National Atmospheric Deposition Program: Mercury Programs

Mark Olson & David Gay University of Wisconsin, State Laboratory of Hygiene



Quick Overview of NAPD Operations



<u>Mercury Deposition</u> <u>Network (MDN)</u>

- Collects one-week precipitationonly samples MDN wet-dry collector
- Measures precipitation with a separate gage
- Analyses
 - Total Mercury
 - Methyl Mercury
 - Other options
- since 1996, currently 84 sites
- 90,000 observations of total Hg

Wet Deposition Collection

<u>Atmospheric Mercury</u> <u>Network (AMNet)</u>

- Gaseous mercury concentrations (speciation)
 - GEM
 - GOM
 - PBM_{2.5}
- estimate of dry deposition flux
- Since 2008, currently 15 sites (2 GEM only)
- 800,000 observations at 24 sites

Operating AMNet Sites

Mercury Litterfall Network (trial network)

- Total and Methyl mercury concentrations (µg/gram biomass)
- estimate of dry mass flux
- Since 2007 (most years), currently ~20 sites
- Currently not a full network, but a trial
- Data not yet available from NADP

NADP New Situation

- NADP was moved from the University of Illinois to the University of Wisconsin in 2018
- All laboratory and data functions are within the Wisconsin State Laboratory for Hygiene now.

Stovall Building University of Wisconsin Madison

Quick Overview of Data Specifics

MDN Data Specifics

- Number of samples: ~87,000
- Current status: 1996-March, 2020
- Valid (A,B), and Invalid (C); both available
- Free for download:

http://nadp.slh.wisc.edu/data/MDN/weekly.aspx

NOTE CODE:

| | | Quality Rating |
|------|--|-------------------|
| Code | Description | (QR) code |
| е | Extended sample time (> 8days) | В |
| | | _ |
| d | debris present | В |
| m | missing information | В |
| Z | site operations problems | В |
| h | sample handling problems | В |
| i | low volume sample $(1.5 \text{ mL} \le \text{ sample} \text{ volume} < 10 \text{ mL})$ (Hg conc. data are reported but they are less certain than samples with a sample volume of at least 10 mL | В |
| b | bulk sample (sample exposed the whole time) | С |
| v | Rain gage indicates precipitation occurred but the sample volume was less than 1.5 mL, or the sample volume was less than 10% of indicated rain gage precipitation amount. | С |
| u | undefined sample (sample exposed for at least 6 hours without precipitation) | С |
| f | serious problems in field operations that compromise sample integrity | С |
| 1 | laboratory error | С |
| с | contamination of sample | С |
| р | no precipitation data from either the rain gage or the sample volume | С |
| n | no sample submitted | С |

Variables

MDN DATA FIELDS

SITE CODE: 2-letter state or province designator followed by a two digit number.

START DATE: (mm/dd/yyyy hh:mm), GMT

END DATE: (mm/dd/yyyy hh:mm), GMT

RGPPT: Precipitation amount as measured by the rain gage in millimeters. Trace amounts are indicated by -7.00 and missing amount by -9.00.

SVOL: Sample Volume, ml. Missing amounts are indicated by a -9.00.

SUBPPT: Rain gage precipitation amount, if available, in mm. If the rain gage value (RGPPT) is missing, the precipitation amount in mm is calculated from the net sample volume caught in the sample bottle. A value of 0.127 is inserted for Trace sample types. Missing amounts are indicated by a -9.00

HGCONC: Total mercury concentration reported by the lab in ng/L. Missing amounts are indicated by a -9.00 $\,$

HGDEP: Total mercury deposition, ng/m₂. The product of SUBPPT and HGCONC. Missing amounts are indicated by a -9.00

Quality rating (QR) CODE:

- A fully qualified with no problems
- B valid data with minor problems, used for summary statistics
- C invalid data, not used for summary statistics
- no sample submitted for this time period

SAMPLE TYPE:

- W wet sample, measurable precipitation (≥ 0.01 in.) on the rain gauge (RG) or net bottle catch (BC) ≥ 1.5 mL if RG data are missing. Concentration and deposition data are reported unless the QR Code is C.
- D dry sample The RG measured a 0 precipitation amount net, or if the RG is missing, the BC < 1.5 mL. No concentration data are reported and are indicated by a -9.00. RGPPT, SUBPPT, and HGDEP are set to zero.
- T trace sample, used when the rain gage detects that an unmeasurable amount of precipitation occurred. No Hg concentration or depositions are shown. SUBPPT is set to 0.127 mm
- -- unknown sample type. Precipitation amount is unknown.

AMNet Data Specifics

- Number of samples: 800,000
- Current status: 2008-March 2020
- Valid (A,B), and Invalid (C); invalid data not available
- Free for download

http://nadp.slh.wisc.edu/data/AMNet/

| Data Flag* nutil L A1 /(A2 /(B0 B B1 B B2 /F B3 B B5 B C0 /(C1 /(| Description Data meets criteria used in the automated scripts (Air cartridge bias, – Air cartridge bais, –)/Air cartridge bias, – 0.15 for 24 consecutive hours Baseline voltage < 0.01V Baseline voltage < 0.05V, or Baseline voltage, – Baseline voltage | Mercury Species All GEM | |
|--|---|-------------------------------|--|
| nutil E A1 ((A2 ((B0 B B1 B B2 (F B3 B B5 B C0 ((C1 () | Data meets criteria used in the automated scripts (Air cartridge bias, – Air cartridge bais;+1)/Air cartridge bias; > 0.10 for 24 consecutive hours (Air cartridge bias, – Air cartridge bais;+1)/Air cartridge bias; > 0.15 for 24 consecutive hours Baseline voltage < 0.01V Baseline voltage < 0.05V, or Baseline voltage > 0.25V Baseline voltage, – Baseline voltage;+1 > 0.01V Baseline deviation > 0.10V for 5 consecutive readings | All GEM | |
| A1 ((A2 () B0 B B1 B B2 [F B3 B B5 B C0 ((C1 () | (Air cartridge bias, – Air cartridge bais,+1)/Air cartridge bias, > 0.10 for 24 consecutive hours (Air cartridge bias, – Air cartridge bais,+1)/Air cartridge bias, > 0.15 for 24 consecutive hours Baseline voltage < 0.01V Baseline voltage < 0.05V, or Baseline voltage > 0.25V Baseline yoltage, – Baseline voltage;+1 > 0.01V Baseline deviation > 0.10V for 5 consecutive readings | GEM | |
| A2 ((B0 E B1 B B2 [F B3 B C0 ((C1 b) | (Air cartridge bias, – Air cartridge bais,:)/Air cartridge bias, > 0.15 for 24 consecutive hours Baseline voltage < 0.01V Baseline voltage < 0.05V, or Baseline voltage > 0.25V Baseline voltage, – Baseline voltage;:) > 0.01V Baseline deviation > 0.10V for 5 consecutive readings | GEM | |
| B0 E B1 B B2 JF B3 B B5 B C0 JC C1 JC | Baseline voltage < 0.01V Baseline voltage < 0.05V, or Baseline voltage > 0.25V Baseline <u>voltage</u> - Baseline voltage _{i+1} > 0.01V Baseline deviation > 0.10V for 5 consecutive readings | | |
| B1 E B2 F B3 E B5 E C0 f(C1 b | Baseline voltage < 0.05V, or Baseline voltage > 0.25V Baseline voltage, - Baseline voltage _{i+1} > 0.01V Baseline deviation > 0.10V for 5 consecutive readings | | |
| B2 JF B3 B B5 B C0 I(0 C1 I(0 | Baseline <u>voltage</u> – Baseline voltage _{i+1} > 0.01V Baseline deviation > 0.10V for 5 consecutive readings |] | |
| B3 E B5 B C0 ((C1 (b) | Baseline deviation > 0.10V for 5 consecutive readings | | |
| B5 E C0 ((C1 () | | - | |
| C0 (C1 (| Baseline deviation > 0.20V | Δ11 | |
| C1 (| (Calibration - Calibration:+)/Calibration > 0.10 | | |
| | (Calibration cartridge bias), – Calibration cartridge bais:+1)/Calibration cartridge bias; > 0.10 | | |
| C2 (| (Calibration cartridge bias, – Calibration cartridge bais, 1)/Calibration cartridge bias, > 0.20 | | |
| C5 (| (Calibration - Calibration +1)/Calibration > 0.05 | 1 | |
| E0 F | First GEM from each cartridge | | |
| E1 G | $GEM \le 1.00 \text{ ng/m}^3$ for same cartridge | GEM | |
| E5 (| (GEMi - GEMi+1)/GEMi > 0.50 for same cartridge | | |
| F1 7. | 72 hours < Time between calibrations < 144 hours | A11 | |
| F2 T | Time between calibrations > 144 hours | | |
| G0 G | $GOM = 0 \text{ pg/m}^3$ for more than 24 hours | | |
| G1 C | Cycle(H) < 0.70 x GOM, or Cycle(I) > 0.20 x GOM, or Cycle(J) > 0.10 x GOM | GOM | |
| G2 G | $GOM < 0 \text{ pg/m}^3$ | | |
| L1 G | GEM cycles < 24 before desorption | GOM | |
| L2 G | GEM cycles 🗢 GEM cyclesbiooxial | PBM _{2.5} | |
| M2 S | Status = M2 (multiple peaks) | Δ 11 | |
| M3 S | Status > M2 (multiple peaks) | All | |
| NP S | Status = NP (no peak) | GEM | |
| OL S | | A 11 | |

Variables

National Atmospheric Deposition Program

Atmospheric Mercury Network (AMNet)

| Field | Data Type | Description |
|-----------|-----------|---|
| SiteID | Char(4) | Site Identifier |
| CollStart | dateTime | Date/Time of Collection Start |
| CollEnd | dateTime | Date/Time of Collection End |
| CollTime | Integer | Collection Time, Minutes |
| PBM | Decimal | Average Particulate Bound |
| | | Mercury concentration, |
| | | picograms/m ³ . Missing or invalid |
| | | values are represented by -9. |
| PBMVal | Char(1) | PBM Validity A or B = valid, C= |
| | | invalid |
| GOM | Decimal | Average Gaseous Oxidized |
| | | Mercury (GOM), picograms/m ³ . |
| | | Missing or invalid values are |
| | | represented by -9. |
| GOMVal | Char(1) | GOM Validity. A or B = valid, C= |
| | | invalid |
| GEM | Decimal | Average Gaseous Elemental |
| | | Mercury (GOM), nanograms/m ³ . |
| | | Missing or invalid values are |
| | | represented by -9. |
| GEMValPct | Decimal | Per cent valid GEM |
| | | measurements |
| GEMVal | Char(1) | GEM Validity. A or B = valid, C= |
| | | invalid |

Measurements are corrected to standard conditions of 0 degrees Celsius and 1 atmosphere of pressure.

Developing Automated Dry Dep System

- *Estimates* of weekly dry deposition
- Further use of AMNet data
- Automated system, using NWS weather observations
- Following Env Canada and the work of Zhang et al.
- Automated weekly estimates of GOM, PBM, with GEM to follow
- To line up with MDN wet deposition

Quality Assurance of Data

- All Data...
 - Three levels of review
 - In the laboratory (not AMNet)
 - By the data management team
 - By the Program Office as final data
 - Full time QA professionals
 - Interlaboratory comparison program
 - Annual external laboratory audits
 - NADP QA Subcommittees

National Atmospheric Deposition Program: Mercury Programs

Mark Olson & David Gay University of Wisconsin, State Laboratory of Hygiene

