Lake Michigan Mass Balance Organics- The Good, the Bad and the Ugly

Marcia Kuehl
Grace Analytical
Project Veteran- June 1994

Atrazine

- **What:** atrazine (Atra), DEA, DIA
- **Where:** open lake, tributaries, atmosphere in vapor (V), particulates (P) and precipitation (T)
- **Who:** Rutgers (RULA, RUTA), ISWS (WSAA), IU (IUAA)
- **How:** Water grab samples, Vapor/Particulates HiVol Quartz filters/XAD-2, Precipitation MIC/XAD-2

Atrazine Analysis

- SPE extraction with DCM/MeOH
- GC/MS DB-5 column, SIM
- On column degradation of DEA/DIA
- pseudo PBMS

FOR MORE INFO...

See LMMB Methods Compendium Volume 2

Atrazine Data Verification

- Surrogate Correction “sometimes”
  - addition not started until after sample analysis began
- DEA/DIA chromatography
  - injection port breakdown, resultant poor QC sample recoveries
- GC/MS threshold integration area inconsistencies
  - set higher at ISWS, increased zeros
    - Not outliers---seasonality!

Atrazine Data Verification Flags

- EHT = Exceeded Holding Time
- FFD = Failed Field Duplicate
- FMS = Failed Matrix Spike
- FSS = Failed Surrogate Spike
- FFR = Failed Field Blank
- FBS = Failed Lab Blank
- OA3 = ±3sd outlier across all stations-QCID-FFRACT
- OS3 = ±3sd outlier within a station-QCID-FFRACT
- HIB = High Bias from LMS, FFR, FBS flags
- LOB = Low Bias from LMS

WSAA Statistics

- Precision
  - 2- 5 field duplicate (FD1) points, constant variability seen in RFS/FD1 pairs
- Accuracy
  - Lab perfomance checks (LPC) % bias at 0.69 to -19%, Lab matrix spikes (LMS) recovery means 82-83%
- Representativeness
  - no contamination in lab reagent blanks (LRB), field blanks (FRB)

WSAA Statistics (cont.)

- Comparability
  - same calibration standard source, but no surrogate correction
- Completeness
  - 96-100% due to lab accidents (LAC), field accidents (FAC)
- Sensitivity
  - 98% vapor results =0
  - 43-50% precipitation results =0
  - 78-87% particulate results=0
- Total Measurement Uncertainty 1.8% particulate samples, 48% precipitation

IUAA Statistics

- Precision
  - 2- 13 field duplicate (FD1) points, used surrogate correction factors for assessment (sd) for precipitation
- Accuracy
  - Lab matrix spikes (LMS) recovery means 80-110%
- Representativeness
  - some contamination in lab reagent blanks (LRB), field blanks (FRB) for vapor and precip

IUAA Statistics (cont.)

- Comparability
  - same calibration standard source, 87% surrogate corrected
- Completeness
  - 98-99% due to lab accidents (LAC), field accidents (FAC)
  - No DEA/DIA measurements
- Sensitivity
  - 83% vapor results below sample specific MDL ; 50% precipitation results below sample specific MDL
  - 87% particulate results below sample specific MDL (MDL flagged)
- Total Measurement Uncertainty 10.5% particulate samples, 2.4% precipitation, 11.6% vapor by Bootstrap Estimation Procedure

RULA Statistics

- Precision
  - 58-59 field duplicate (FD1) points, FD1 bias from RFS, surrogate correction factors sd 25%
- Accuracy
  - Used surrogate correction factors mean 0.913
- Representativeness
  - no contamination in lab reagent blanks (LRB) (No field or trip blanks collected)

RULA Statistics (cont.)

- Comparability
  - same calibration standard source, and surrogate correction
- Completeness
  - 69%, no collection May-October 1995
- Sensitivity
  - 100% Atra and DEA > MDL
  - 5% DIA < MDL
- Total Measurement Uncertainty using Bootstrap Procedure 20.1 %

RUTA Statistics

- Precision
  - 5 field duplicate (FD1) points, mean RPDs 8.5-13% analyte dependent , Surrogate correction factors sd 25%
- Accuracy
  - Used surrogate correction factors mean 0.87
- Representativeness
  - no contamination in lab reagent blanks (LRB) (No field or trip blanks collected)

RUTA Statistics (cont.)

- Comparability
  - same calibration standard source, and surrogate correction
- Completeness
  - 29%, no collection in 1994 season
- Sensitivity
  - 99% Atra > MDL
  - 90% DEA > MDL
  - 85% DIA < MDL
- Total Measurement Uncertainty using Bootstrap Procedure 0.58 %

PCBs and trans-nonachlor

- **What:** 130-180 congeners and trans-nonachlor
- **Where:** open lake (dissolved and particulate), tributaries (dissolved and particulate), atmosphere in vapor (V), particulates (P) and precipitation (T), sediment, dry deposition, plankton and fish
- **Who:** Rutgers (RUAP), ISWS (WSAP), IU (IUAP), Battelle (BALP), WSLH (LHTP), U Minnesota (MNPP), NOAA (NASP), USFWS/USGS (BSFP)
- **How:** Water Pentaplate/XAD-2, Vapor/Particulates HiVol Quartz filters/XAD-2, Precipitation MIC/XAD-2, Dry deposition greased Mylar strips, sediment traps, grabs and cores, plankton net and Phytovibe, mysis/diporeia sled tow, fish nets

PCBs and tNona Analysis

- 60 m DB-5 column, GC/EC, fish and tNona GC/NCI-MS
- pseudo-PBMS
- internal standards 30, 204
- surrogates 14, 65, 166, DBCE
- MDL determination
- single source quant mix and PE study

FOR MORE INFO...

See LMMB Methods Compendium Volume 2

PCB and tNona Data Verification

- Surrogate Correction “sometimes”
  - none for RUAP, sporadic tNona correction
- tNona/99 chromatography
  - coelution, carryover in silica gel fractionation
- congener reporting
  - 1 invalidated for WSAP, 99 HIB for WSAP from method change
  - interferences

PCB/tNona Data Verification Flags

- same as atrazine flags PLUS
- CON = Confirmed by alternate column
- FFT = Failed trip blank , FSB = Failed Solvent Blank
- FPC = Failed Lab Performance Check, FPS = Failed Lab performance Spike
- REJ = Rejected by PI , EST = Estimated value
- NAI = Not Analyzed due to Interference
- OA3 = ±3sd outlier across all stations-QCID-FFRACT
- OS3 = ±3sd outlier within a station-QCID-FFRACT
- HIB = High Bias
- LOB = Low Bias
- INV = Invalid

PCB/tNona Manual Flag Philosophy

- High Bias (HIB)
  - two or more failed blank codes present (FFT, FFR, FBS, FBK), or > 200% LMS recovery
  - field conditions
- Low Bias (LOB)
  - < 10% LMS or LPS or SLB recovery and result detected
  - < 25% LSS recovery (WSAP)
  - field conditions
- Invalid
  - < 10% LMS or LPS or SLB recovery and result undetected
  - < 10% LSS recovery
  - sampler bias (WSAP Lake Guardian)
  - FMB concentration indistinguishable from RFS (RUAP)

PCB/tNona Statistical Assessments

- Limit to Modeler's hit list of congeners
- In process

Manual Flag Highlights

- High bias from blank detects
  - 8+5, 15+17, 28+31, 44, 52, 56+60, 92+84, 87, 95, 101, 208+195
- Low bias or INV from matrix spike recoveries
  - 4+10, 209 12, 13, 134

RLP Pesticides and Polynuclear Aromatics

- **What:** 12 pesticides and 18 PNAs
- **Where:** tributaries (dissolved and particulate), atmosphere in vapor (V), particulates (P) and precipitation (T)
- **Who:** ISWS (WSAP and WSAU), IU (IUAP and IUAU), WSLH (LHTP)
- **How:** Water Pentaplate/XAD-2, Vapor/Particulates HiVol Quartz filters/XAD-2, Precipitation MIC/XAD-2

RLP Pesticides and Polynuclear Aromatics Analysis

- 60 m DB-5 column, GC/EC
- pseudo-PBMS
- fractionation from silica gel column
- surrogates 65, 155, or DBCE (IUAP) for pesticides
- MDL determination
- internal standards DDE, d_{10}-anthracene, d_{12} BAP, d_{12}-perlene, triphenylmethane

FOR MORE INFO...

See LMMB Methods Compendium Volume 2

RLP Pesticides and Polynuclear Aromatics Data Verification

- Pesticides verified with PCB/tNona
- pesticide blanks clean
- Low matrix recoveries for HCHA, HCHG, HCB
- PNA data not verified yet, need WSAU

The GOOD

- Passion persists
- Quality is known and ignorance is NOT bliss

The BAD

- Data “diplomacy”
- Still finding data to add to verified sets

The UGLY

- QC Coordinators mood
- Modelers mood

ORGANICS LESSONS LEARNED

- Indicate direction of bias on flags
  - I.e. FMH (Failed matrix spike High) aid in dv process and HIB, LOB assignment
- Define analytical Batch and QC sample linkages at start
- Define field QC sample linkages and flagging policy prior to collection
- Define sample collection start/end date and time meanings at start
- MQOs should detail when flags added and not added
- Involve PI on flag philosophy for LOB, HIB, INV codes up front