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APHL

# Combined Frequency and Time-Domain Analysis Reveals Persistent Annual and Semi-Annual Periodicity in Wet and Dry Atmospheric Deposition Across the United States

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## Abstract

**Background/Objectives**: Atmospheric deposition refers to the transfer of pollutants from the atmosphere into the environment via wet or dry processes. The significance of monitoring the seasonality of atmospheric deposition cannot be overstated, as it has direct implications for human health, crop yields, and aquatic environments. While the seasonality of deposition events has been widely reported for decades, their persistence over time, consistency across wet and dry deposition, and responses to non-stationary processes have not yet been fully quantified. **Methods**: In this study, we developed an automated, scalable analysis approach with no stationarity assumptions, employing strict data quality control procedures, Box-Cox transformation based on segments, and frequency (FFT) and autocorrelation function (ACF) based approaches, applied to multiple high-quality data segments of the major ions across the USA measured by CASTNET and NADP/NTN (3 years vs 5 years vs longest length). **Results**: FFT and ACF analyses of co-located sites (WFM105–NY98) and proximal sites (WFM105–VT99) showed highly consistent annual periodicity (48–54 weeks) between the CASTNET and NADP/NTN networks. This annual cycle (50–54 weeks) was also dominant across the full CASTNET and NADP/NTN datasets. ACF analysis detected fine-scale phase differences in the timing of peak concentrations through variations in lag windows at individual sites. When combined across multiple sites, these ACF lags revealed transport-driven spatial patterns in the Southeast and Midwest regions. **Conclusions**: The technique allows us to identify the same dominant annual Periodicity and a secondary semi-annual Periodicity in depositions of various ions and chemical species under both wet and dry conditions at co-located or proximal stations. Furthermore, this analysis provides additional information unavailable from stationary analysis, such as phase relationships between maxima and flow-directionality patterns.

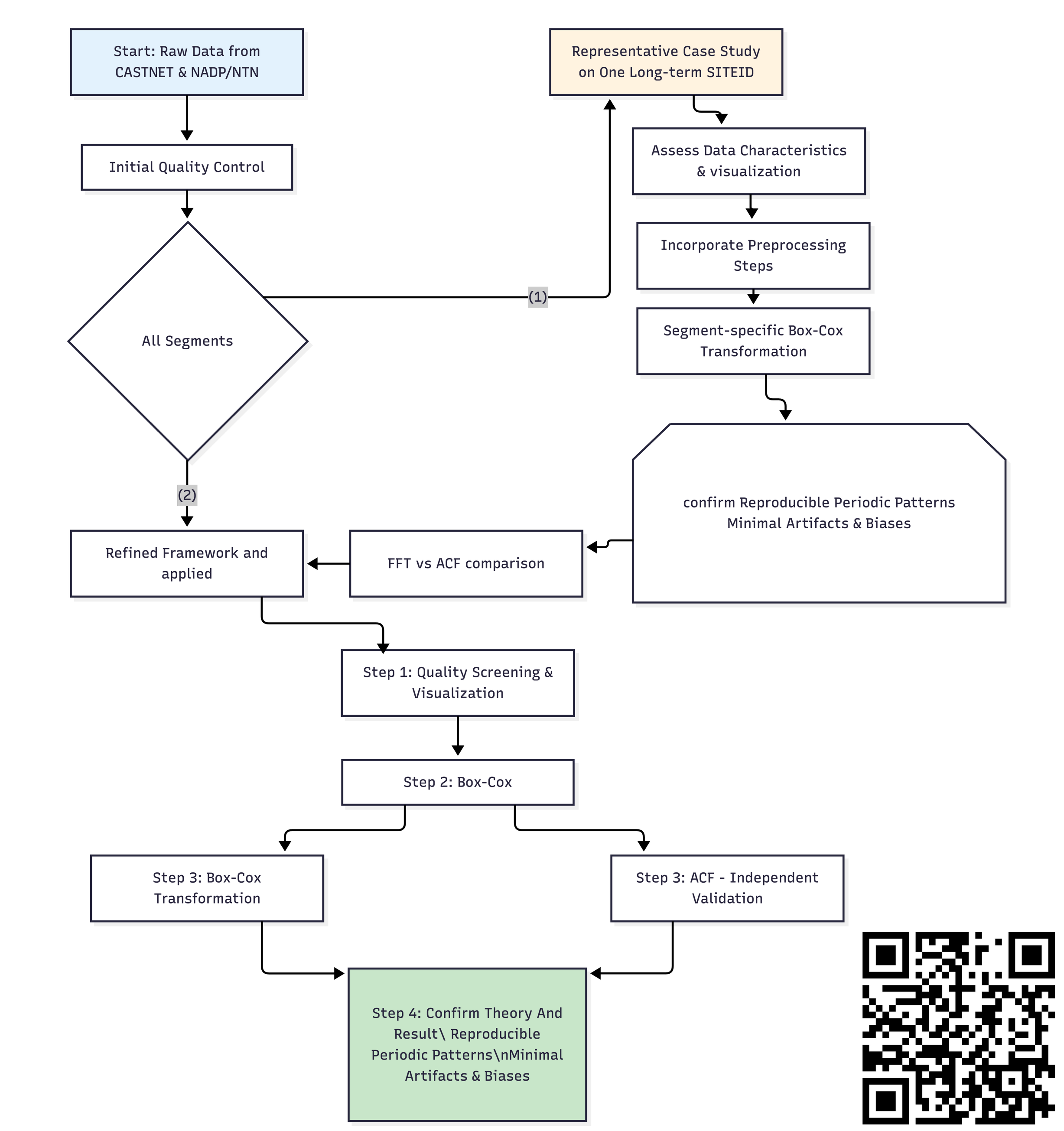


**Fig. 1** Schematic representation of the iterative analytical approach for periodicity analysis of the atmospheric deposition chemistry. The process starts with rigorous quality control standards, fewer than 10% missing values, and no more than 1 consecutive missing row, where a row is considered missing if any of the chemical variables are NA. The iterative analytical approach was validated using a selected example site within the SITEID with a complete record. After that, temporal segmentation was performed, followed by the application of the Box-Cox transformation to each individual segment. Quality assurance/control tests were carried out after each preprocessing phase. Then, the refined approach was applied consistently to all eligible segments from CASTNET and NADP/NTN sites

## FFT/ ACF at a co-located and proximal site

| Variable | CASTNET WFM105 Seg 120 (Dry) | NTN NY98 Seg 1 (Wet) | NTN VT99 Seg 3 (Wet) | Overall Consistency |
|---|---|---|---|---|
| $SO_4^{2-}$ | ACF: Lag 32 (0.184, PASS) | ACF: Lag 54 (0.208, PASS) | ACF: Lag 49 (0.219, PASS) | High |
| | FFT: ~54.0 wk (PASS) | FFT: ~50.0 wk (PASS) | FFT: ~48 wk (PASS) | |
| $NO_3^-$ | ACF: Lag 55 (0.151, PASS) | ACF: Lag 54 (0.177, PASS) | ACF: Lag 17 (0.177, PASS) | High |
| | FFT: ~54.0 wk (PASS) | FFT: ~50.0 wk (PASS) | FFT: ~48 wk (PASS) | |
| $NH_4^+$ | ACF: Lag 32 (0.149, PASS) | ACF: Lag 54 (0.142, PASS) | ACF: Lag 49 (0.193, PASS) | Good |
| | FFT: 7.94 & 54.0 wk (PASS) | FFT: ~55.6 wk (PASS) | FFT: ~57.6 wk (PASS) | |
| $Ca^{2+}$ | ACF: Lag 4 (0.135, PASS) | ACF: Lag 125 (0.128, PASS) | ACF: Lag 105 (0.189, PASS) | High |
| | FFT: ~54.0 wk (PASS) | FFT: ~50.0 wk (PASS) | FFT: ~26,Äì57 wk (PASS) | |
| $Na^+$ | ACF: Lag 22 (0.207, PASS) | Failed Box-Cox | ACF: Lag 82 (0.157, PASS) | Moderate |
| | FFT: ~54.0 wk (PASS) | | FFT: ~48 wk (PASS) | |
| $K^+$ | ACF: Lag 66 (0.184, PASS) | Failed Box-Cox | Failed Box-Cox | Limited |
| | FFT: ~54.0 wk (PASS) | | | |
| $Mg^{2+}$ | Failed Box-Cox | Failed Box-Cox | ACF: Lag 21 (0.186, PASS) | Limited |
| | | | FFT: ~26.2 wk (PASS) | |
| $HNO_3$ | ACF: Lag 17 (0.127, PASS) | -- | -- | -- |
| | FFT: ~7.94 wk (PASS) | | | |
| $SO_2$ | ACF: Lag 142 (0.152, PASS) | -- | -- | -- |
| | FFT: ~54.0 wk (PASS) | | | |
| $TNO_3$ | ACF: Lag 32 (0.158, PASS) | -- | -- | -- |
| | FFT: ~54.0 wk (PASS) | | | |

*Table 1: Assessment of periodicity of variables for a representative sample of a CASTNET dry deposition site (WFM105, CASTNET Seg. 120) in comparison to two NADP/NTN wet deposition sites (NY98, NTN Seg. 1, and VT99, NTN Seg. 3). Data are presented based on a combination of time domain analysis using the autocorrelation function (ACF) and frequency domain analysis using fast Fourier transform (FFT) after a segment-specific Box-Cox transformation. Failed Box-Cox refers to cases where the variables did not meet QA/QC requirements ($R^2$ of the Q-Q plot > 0.95 and the bimodality test).*

## FFT and ACF of CASTNET

| Variable | Longest Qualifying Segments (Success Rate / Dominant FFT / ACF Lag) | 5-Year Segments (188 total) (Success Rate / Dominant FFT / ACF Lag) | 3-Year Segments (~435 total) (Success Rate / Dominant FFT / ACF Lag) | Overall Periodicity Strength |
|---|---|---|---|---|
| $SO_4^{2-}$ | High / Annual (~50–54 w) / ~50–110 w | 188/188 (100%) / Annual (~50–54 w) / ~50–110 w | 420/435 (~96.6%) / Annual (~50–54 w) / ~30–110 w | Strong Annual |
| $TNO_3$ | High / Annual (~50–54 w) / ~50–160 w | 188/188 (100%) / Annual (~50–54 w) / ~50–160 w | 435/435 (100%) / Annual (~50–54 w) / ~40–160 w | Strong Annual |
| $NH_4^+$ | High / Annual (~50–55 w) / ~25–160 w | 188/188 (100%) / Annual (~50–55 w) / ~25–160 w | 435/435 (100%) / Annual (~50–55 w) / ~25–160 w | Annual + Semi-annual |
| $Ca^{2+}$ | High / Annual (~50–54 w) / ~50–200 w | 187/188 (~99.5%) / Annual (~50–54 w) / ~50–200 w | ~430/435 (~98.9%) / Annual (~50–54 w) / ~40–150 w | Strong Annual |
| $SO_2$ | High / Annual (~50–54 w) / ~50–170 w | 184/188 (~97.9%) / Annual (~50–54 w) / ~50–170 w | ~415/435 (~95.4%) / Annual (~50–54 w) / ~30–170 w | Strong Annual |
| $HNO_3$ | High / Annual (~50–54 w) / ~50–180 w | 184/188 (~97.9%) / Annual (~50–54 w) / ~50–180 w | ~415/435 (~95.4%) / Annual (~50–54 w) / ~40–180 w | Strong Annual |
| $Na^+$ | Good / Annual (~50–54 w) / ~50–150 w | 169/188 (~89.9%) / Annual (~50–54 w) / ~50–150 w | ~400/435 (~92.0%) / Annual (~50–54 w) / ~30–150 w | Strong Annual |
| $NO_3^-$ | Good / Annual (~50–54 w) / ~50–150 w | 155/188 (~82.4%) / Annual (~50–54 w) / ~50–150 w | ~380/435 (~87.4%) / Annual (~50–54 w) / ~30–150 w | Strong Annual |
| $K^+$ | Moderate / Semi-annual (~25–27 w) / ~25–60 w | 152/188 (~80.9%) / Semi-annual (~25–27 w) / ~25–60 w | ~370/435 (~85.1%) / Semi-annual (~25–27 w) / ~20–60 w | Semi-annual Dominant |
| $Mg^{2+}$ | Moderate / Semi-annual (~25–27 w) / ~25–60 w | 144/188 (~76.6%) / Semi-annual (~25–27 w) / ~25–60 w | ~360/435 (~82.8%) / Semi-annual (~25–27 w) / ~20–60 w | Semi-annual Dominant |

*Table 2:* Comparison of periodicity detection robustness across segment lengths in the CASTNET network. Longest qualifying segments refer to the maximum continuous periods meeting quality criteria (up to ~22 years). All results are based on segment-specific Box-Cox transformations followed by dual FFT (frequency domain) and ACF (time domain) analyses. Success rates decrease modestly with shorter segments due to increased sensitivity to non-stationarity, but dominant annual (~48–57 weeks) and semi-annual (~25–27 weeks) cycles remain highly consistent.

## FFT and ACF of NTN/NADP

| Variable | Longest Qualifying Segments (Success Rate / Dominant FFT / ACF Lag) | 5-Year Segments (3 total) (Success Rate / Dominant FFT / ACF Lag) | 3-Year Segments (Success Rate / Dominant FFT / ACF Lag) | Overall Periodicity Strength |
|---|---|---|---|---|
| $SO_4^{2-}$ | 3/3 (100%) / Annual (~50–55 w) / ~40–54 w | 3/3 (100%) / Annual (~50–55 w) / ~40–54 w | High (~95%+) / Annual (~50–55 w) / ~30–60 w | Strong Annual |
| $NO_3^-$ | 3/3 (100%) / Annual (~48–57 w) / ~40–54 w | 3/3 (100%) / Annual (~50–55 w) / ~40–54 w | High (~90%+) / Annual (~50–55 w) / ~30–60 w | Strong Annual |
| $NH_4^+$ | 3/3 (100%) / Annual (~50–55 w) / ~40–54 w | 3/3 (100%) / Annual (~50–55 w) / ~40–54 w | High (~90%+) / Annual (~50–55 w) / ~30–60 w | Strong Annual |
| $Ca^{2+}$ | 2/3 (~67%) / Annual (~50–55 w) / ~40–105 w | 2/3 (~67%) / Annual (~50–55 w) / ~40–105 w | Moderate-High / Annual (~50–55 w) / ~30–100 w | Strong Annual |
| $K^+$ | Low (~33–50%) / Semi-annual (~25–27 w) where successful | Low / Semi-annual where successful | Moderate / Semi-annual (~25–27 w) where successful | Semi-annual (when passing) |
| $Mg^{2+}$ | Low (~33–50%) / Semi-annual (~25–27 w) where successful | Low / Semi-annual where successful | Moderate / Semi-annual (~25–27 w) where successful | Semi-annual (when passing) |
| $Na^+$ | Low-Moderate / Annual (~50–55 w) where successful | Low-Moderate / Annual (~50–55 w) where successful | Moderate / Annual (~50–55 w) where successful | Annual (when passing) |

*Table 3:* Comparison of periodicity detection robustness across segment lengths in the NADP/NTN network. Longest qualifying segments refer to the maximum continuous high-quality periods (up to ~9.43 years). Results are based on segment-specific Box-Cox transformations followed by dual FFT (frequency domain) and ACF (time domain) analyses. Success rates are lower and more variable than in CASTNET due to the inherently sparser nature of wet deposition data, but dominant annual (~48–57 weeks) cycles remain consistent across species that pass QA/QC. Semi-annual signals (~25–27 weeks) appear for base cations in passing segments.

## Single-Site Trend Detection and Early Warning Potential

| Seg_ID | SITE_ID | Start_Date | End_Date | Num_Years | acf_SO2_Lag | acf_SO2_Status | acf_SO4_Lag | acf_SO4_Status | acf_HNO3_Lag | acf_HNO3_Status | acf_NO3_Lag | acf_NO3_Status | acf_TNO3_Lag | acf_TNO3_Status | acf_NH4_Lag | acf_NH4_Status | acf_CA_Lag | acf_CA_Status | acf_K_Lag | acf_K_Status | acf_MG_Lag | acf_MG_Status | acf_Sodium_Lag | acf_Sodium_Status |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 94 | PSU106 | 1/4/00 | 5/10/22 | 22.35 | 107 | PASS | 114 | PASS | 179 | PASS | 255 | PASS | 164 | PASS | 125 | PASS | 11 | PASS | NA | FAIL BOXCOX | NA | FAIL BOXCOX | NA | FAIL |
| SUB_139 | PSU106 | 1/4/15 | 1/4/20 | 5 | 38 | PASS | 12 | PASS | 41 | PASS | 61 | FAIL | 35 | PASS | 12 | PASS | 85 | PASS | 25 | FAIL | 56 | PASS | 81 | FAIL |
| SUB_140 | PSU106 | 1/4/10 | 1/4/15 | 5 | 25 | PASS | 133 | PASS | 22 | PASS | 40 | PASS | 27 | PASS | 25 | PASS | 40 | PASS | 47 | PASS | 40 | PASS | 6 | PASS |
| SUB_141 | PSU106 | 1/4/05 | 1/4/10 | 5 | 114 | PASS | 6 | PASS | 46 | PASS | 59 | PASS | 91 | PASS | 32 | PASS | 17 | PASS | 60 | PASS | 17 | PASS | 54 | PASS |
| SUB_142 | PSU106 | 1/4/00 | 1/4/05 | 5 | 47 | PASS | 15 | PASS | 78 | PASS | 62 | PASS | 167 | PASS | 110 | PASS | 42 | PASS | NA | FAIL BOXCOX | NA | FAIL BOXCOX | 112 | FAIL |
| 27 | CHA467 | 7/29/03 | 12/18/18 | 15.39 | 20 | PASS | 162 | PASS | 55 | PASS | 95 | PASS | 101 | PASS | 20 | PASS | 204 | PASS | 222 | PASS | 200 | PASS | 4 | PASS |
| SUB_38 | CHA467 | 7/29/13 | 7/29/18 | 5 | 38 | PASS | 35 | PASS | 14 | PASS | 17 | PASS | 7 | PASS | 35 | PASS | 7 | PASS | 7 | PASS | 72 | PASS | 31 | FAIL |
| SUB_39 | CHA467 | 7/29/08 | 7/29/13 | 5 | 20 | PASS | 54 | PASS | 6 | PASS | 4 | PASS | 9 | PASS | 54 | PASS | 56 | FAIL | 124 | PASS | 86 | PASS | 4 | PASS |
| SUB_40 | CHA467 | 7/29/03 | 7/29/08 | 5 | 22 | PASS | 105 | PASS | 22 | PASS | 57 | PASS | 22 | PASS | 87 | PASS | 26 | PASS | 26 | PASS | 46 | PASS | 38 | PASS |
| 50 | GAS153 | 7/18/00 | 7/9/24 | 23.98 | NA | FAIL BOXCOX | 81 | PASS | 187 | PASS | NA | FAIL BOXCOX | 228 | PASS | 97 | PASS | 81 | PASS | NA | FAIL BOXCOX | NA | FAIL BOXCOX | 147 | PASS |
| SUB_75 | GAS153 | 7/18/15 | 7/18/20 | 5 | 31 | PASS | 81 | PASS | 20 | PASS | 54 | PASS | 11 | PASS | 42 | PASS | 32 | PASS | 57 | PASS | 48 | PASS | 20 | PASS |
| SUB_76 | GAS153 | 7/18/10 | 7/18/15 | 5 | 26 | PASS | 9 | PASS | 52 | PASS | 140 | PASS | 26 | PASS | 5 | FAIL | 51 | PASS | 55 | PASS | 39 | PASS | 22 | PASS |
| SUB_77 | GAS153 | 7/18/05 | 7/18/10 | 5 | 25 | PASS | 67 | PASS | 22 | PASS | 45 | PASS | 127 | PASS | 10 | PASS | 66 | PASS | 17 | PASS | 164 | PASS | 78 | PASS |
| SUB_78 | GAS153 | 7/18/00 | 7/18/05 | 5 | 28 | PASS | 37 | PASS | 5 | PASS | NA | FAIL BOXCOX | 32 | PASS | 46 | PASS | 48 | PASS | 29 | PASS | 54 | PASS | 7 | FAIL |

*Table 4:* ACF findings on all chemical species levels at three CASTNET stations (PSU106, CHA467, and GAS153). In this table, findings from multiple 5-year sub-samples regarding lags and their significance are compared with those from the longest qualifying segment. These changes may occur due to seasonal phase shifts

## Inverse Time Dominant ACF Lag-Based Spatial-Temporal Mapping and Its Relevance to the Atmospheric Transport Process

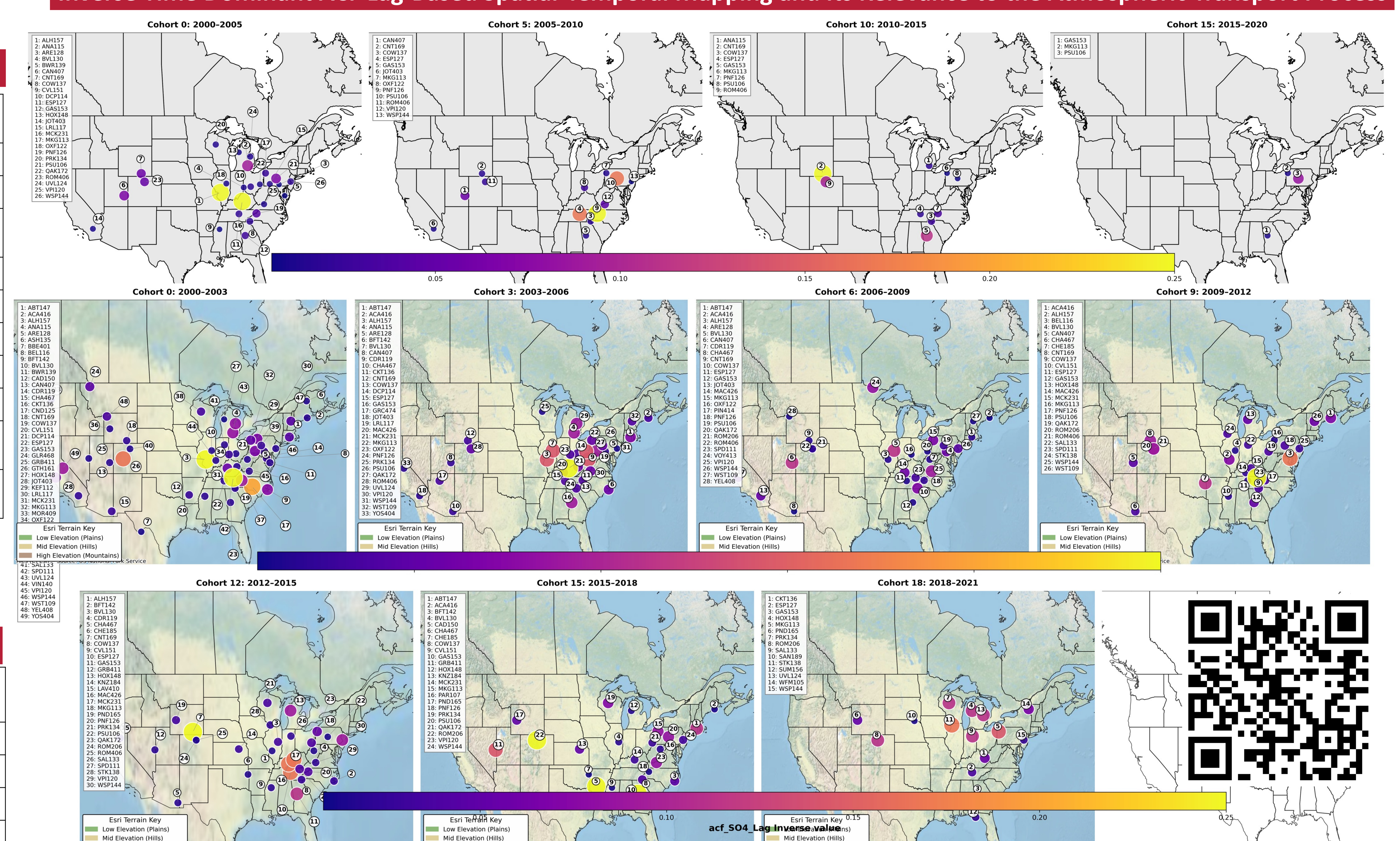


*Fig 2. Spatial-temporal maps of the inverse dominant ACF lag for SO4 across the CASTNET network, using non-overlapping 5 and 3-year cohorts from 2000 to 2021. The inverse ACF lag serves as a proxy for seasonal signal coherence, and the timing of peak concentrations — higher values (warmer colors) indicate stronger seasonal coherence or earlier seasonal peaks. Panels (a–g) show the evolution of spatial patterns over time. Terrain elevation is overlaid to assess potential topographic influences on seasonal dynamics: low-elevation (plains), mid-elevation (hills), and high-elevation (mountains). Note that some sites appear only in certain cohorts due to strict data quality criteria (≥5 years total record,*

## Summary

Our study establishes the dual FFT–ACF framework as a robust method that reliably detects persistent annual (48–57 weeks) and semi-annual (25–27 weeks) cycles in atmospheric deposition chemistry. FFT identifies the dominant frequencies while ACF validates them in the time domain and reveals fine-scale phase shifts in peak concentration timing. Analyses at co-located (WFM105–NY98) and proximal (WFM105–VT99) sites confirm high consistency between CASTNET and NADP/NTN networks. When applied across hundreds of segments, the approach uncovers transport-driven seasonal coherence patterns in the Southeast and Midwest regions.

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