Supplementary Information

Tables S1 – S3

Figures S1 – S5

Table S1. Detection limits* of instruments used between 2002 and 2010.

Parameter	units	Instrument	Method	2002	2003	2004	2005	2006	2007	2008	2009	2010
TOC, DOC	mg C/L	Shimadzu TOC-5000A	High temp catalytic oxidation	NP	NP	NP	NP	NP	NP	NU	NU	NU
DOC	mg C/L	Shimadzu TOC-V csn		NU	NU	NU	NU	NU	NU	0.12	0.09	0.07
TN, TDN	uEQ/L	Quik Chem 8000	Potassium persulfate digestion	0.11	0.12	NU	NU	NU	NU	NU	NU	NU
TN, TDN	uEQ/L	FS 4	Potassium persulfate digestion	NU	NU	0.03	0.24	0.45	0.92	1.12	NU	NU
TDN	uEQ/L	Shimadzu TOC-V csn		NU	NU	NU	NU	NU	NU	1.49	1.14	1.02
NH4+	uEQ/L	Quik Chem 8000	phenol color	0.29	0.38	NU	NU	NU	NU	NU	NU	NU
NH4+	uEQ/L	FS 4	phenol color	NU	NU	0.11	0.14	0.13	0.1	NP	NU	NU
NH4+	uEQ/L	Biotek Synergy 2		NU	NU	NU	NU	NU	NU	0.46	0.46	0.63
NO3-	uEQ/L	Dionex DX 500		0.07	NU	NU	NU	NU	NU	NU	NU	NU
NO3-	uEQ/L	Metrohm 761	Compact IC	NU	0.02	0.03	0.02	0.02	0.04	0.04	0.02	0.09
TP, TDP	uMOLE/L	Quik Chem 8000	Persulfate digestion	0.05	0.07	0.01	0.03	0.04	0.03	0.03	0.05	NU
TDP	uMOLE/L	Quik Chem 8500	Persulfate digestion	NU	NU	NU	NU	NU	NU	NU	NU	0.03
PO4 3-	uEQ/L	Lachat Quik Chem 8000		0.21	0.16	0.03	0.03	0.11	0.16	0.16	0.16	NU
PO4 3-	uEQ/L	Lachat Quik Chem 8500		NU	NU	NU	NU	NU	NU	NU	NU	0.06
Ca 2+	uEQ/L	Perkin Elmer AA100		0.06	0.06	0.06	0.19	0.26	0.17	0.06	0.25	NU
Ca 2+	uEQ/L	Perkin Elmer AA200		NU	NU	NU	NU	NU	0.11	NU	NU	0.38
SO4 2-	uEQ/L	Dionex DX 500		0.07	NU	NU	NU	NU	NU	NU	NU	NU
SO4 2-	uEQ/L	Metrohm 761	Compact IC	NU	0.03	0.04	0.08	0.04	0.63	0.29	0.07	0.56

* NP = not performed, but three replicate analyses yielded standard deviations of 0.06 mg C/L with a range of 0.01 to 0.22 mg C/L (Williams et al., 2009); NU = instrument not in use.

Table S2. Volume weighted mean (VWM) concentrations, solute loadings, and Redfield ratios for wet deposition (from 2002 – 2010) at the Soddie collector, with standard deviation (δ) and number of samples (N).

Solute or parameter	Mean	δ	N
WT (g)	584	652	402
pH	5.34	0.50	353
Conductivity (µS/cm)	7.3	6.4	356
Ca^{2+} (µEQ/L)	16	40	353
NH_4^+ (µEQ/L)	16	16	357
NO_3^- (µEQ/L)	16	14	358
SO_4^{2-} (µEQ/L)	11	11	358
PO_4^{3-} (µEQ/L)	0.11	0.23	349
$\delta^{18}O$ (‰)	-9.4	6.7	219
Deuterium (‰)	-65	53	206
DOC (mg/L)	1.2	1.6	331
TDN (µmol/L)	34	29	339
DON (µmol/L)	2.3	3.6	339
TDP (µmol/L)	0.11	0.19	332
DOP (µmol/L)	0.08	0.14	330
DOC loading (kg/ha/yr)	9.9	4.2	235
TDN loading (kg/ha/yr)	3.8	1.1	332
DON loading (kg/ha/yr)	0.29	0.19	235
TDP loading (kg/ha/yr)	0.030	0.014	330
DOP loading (kg/ha/yr))	0.020	0.011	349
Ca^{2+} loading (kg/ha/yr)	2.6	1.7	219
DOC:DON	105	481	252
DOC:DOP	1681	3974	204
DON:DOP	43	98	204
DOC:TDN	3.6	2.8	339
DOC:TDP	1076	1522	218
TDN:TDP	342	360	218

Table S3. DOC concentrations and optical properties* for the Soddie wet deposition collector during 2010.

Sampling date	DOC (mg/L)	FI	FrI	FI Peak (nm)	HIX	$SUVA_{254}$ ($L\ mg^{-1}\ m^{-1}$)	$S_{275\text{-}295}$ (nm^{-1})	$S_{350\text{-}400}$ (nm^{-1})	S_R	a_{250} (m^{-1})	a_{320} (m^{-1})	LC1 (RU)	LC2 (RU)	LC3 (RU)	Sum (RU)	%C1	%C2	%C3	MW (Da)	Polydispersity (d-less)
1/5/2010	0.39	1.35	0.60	472	0.38	R	R	R	R	R	R	0.07	0.24	0.00	0.37	19%	64%	17%	3720	8.50
1/12/2010	0.77																		1997	5.19
2/2/2010	0.58	1.36	0.65	452	0.35	R	R	R	R	R	R	0.03	0.23	0.01	0.34	10%	68%	22%	2357	6.36
2/9/2010	0.70	1.54	0.66	446	0.26	1.26	0.0113	0.0055	2.0	0.45	0.20	0.07	0.30	0.00	0.46	14%	64%	22%		
2/16/2010	0.54	1.39	0.71	468	0.54	1.78	0.0190	0.0126	1.5	0.48	0.14	0.20	0.94	0.08	1.36	14%	69%	16%	1507	4.09
2/23/2010	0.31	1.35	0.57	452	0.42	1.08	0.0197	0.0123	1.6	0.17	0.04	0.08	0.26	0.02	0.41	19%	63%	18%		
3/16/2010	1.15	1.42	0.62	444	0.46	0.85	0.0121	0.0053	2.3	0.49	0.21	0.18	0.37	0.05	0.69	26%	53%	20%	1321	3.21
3/23/2010	0.49	1.27	0.61	452	0.45	R	R	R	R	R	R	0.12	0.29	0.01	0.51	23%	58%	19%	1703	4.26
3/30/2010	0.53	1.29	0.54	456	0.49	1.11	0.0161	0.0145	1.1	0.30	0.09	0.13	0.36	0.02	0.60	21%	61%	18%	1485	3.89
4/9/2010	0.30	1.26	0.84	468	0.54	2.57	0.0153	0.0130	1.2	0.38	0.12	0.34	0.39	0.14	0.84	41%	46%	13%	1587	3.00
4/27/2010	0.56	x	0.61	422	0.42	1.53	0.0136	0.0097	1.4	0.43	0.15	0.11	0.27	0.04	0.48	23%	57%	20%	1825	4.24
5/4/2010	1.03	1.47	0.70	452	0.65	R	R	R	R	R	R	0.66	0.70	0.19	1.61	41%	44%	15%	1289	2.54
5/11/2010	2.12	1.40	0.62	458	0.67	1.29	0.0165	0.0119	1.4	1.33	0.48	1.46	1.17	0.25	3.22	45%	36%	18%	1128	2.43
5/18/2010	0.71	1.30	0.53	462	0.71	2.22	0.0147	0.0095	1.5	0.77	0.31	0.75	0.51	0.07	1.48	50%	35%	15%	970	1.94
5/25/2010	3.16	1.31	0.58	454	0.53	0.48	0.0184	0.0120	1.5	0.74	0.23	0.67	1.19	0.07	2.22	30%	53%	16%		
6/15/2010	1.62	x	0.65	512	0.52	R	R	R	R	R	R	0.41	0.46	0.09	1.05	39%	44%	17%	1265	3.17
7/6/2010	3.03	1.27	0.56	462	0.49	0.45	0.0269	0.0093	2.9	0.68	0.15	0.44	0.73	0.09	1.53	29%	48%	23%	992	2.89
7/13/2010	1.86	1.22	0.58	464	0.51	R	R	R	R	R	R	0.44	0.63	0.06	1.29	34%	49%	17%	1021	2.85
7/20/2010	4.42																		800	2.42
7/27/2010	5.05	1.39	0.62	458	0.62	0.40	0.0316	0.0215	1.5	1.01	0.17	1.07	2.16	0.18	3.93	27%	55%	18%	808	2.38
8/3/2010	1.45	1.30	0.56	460	0.52	R	R	R	R	R	R	0.16	0.32	0.00	0.62	26%	52%	22%	1353	2.86
8/10/2010	1.65	1.48	0.54	454	0.51	R	R	R	R	R	R	0.17	0.35	0.00	0.65	26%	53%	21%	1011	3.21
8/24/2010**	1.31	x	0.47	408	0.57	0.83	0.0158	0.0107	1.5	0.54	0.17	0.00	1.32	0.00	1.32	0%	100%	0%	1700	4.36
8/31/2010	4.14	1.42	0.48	446	0.64	0.36	0.0215	0.0135	1.6	0.73	0.21	0.59	1.13	0.00	2.47	24%	46%	30%		
9/14/2010	2.13	1.35	0.53	458	0.39	1.20	0.0134	0.0058	2.3	1.25	0.55	0.23	0.45	0.00	0.82	28%	55%	18%	1243	3.60
9/28/2010	3.94	1.32	0.64	462	0.30	0.27	0.0288	0.0248	1.2	0.51	0.12	0.30	0.75	0.00	1.26	24%	60%	16%	1348	3.49
10/12/2010	0.66																			
10/19/2010	0.75	1.23	0.65	458	0.43	R	R	R	R	R	R	0.10	0.30	0.06	0.47	22%	64%	14%	1326	3.81
10/26/2010	0.61	x	0.61	382	0.48	0.68	0.0191	0.0143	1.3	0.22	0.07	0.14	0.23	0.02	0.44	32%	54%	14%	2213	5.07
11/2/2010	0.96	1.39	0.75	458	0.63	R	R	R	R	R	R	0.33	0.76	0.10	1.25	27%	61%	13%	1273	3.34
11/16/2010	0.74	1.41	0.80	470	0.51	R	R	R	R	R	R	0.16	0.29	0.11	0.54	30%	54%	16%	1574	3.89
11/23/2010	0.55	1.31	0.68	464	0.60	R	R	R	R	R	R	0.20	0.44	0.04	0.72	28%	60%	11%	1501	2.63
11/30/2010	0.92																			
12/7/2010	0.81																			
12/14/2010	0.99	1.31	0.68	466	0.53	R	R	R	R	R	R	0.20	0.36	0.03	0.66	31%	55%	15%	2191	4.71
12/21/2010	0.31	1.25	0.68	474	0.47	5.91	0.0062	0.0082	0.8	0.97	0.30	0.06	0.18	0.01	0.27	23%	65%	12%	2328	4.74

* DOC = dissolved organic carbon; FI = fluorescence index at ex 370 nm; FrI = freshness index; FI peak = peak wavelength of the fluorescence index curve; HIX = humification index; *S* = spectral slope; S_R = spectral slope ratio; *a* = Naperian absorption coefficient; LCN = concentration of component N; Sum = sum of concentrations; %CN = relative amount of component N; MW = molecular weight; R = UV-vis absorbance values were near instrument detection limits and data were removed; x = peak of FI curve out of range (440-470 nm) and FI value could not be calculated; Missing values due to insufficient volume for analyses.
** Fluorescence values were outliers and not used in statistical analyses.

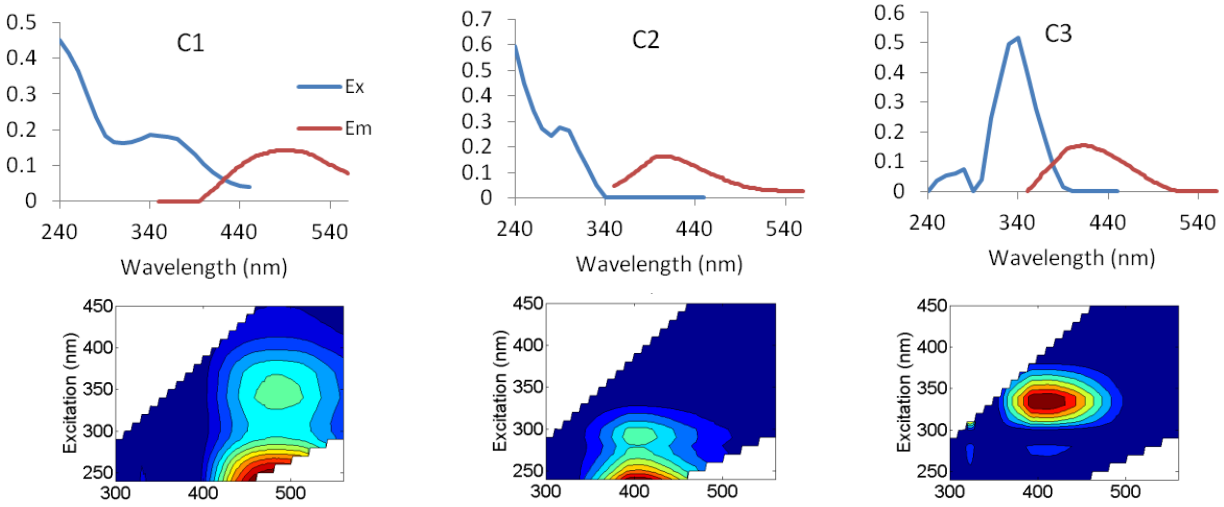

Figure S1. Excitation and emission peaks of PARAFAC components, C1 (with an ex/em peak at <240(340)/492 nm), C2 (with an ex/em peak at <240(290)/406 nm), and C3 (with an ex/em peak at 340/414 nm). C3 is called component 5 in Mladenov et al. (2011). Tyrosine- and tryptophan-like components C4 and C5 were not used in the current study. Source: Mladenov et al. (2011).

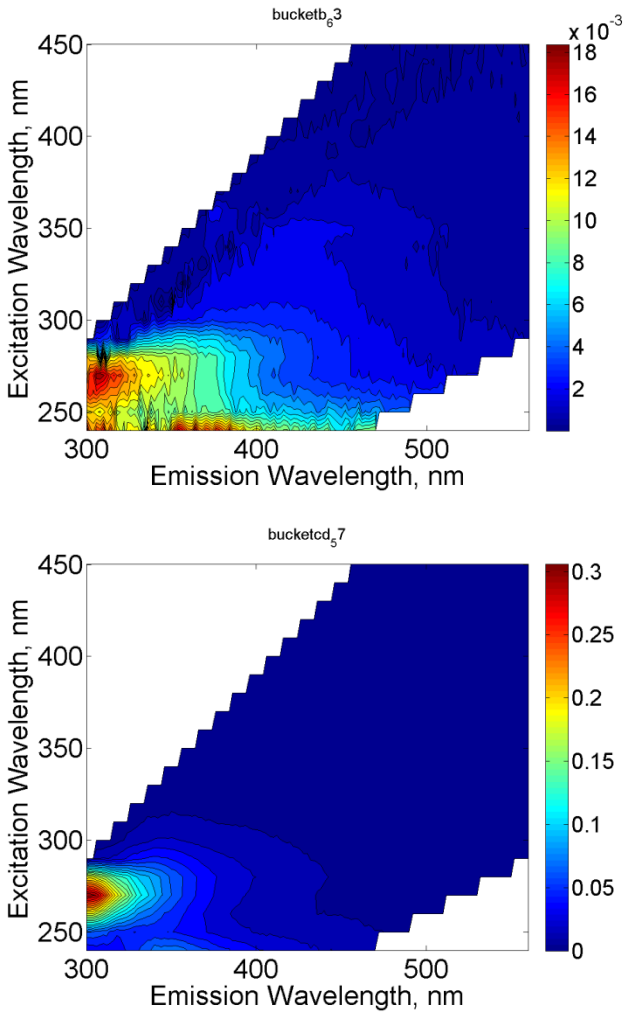

Figure S2. Fluorescence due to 1-d (top) and 7-d (bottom) of contact between atmospheric deposition collection bucket with 1 L of ultrapure water. Colorbar shows intensities of fluorescence in Raman units (RU). Note that for atmospheric deposition samples the fluorescence intensities at >350 nm emission are generally >0.10 RU. Therefore, leaching from the plastic bucket has negligible influence at wavelengths > 350 nm emission. Seven days of leaching does produce a notable effect on the fluorescence at wavelengths <350 nm emission, and 1 day of leaching is negligible at all wavelengths.

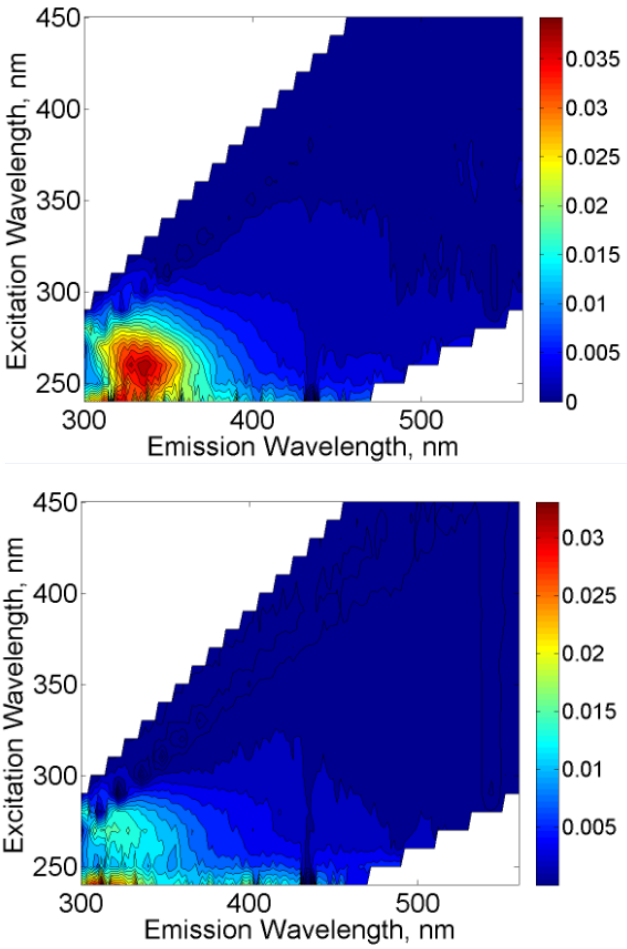

Figure S3. Fluorescence EEM spectra of 20 mg *Pinus contorta* (top) and 11 mg *P. ponderosa* (bottom) pollen leached in 550 mL of ultra-pure water.

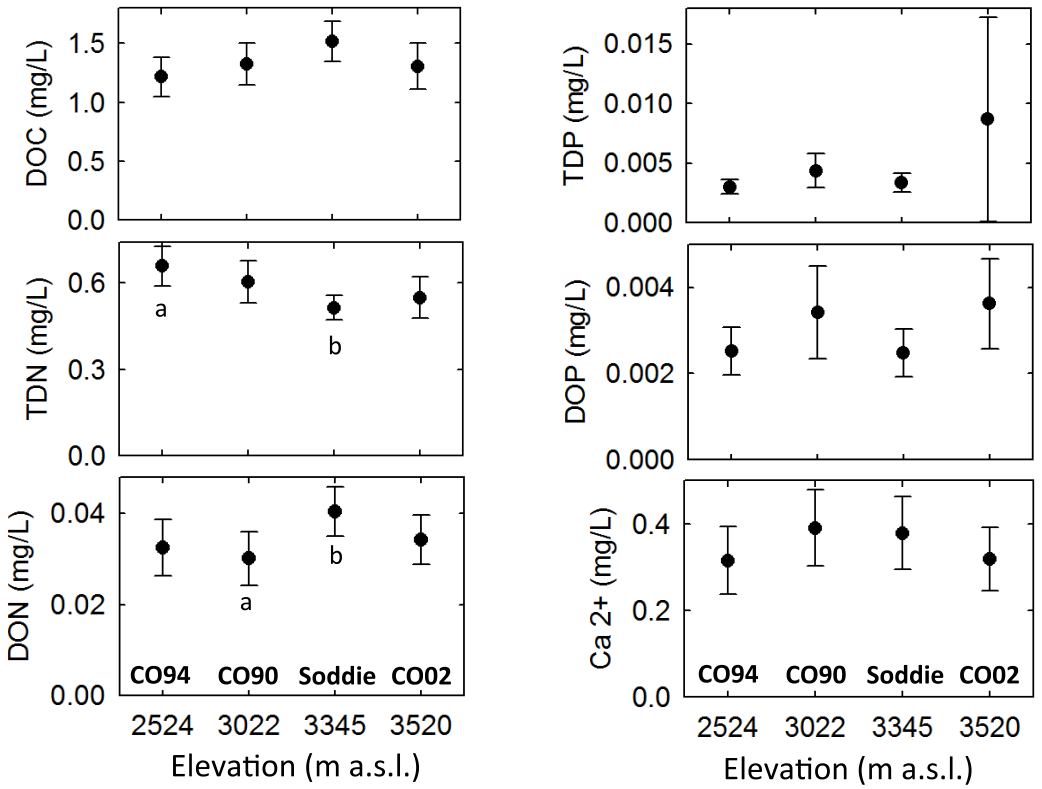

Figure S4. Mean concentrations with 95% confidence intervals for dissolved organic carbon (DOC), total dissolved nitrogen (TDN), dissolved organic nitrogen (DON), total dissolved phosphorus (TDP), dissolved organic phosphorus (TDP) and calcium (Ca) from 2002-2010 for the Soddie collector and CO94 (Sugarloaf), CO90 (Niwot Ridge-Southeast), and CO02 (Niwot Saddle) NADP collectors. Because the first 200 g of NADP wet deposition was reserved for NADP purposes and not available for DOC, DON, and DOP analyses, only samples with precipitation > 250 g were considered for this comparison. Only values marked with "a" and "b" were significantly different from each other at a level of $p \leq 0.01$.

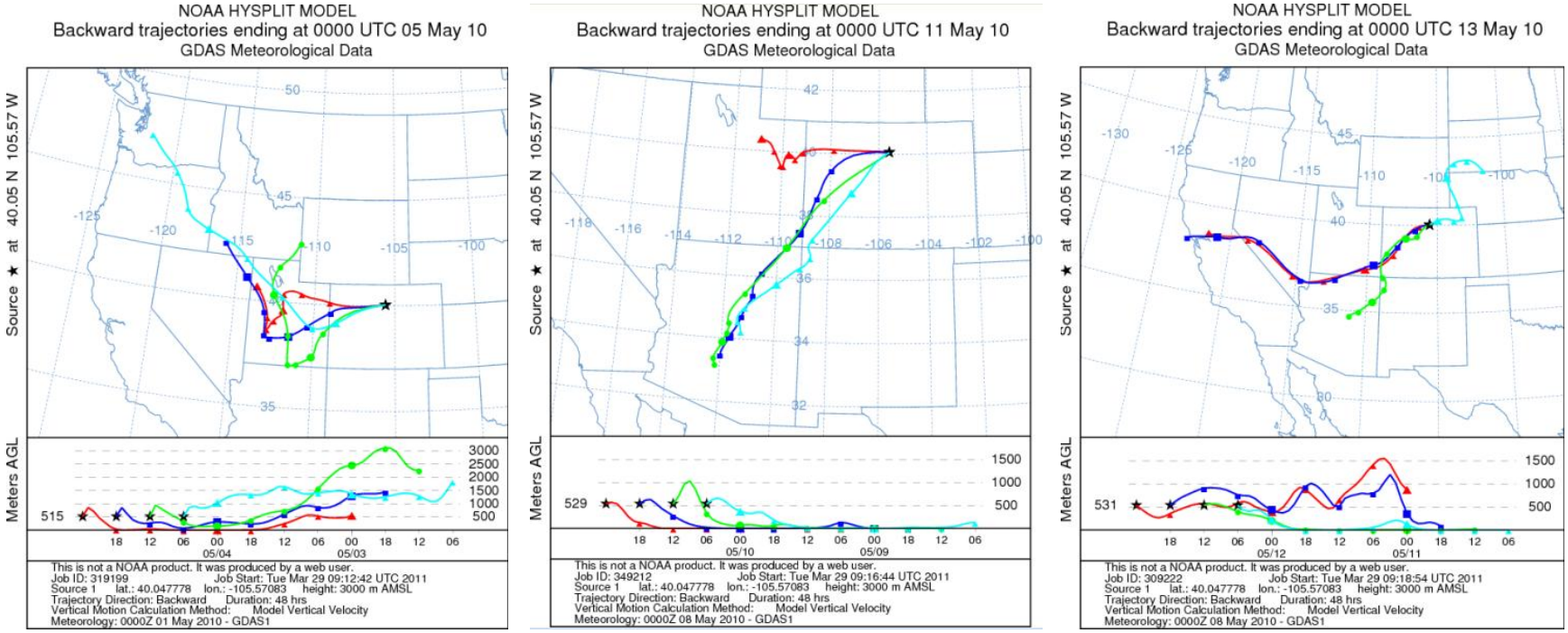

Figure S5. NOAA HYSPLIT model airmass backward trajectories (48 hour duration) for weekly wet deposition events ending on a) 4 May 2010, b) 11 May 2010, and c) 18 May 2010. Backward trajectories are modeled from GDAS archive data at 6 hour increments ending at 0000 UTC on the date during which precipitation was measured at the NADP gage (date is specified in each backward trajectory figure).