in C export from alpine zones. Given the uncertainties associated with aboveground biomass, we explain in Section 5.1 that these estimates need to be better constrained.

Comment: Overall, this paper makes a nice contribution to our understanding of the biogeochemistry of high mountain catchments. Although not the focus of this paper, the potential importance of organic deposition to soil development in these regions is an interesting aspect to this reader.

Minor comments:

Abstract – please clarify that the autotrophs you refer to are microbial

NM: We have made this change in the manuscript.

Use common units – it is confusing to jump between – cm – m – mm precipitation – kg – kg/ha.

NM: We have made these changes and in the case where multiple units are used, we have included those in parentheses to appeal to a broader range of readers.

Can you clarify how were POM compounds analyzed? On filters? Please add that to the methods so others can build on this work.

NM: This omission has been corrected. We have added the methods describing the POC, PN, and PP measurements to the Methods section.

Can you be more clear that you are looking at water soluble and water insoluble compounds less than 0.7µm?

NM: Yes, we have added this information to the Introduction where we first discuss water soluble compounds.

In the back trajectory analyses do you assume most deposition occurs during storms? What about dry deposition between precipitation events? I wasn't clear on the distinction here – is this analysis only for fresh precipitation samples?

NM: Yes, the analysis shown in Figure is for wet deposition samples. We have rewritten this (Section 3.8) to clarify what was done. Backward trajectories ending on the date of precipitation and at six hour increments before the date of precipitation were acquired.

Page 2390 line 15 – it is more correct to say that there was no relationship, rather than the relationship was insignificant

NM: Thank you. We have made this change.

GLV is a windy place – can you determine what fraction of deposition is local (sourcing and deposition within the catchment) vs. what is a net input to the watershed?

NM: In terms of soil provenance and long range transport of dust as an influence on soil formation, this is an important question. This is part of our ongoing investigation and we are conducting XRD analyses on dust in snow to determine dry deposition sources. Clow et al (1997) suggest that as high as 25% of the Ca deposition in the Rocky Mountains near Boulder, CO may be aeolian. In terms of organic carbon and P, we know that the alpine soils are C and P limited, and redistribution of C and P from local alpine sources is unlikely. We address possibilities that summer upslope conditions could transport C and nutrients from nearby urban and forested areas. We have augmented our discussion (end of Section 5.1 and parts of Section 5.2) to include the Clow et al (1997) findings and address the ongoing work in determining atmospheric deposition sources.

It would be helpful to present the C:N:P ratios (Redfield) you discuss more explicitly. Also, the

ratio of base cations would be great for mineral weathering folks if you have the data.

NM: A table that includes C:N:P ratios and base cation information is included as Supplemental Table S2. In efforts to shorten the Discussion (see Reviewer #2 comments in text), we have kept this information in the Supplement and removed the more speculative discussion related to Redfield ratios and bioavailability.

Page 2394 line 15 – difficult to “determine” rather than to “tell”

NM: We have made this change.

Page 2395 lines 17-18 please expand on what similar to Saharan dust means for this location.

NM: We initially intended to use the similarities in wet deposition fluorescence between Saharan and, in our case, SW US dust to make a connection between the processes responsible for the often surprisingly large organic carbon load associated with dust events. However, this area of research is at an early stage and we have removed this more speculative interpretation from the discussion.

Figure 2 – I don’t think the temporal lake data add to your story given the issue and unknowns you raise re lake productivity.

NM: We agree and we have removed the lake figure from the multi-panel figure.

Figure 3 and 4 – should these be column graphs as you are comparing categories now and not times series (although the categories are seasons).

NM: Given that the inset of Figure 3 has months on the x-axis (this has been added and enlarged) and that these graphs really do explore the temporal variability, we have kept them in this configuration. Figure 4 was removed along with discussions regarding bioavailability and Redfield ratios, as mentioned previously.

Figure 5 – I suggest that you change your axes – the independent variables in these scatter plots are wet dep volume and 18O which are used in the text to infer timing and source of DOC and Ca. As plotted DOC and Ca are treated as the independent variables that predict wet dep and 18O.

NM: In response to comments from Referee #2, we decided that the DOC-18O and Ca-18O relationships were not central to the main thesis of this paper. Therefore, the interpretation of these results and Figure 5 were removed.

Figure 10 – the spatial distribution of landscape types does not add to this figure – the take home point is the carbon balance, yet my eyes and perhaps other readers are drawn to the colors that represent landscapes.

NM: We feel that it is important to illustrate both that there is a low proportion of vegetated landscape and that the catchment is not uniform in terms of vegetation types. We have, therefore, kept the colors but made them less contrasting.

Anonymous Referee #2

The Mladenov et al. manuscript describes original research on carbon, nitrogen, and phosphorus inputs to and outputs from an alpine catchment at the Niwot Ridge LTER/CZO site in the Rocky Mountains of Colorado, USA. The manuscript presents data that document substantial inputs of C, N, and P via atmospheric deposition, particularly with infrequent yet large-magnitude dry deposition events. The calculated atmospheric inputs are sometimes a remarkably large proportion of the solute yields in streams leading to a realization that solute yields from these catchments may be more sensitive to atmospheric deposition and atmospheric pollutants than is commonly conceptualized. This latter point is novel and the strength of the research. The study also includes compositional measures of DOM and this aspect may constitute a novel application of metrics that are now common for surface waters but rarely measured in precipitation. With major revision, the content may constitute an important contribution to Biogeosciences Discussions.

Comment: The most substantial of revisions should address: 1) validation data that are needed to extrapolate knowledge of spectral properties known for surface waters to precipitation; 2) uncertainty of calculated values that needs to be discussed and quantified; and 3) removal of content related to biogeochemical processes for which no direct measurements or strong evidence is provided.

NM: please see detailed responses below.

1) validation data are needed to extrapolate knowledge of spectral properties known for surface waters to precipitation

Data are presented on spectral properties of DOM that were measured for surface and precipitation waters. The authors use these data to interpret a variety of compositional or functional properties of DOM. For these compositional and functional properties, the authors extrapolate relationships that have been quantified for surface waters to precipitation without providing any evidence that these extrapolations are valid. Validation and discussion of the appropriateness of these extrapolations from surface waters to precipitation is needed.

NM: We have now provided more references to the body of knowledge on this topic. In particular, a number of recent studies (Duarte et al. 2005, 2007 and Kieber et al. 2007) have shown that UV absorbance and fluorescence can be used as indicators of organic aerosol source and may reflect photodegradation processes. For example, Duarte et al. (2005 and 2007) isolated fulvic acids and compared aromatic peaks from ¹³C-NMR and FT-IR with specific absorbance and fluorescence measurements to show that those more rapid techniques could be used to reflect changes in organic aerosol source. We have added relevant information from this and other studies to the Introduction. Nevertheless, we agree with the reviewer that further research is needed on this topic and this is one of the foci of our ongoing research. We have therefore, removed the more speculative parts of the discussion in which we use absorbance and fluorescence to make interpretations about bioavailability and Redfield ratios.

2) uncertainty of calculated values that needs to be discussed and quantified

Many values are calculated without mention of uncertainty. Uncertainty does need to be acknowledged and substantively discussed, preferably via quantitative analysis. This aspect is especially pertinent to measures of DOC, DON, and DOP that may be very close to the limits of detection without any mention of how non-detects or values below detection limits are

used in calculations of atmospheric deposition and stream solute yields. Another example is upscaling of point measurements of precipitation chemistry from a mix of synoptic snow surveys and repeated measures made at a single atmospheric deposition monitoring station. The calculation of dry deposition is another particularly important calculation to bound with uncertainty analysis.

NM: We thank the reviewer for noting this. Indeed, the detection limits and uncertainty were omitted. To address this, we have included a detailed table of instruments used and uncertainty for each chemical measurement in Supplemental Table S1. Standard deviations have also been added for values that were directly measured. In the case of back-of-the-envelope calculations used for the C budget, most terms are approximations. We have discussed the high standard deviations associated.

NM: Consistent with Williams et al. (2006), non-detects were set at zero values. However, upon close scrutiny, we found that some wet deposition years had undetected values treated as missing values. We have double checked all calculations of atmospheric deposition against the raw data and corrected this error to ensure that all values below detection limits are counted as zero. This correction resulted in changes to VWM solute concentrations and standard deviations of N and P species that can be seen when comparing new Supplemental Table S2 with old Table S1. No DOC, TDN, TDP, or Ca loading or yield calculations or conclusions of the paper were affected.

NM: The Green Lake 4 watershed is a protected watershed that is the drinking water supply for the City of Boulder. Because of this designation, it is not possible to instrument the watershed with one or more atmospheric deposition collectors. To justify use of the Soddie atmospheric deposition collector, we used ANOVA analyses of unweighted concentrations to compare DOC, TDN, DON, TDP, and DOP deposition (areal flux and concentration values) from the Soddie station to three other NADP stations at elevations above and below treeline and near the Soddie site and GL4 catchment. We found no significant difference between values for the Soddie station and the CO02 NADP station. Only TDN and DON concentrations were significantly different between Soddie and the two collectors located below treeline using ANOVA analyses (Supplemental Figure S4. T-tests performed on VWM concentrations showed that only the highest (CO02) and lowest (CO94) elevation atmospheric deposition sites had significantly different TDN concentrations. We have added a sentence addressing the similarity between Soddie and the CO02 collector data to the Discussion (beginning of Section 5.1).

3) removal of content related biogeochemical processes for which no direct measurements or strong evidence is provided.

The deposition and stream solute yield data document patterns and the spectral data are suggestive of some biogeochemical processes, but none of the presented data are direct measurements of biogeochemical transformations. Interpretations based on the patterns and magnitudes of the deposition and yield data are sound and well developed. In contrast, interpretations related to unmeasured biogeochemical processes are highly speculative and there is little basis for delving into topic areas that are not directly supported by the presented data. While the patterns may be suggestive of processes, many of the processes that are mentioned in the discussions cannot be definitively pinpointed with the information that has been presented and many other unmentioned processes may also be relevant. I suggest a focus on documenting and interpreting deposition/yield patterns while avoiding speculation on processes that were not measured or are not definitive without validated spectral data. Removal of speculation and extraneous content that is not well supported would tighten the focus and strengthen the interpretation while leading to a more concise and well-formulated manuscript. The manuscript could easily be trimmed by several pages without com-

promising the quality of the best described and interpreted research findings.

NM: We have removed the more speculative discussion points related to processes, such as bioavailability and photobleaching. Essentially most of previous Section 5.2. We kept only interpretations related to aromaticity and photodegradation that have been used in other studies of organic aerosols or rainwater.

Comment: Beyond that, I encourage the authors to thoroughly review the manuscript for wordsmithing, to standardize terminology, add additional details, specify vaguely presented information, define all formulas/acronyms/abbreviations, and remove redundancies.

NM: We have thoroughly reviewed and revised the manuscript in the attached version. We have also restructured the manuscript to deemphasize speculation and unmeasured processes. For example, we removed speculations about the bioavailability and recalcitrance of atmospheric organic matter based on evidence from MW measurements and UV-vis and fluorescence. We have moved previous Section 5.3 (“Relevance of wet and dry deposition...”) to the beginning of the Discussion (now Section 5.1.).

Comment: I am providing a marked manuscript with many suggestions and comments for the authors to consider; these comments are not exhaustive – the authors should consider these as guideposts to revise for consistency, relevance, and salience.

NM: We have addressed the major concerns of the referee in the attached manuscript. The most important changes were:

Title: As per the referee's suggestion, we have changed the title to “Atmospheric deposition as a source of carbon and nutrients to an alpine catchment of the Colorado Rocky Mountains”.

P2376 L10-11: We have replaced approximate values with exact means and standard deviations, where appropriate.

P2376 L15: We have revised the abstract to better explain the relevance of relationships between DOC concentrations and other solute concentrations and the importance of optical spectroscopic analyses.

P2380 L1: In response to questions about whether climate is really recorded, the statements we used are accurate. At D-1, air temperature and precipitation are continuously recorded on a chart recorder to ensure a homogeneous climate record (Williams et al. 1996, L&O).

P2381 L26: Omissions in DON and POC (also DOP, PN and PP) methods have been corrected.

P2387 L12: The referee has suggested we remove the word, “loading”. Our study includes atmospheric fluxes into the catchment, which are referred to as “loadings” in many studies on atmospheric deposition (e.g., see articles in Atmospheric Environment). To appeal to a broader audience and to avoid confusion with other measures, such as concentration of the solutes in atmospheric deposition, respiration fluxes to the atmosphere, and yields from the catchment, we have respectfully decided to keep the word, “loading”.

P2392 L12: For clarity, we have replaced the term WINSOC with POC and have improved the description of all terms in this section (4.4).

P2393 L7-15: We agree with the referee that our interpretation of the $\delta^{18}\text{O}$ and DOC and Ca relationships was flawed. We also agree that an in-depth discussion of the processes that lead to enrichment and depletion of ^{18}O is not relevant to the thesis of this paper. Therefore, we have removed this discussion point along with Figure 5.

P2393 L20: As per the referee's comment, we performed a pollen leaching experiment and measured DOC leached per g pollen, SUVA, and FI. We have added these results to section 4.4. We have discovered that, despite its noticeable presence in wet deposition during summer months, pollen does not contribute substantially to DOC in wet deposition.

P2399 L8: The referee was concerned with the use of pollen deposition rates from a different (remote, but forested) site in Wisconsin. We found that Fall (1992) measured pollen deposition rates for the Rocky Mountains and we have used this more relevant rate to in our C budget calculation.

Tables: we have standardized the style for all tables so that units are included in the title.

Table 5: We have revised this table so that each parameter is described and standard deviations are included, where applicable.

Figure 1: We have set this figure to "landscape" orientation so that its high resolution is visible.

Figure 3: We have labeled the x-axis.

Figure 4: We have removed this figure.

Figure 5: We have removed this figure.

Figure 6: These data were indeed better suited to a log-normal distribution and the figures have been changed accordingly. This has also been corrected for old Figure 9 (new Figure 7).

Comment: Also, despite mention in the first sentence of the introduction, the focus of the manuscript is not climate change and the authors should address this topic more specifically or remove if not highly relevant.

NM: We have removed the climate change justification from the first sentence of the introduction.

Short Comment by Caitlin Glover

It was interesting to see the contribution that wet deposits can make in a remote region. Since the organic matter is so varied and from such different sources, I am wondering if there are other studies that further characterize it. Have the dust events been characterized for the contaminants present?

NM: There are other studies in the literature that have characterized both dust and pollutant influences in PM₁₀ and PM_{2.5} aerosols. In Mladenov et al. (2010, Atmospheric Environment), we also examined PM₁₀ aerosols that had both dust and continental pollution influences.

If so, which ones persist? And have the EEMs shown any regions where these contaminants might be present?

NM: We have seen diesel and gasoline compounds with high fluorescence intensities in the low excitation and emission wavelengths, where naphthalene, benzene, xylene, and toluene fluoresce. However, depending on the concentrations of pollutants in the atmosphere and the presence of other organic compounds, such as the intense HULIS fluorescence, the influence of contaminants can be difficult to tease out with fluorescence alone.

I have seen a couple of papers that trace contaminants in rain water over seasonal variation, but have there been others that went further to look at the concentrations found in receiving water bodies? Is it possible these contaminants are degraded by natural processes or is the dilution factor into the receiving stream too high to have any detection level?

NM: These answers will depend on the concentrations of pollutants in the atmosphere and DOC concentrations in lakes and rivers. Although this was outside of the scope of the current study, Mladenov et al. (2008, JGR and 2009, Limnology and Oceanography) did examine the influence of atmospheric deposition on two alpine lakes in the Sierra Nevada Mountains of Spain.