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Intra- and Intercorrelations among Soil Constituents and MeHg Bioaccumulation in the Mudworm (*Lumbriculus variegatus*) Exposed to a Set of South Florida Peat Soils in a 28-Day Wet Soil Bioassay

by Larry E. Fink, Private Consultant,
Boynton Beach, FL

Abstract

Soil core (0-4 cm) composites were collected from 5 subunits of each of 50, 1,000-acre operational units (OUs) in the potential footprint of the ~30,000-acre storage reservoir complex in the Everglades Agricultural Area in South Florida. The first-flush methylmercury (MeHg) production potential and bioavailability of these predominately peat soils were evaluated for 10 randomly selected OUs using the mudworm (*Lumbriculus variegatus*) in a standard 28-day wet sediment bioaccumulation bioassay. In addition to total mercury (THg) and MeHg, post-bioassay wet soils were analyzed for moisture and ash content; total iron, manganese, and sulfur; and acid volatile sulfide (AVS). Although the data set is small (n = 10 x 10 for soil constituents; 8 x 8 for MeHg and %MeHg), the results of exploratory intra- and intercorrelation analyses using parametric (Pearson) and nonparametric (Spearman) statistics are informative.

Abstract

(continued)

Perhaps surprisingly, wet soil MeHg was not statistically significantly ($p < 0.05$) correlated with any soil constituent, but %MeHg was strongly positively correlated with %ash and inversely correlated with moisture, manganese and sulfur. Worm MeHg concentration was strongly positively correlated with soil THg and %ash but not MeHg and strongly inversely correlated with moisture, manganese, and sulfur, while the correlations weakened for worm %MeHg. The worm THg and MeHg bioaccumulation factors were most strongly positively correlated with ash and inversely correlated with moisture, manganese, and sulfur. AVS was not intra- or intercorrelated with any other constituent, factor, or ratio thereof, as was the case for the ratio of post-/pre-wet soil THg, MeHg, and %MeHg.

Resource Management Questions

- Will any parcels in the EAA Storage Reservoir Project (EAASRP) experience a first-flush methylmercury (MeHg) anomaly of unacceptable magnitude, duration, and frequency of recurrence? … associated ecotox risks to fish-eating wildlife foraging there preferentially?
- Which soil factors influence the magnitude, duration, and frequency of first-flush MeHg anomaly potential?
- Which soil factors influence MeHg bioavailability to and bioaccumulation in the benthos-based reservoir aquatic food chain?

Background

- The ~30,000-acre Everglades Agricultural Area (EAA) Storage Reservoir Project (EAASRP) is the centerpiece of Everglades restoration effort.
- The proposed EAASRP footprint (Fig. 1) included up to 50,000 acres of EAA lands.
- Frequent drying and reflooding of the EAASRP during routine operation suggested the potential for a first-flush methylmercury (MeHg) anomaly.
- Such anomalies had already been encountered in wetlands constructed on EAA lands in Stormwater Treatment Areas (STAs) 2 and 6.

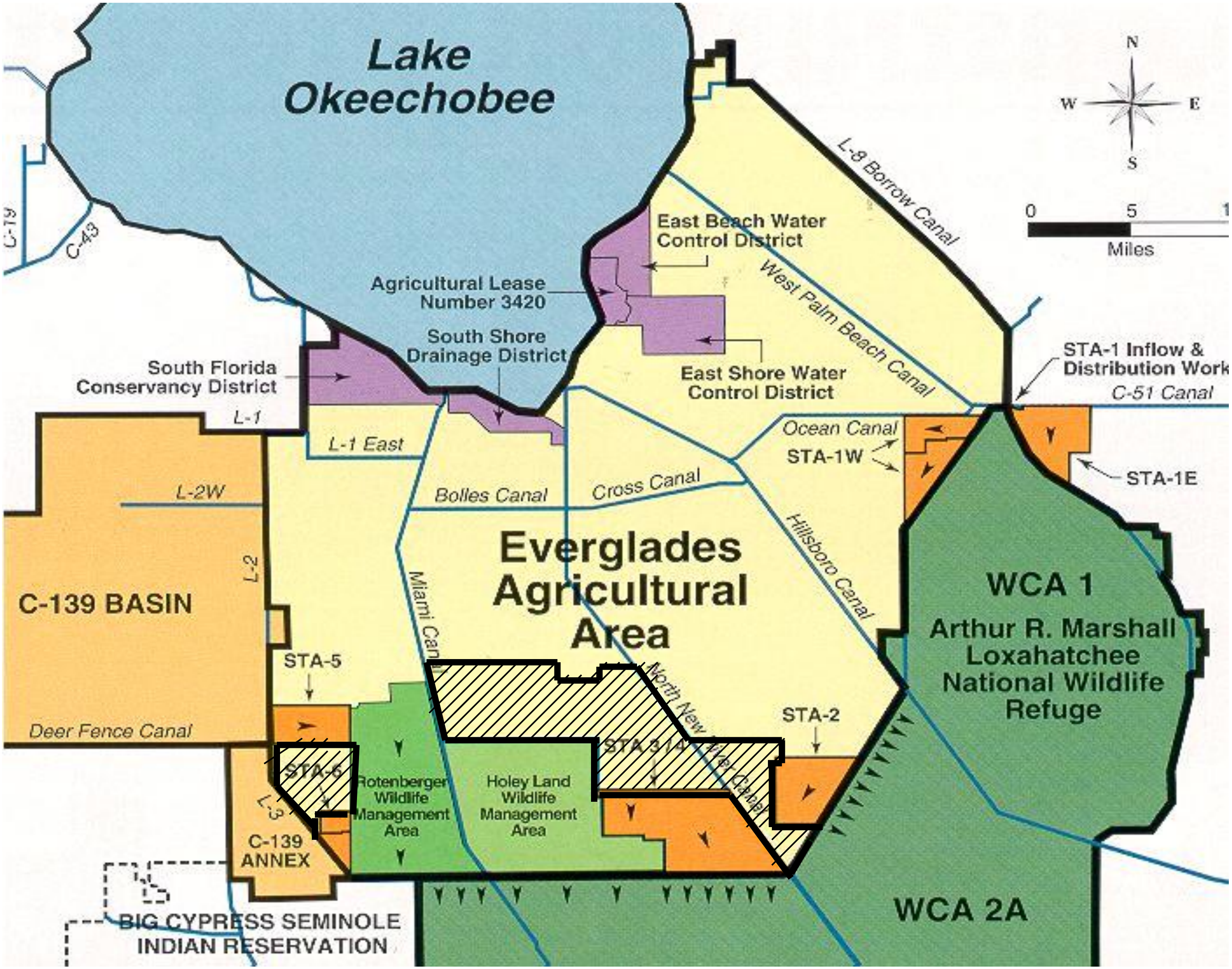


Figure 1. Proposed footprint of the Everglades Agricultural Area (EAA) Storage Reservoir Project (EAASRP)

Study Design

- To evaluate MeHg first-flush potential, in Phase I (P1) 6, 4-cm core samples were obtained from each of 5, 200-acre subunits and composited for each of 50, 1,000-acre operational units (OUs) [Fig. 2], and dry soil composites were analyzed for THg and MeHg.
- In Phase II (P2), 10 of the 50 [Fig. 2] were randomly selected for a 28-day mudworm (*Lumbriculus variegatus*) bioassay with wet worm and wet soil analysis for THg and MeHg and wet soil analysis for ash, moisture, TFe, TS, TMn, AVS, THg and MeHg.

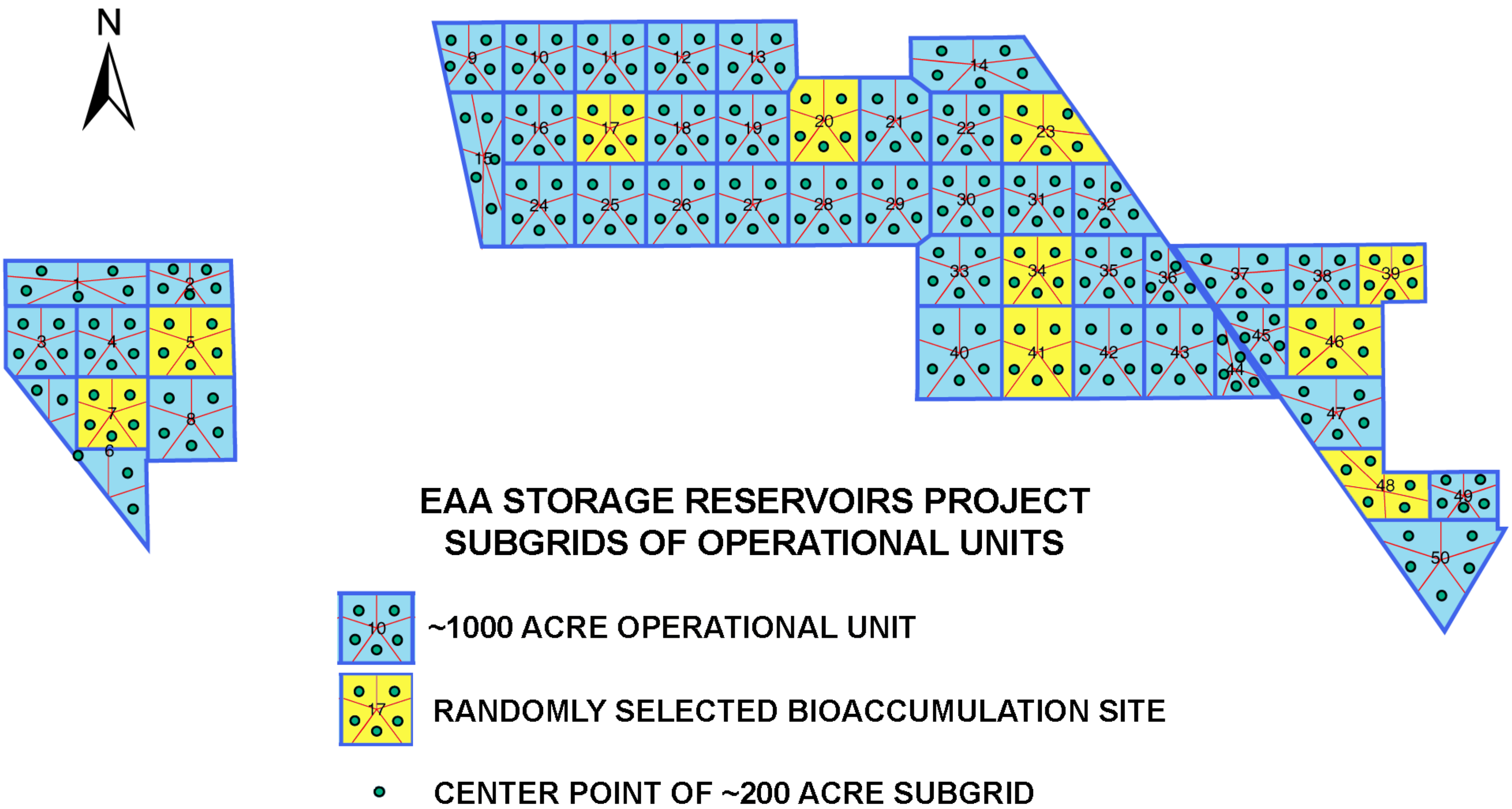


Figure 2. Proposed footprint of the Everglades Agricultural Area (EAA) Storage Reservoir Project (EAASRP)

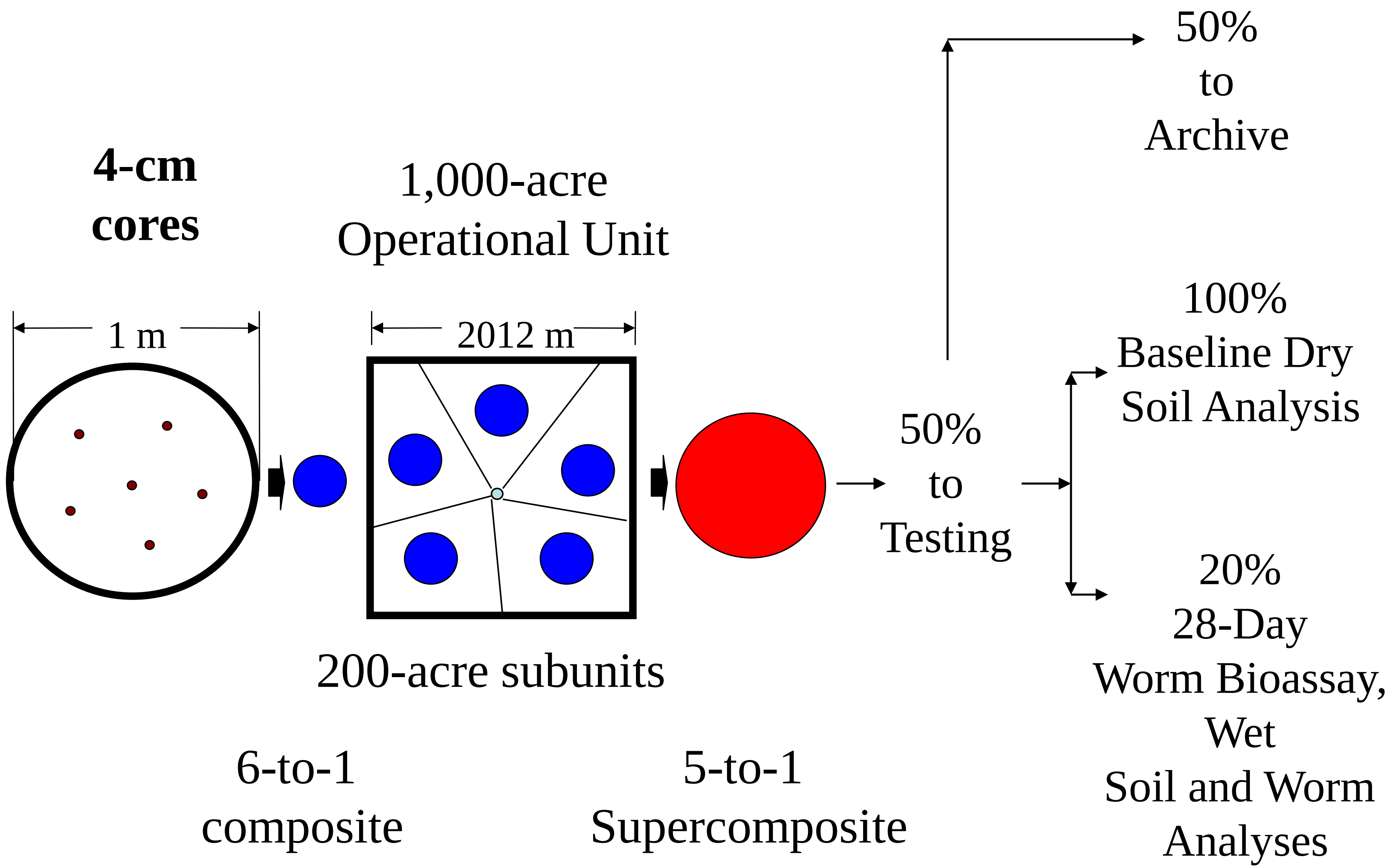


Figure 3. Soil Field Sampling and Sample Processing Protocol for the EAASRP

Methods

- Dry-soil 4-cm soil cores collected with acid precleaned polyurethane corer; cut with stainless steel spatula; homogenized in new polyurethane pans in mercury-uncontaminated lab.
- 28-day mudworm bioassay per USEPA (2000) using clean sand admixed with algae flake as reference medium.
- Mudworm guts not purged prior to homogenizing for chemical analysis.
- (Mudworms delayed burrowing for ~ 7 days until peat rehydrated sufficiently.)
- Statistical analysis performed using Microsoft XLSTAT®.

Methods

- Dry-, bioassay wet-soil composites and organism homogenates analyzed for THg and MeHg per USEPA Methods 1631 and 1630, respectively, by Frontier Geoscience (FGS) of Seattle, WA.
- Post-bioassay salmon and algae rations and mudworms rerun by Florida Dept. Environmental Protection ultra-trace mercury lab in Tallahassee when 8 of 10 FGS results were non-detect.
- Bioassay wet-soil ash, moisture, TFe, TMn, TS, and AVS analysis using standard or literature methods by DB Environmental Laboratory of Rockledge, FL.

Phase II Results

	Soil ASH DRY WT (%)	MOIST DRY WT (%)	TFE DRY WT (mg/Kg)	TMN DRY WT (mg/Kg)	TS DRY WT (mg/Kg)	AVS DRY WT (mg/Kg)
SEAAOU5	62.3	36.7	4300	59	1700	152
SEAAOU7	89.1	25.1	2100	21	800	130
SEAAOU17	34.5	64.26	8500	170	3600	250
SEAAOU20	18.5	67.38	6500	170	4200	319
SEAAOU23	23.6	64.45	6800	170	4900	269
SEAAOU34	28.3	63.06	5000	130	4000	239
SEAAOU39	16.7	71.93	3100	180	5100	76
SEAAOU41	26.5	62.47	5100	130	3800	61
SEAAOU46	14.6	79.95	2400	230	4900	550
SEAAOU48	25	64.51	3500	99	3500	241
LABQC 0	92.4	63.58	21000	180	6600	501

	THg DRY WT (mg/Kg)	MeHg DRY WT (mg/Kg)	%MeHg	RATIO Phase 2-to-1 Soil THg	MeHg	%MeHg
SEAAOU5	0.01970	0.00047	2.40	1.24	3.94241	3.14269
SEAAOU7	0.00910	0.00024	2.62	0.85714	3.7619	4.35897
SEAAOU17	0.03000	0.00015	0.50	1.09091	1.09254	0.99632
SEAAOU20	0.03090	0.00027	0.88	1	1.67906	1.68196
SEAAOU23	0.03280	0.00036	1.09	0.93069	2.0501	2.20917
SEAAOU34	0.03100	0.00046	1.49	1.07143	1.63241	1.51703
SEAAOU39	0.01940	0.00019	0.98	0.91667	2.21306	2.42321
SEAAOU41	0.03280	0.00086	2.62	0.97872	2.75431	2.82637
SEAAOU46	0.01750	0.00034	1.93	0.97647	2.61375	2.67898
SEAAOU48	0.03440	0.00053	1.53	1.14458	1.981	1.72529
LABQC 0	0.04710	0.00188	4.00			

Phase II Results

Worm

	THg DRY WT (mg/Kg)	MeHg DRY WT (mg/Kg)	DRY FRACTION (unitless)	THg WET WT (mg/Kg)	MeHg WET WT (mg/Kg)	%MeHg (unitless)	THg SBAF	MeHg SBAF	RATIO %MeHg
SEAAOU5	0.04481	0.0135	0.097	0.00435	0.00170	39.08	9.20	3.59	16.28
SEAAOU7	0.04653	0.0108	0.086	0.00400	0.00150	37.50	16.81	6.30	14.34
SEAAOU17	0.05412	< MDL	0.017	0.00092			6.09		
SEAAOU20	0.02777	0.008	0.048	0.00133	0.00037	27.82	4.91	1.37	31.72
SEAAOU23	0.03582	0.0021	0.087	0.00312	0.00051	16.35	8.72	1.42	14.98
SEAAOU34	0.03902	0.0034	0.09	0.00351	0.00057	16.24	7.58	1.23	10.87
SEAAOU39	0.0185	0.0012	0.084	0.00155	0.00037	23.87	8.16	1.95	24.37
SEAAOU41	0.03695	0.0008	0.091	0.00336	0.00060	17.86	3.91	0.70	6.82
SEAAOU46	0.02453	< MDL	0.097	0.00238			7.06		
SEAAOU48	0.03795	0.0111	0.092	0.00349	0.00037	10.60	6.62	0.70	6.92
LABQC 0	0.10855	0.0131	0.083	0.00901	0.00150	16.65	4.78	0.80	4.16

Results of Intracorrelation Analysis (Covariance Matrix): Soil vs. Soil

Spearman Covariance Matrix	THg	MeHg	%MeHg	ASH	MOIST	TFE	TMN	TS	AVS
Soil THg	1	**0.743**	0.060	-0.216	0.216	0.551	0.121	0.132	0.335
Soil MeHg	**0.743**	1	0.571	0.310	-0.310	0.310	-0.361	-0.381	-0.071
Soil %MeHg	0.060	0.571	1	**0.786**	**-0.833**	-0.310	**-0.771**	**-0.786**	-0.619
ASH	-0.216	0.310	**0.786**	1	**-0.952**	-0.333	**-0.916**	**-0.881**	-0.286
MOIST	0.216	-0.310	**-0.833**	**-0.952**	1	0.190	**0.831**	**0.810**	0.357
TFE	0.551	0.310	-0.310	-0.333	0.190	1	0.458	0.452	0.524
TMN	0.121	-0.361	**-0.771**	**-0.916**	**0.831**	0.458	1	**0.988**	0.181
TS	0.132	-0.381	**-0.786**	**-0.881**	**0.810**	0.452	**0.988**	1	0.214
AVS	0.335	-0.071	-0.619	-0.286	0.357	0.524	0.181	0.214	1
MeHg/fom	-0.108	0.429	**0.905**	**0.929**	**-0.929**	-0.357	**-0.952**	**-0.952**	-0.357
%MeHg/%fom	0.611	0.476	0.024	-0.452	0.476	0.119	0.386	0.333	-0.262
MeHg/fH20	0.156	**0.714**	**0.952**	**0.786**	**-0.833**	-0.119	**-0.783**	**-0.810**	-0.452
THg P2/P1	0.443	0.667	0.048	0.167	-0.024	0.214	-0.265	-0.262	0.333
MeHg P2/P1	-0.455	0.024	0.619	0.452	-0.595	-0.405	-0.470	-0.500	-0.619
%MeHg P2/P1	-0.503	-0.071	0.643	0.476	-0.619	-0.476	-0.494	-0.524	-0.643

Spearman Nonparametric Correlation Analysis (bold = stat. sig. $p < 0.05$)

Results of Intercorrelation Analysis (Covariance Matrix): Worm vs. Soil

Spearman Covariance Matrix	**Worm THg**	**Worm MeHg**	**Worm %MeHg**	**THg SBAF**	**MeHg SBAF**	**MeHg SBAFOM**	**RATIO %MeHg**
Worm THg	1	**0.805**	0.214	**0.952**	0.310	-0.238	-0.405
Worm MeHg	**0.805**	1	0.512	**0.878**	0.366	-0.171	-0.268
Worm %MeHg	0.214	0.512	1	0.262	**0.738**	0.476	0.571
THg SBAF	**0.952**	**0.878**	0.262	1	0.310	-0.357	-0.476
MeHg SBAF	0.310	0.366	**0.738**	0.310	1	0.595	0.595
MeHg SBAFOM	-0.238	-0.171	0.476	-0.357	0.595	1	**0.905**
Ratio %MeHg	-0.405	-0.268	0.571	-0.476	0.595	**0.905**	1

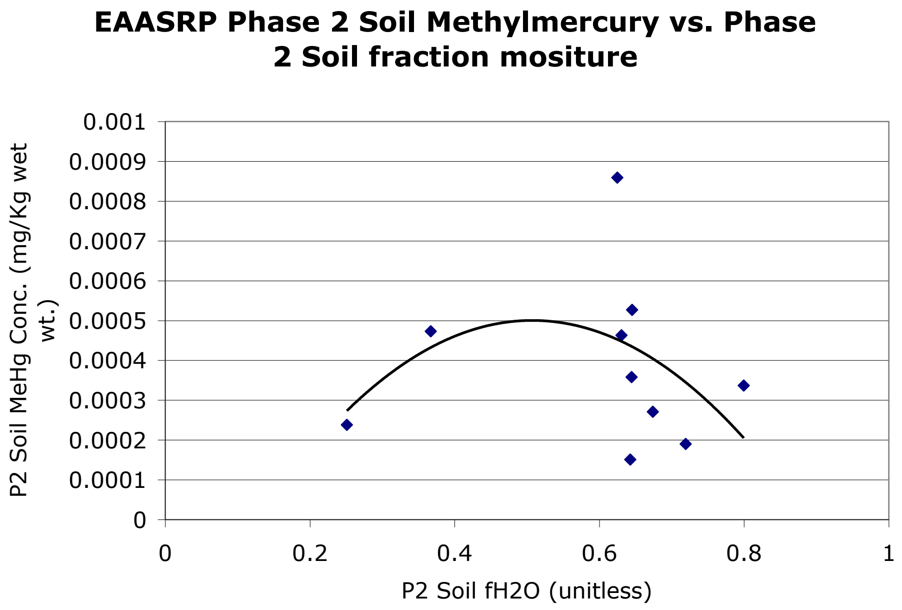
Spearman Covariance Matrix	**Soil THg**	**Soil MeHg**	**Soil %MeHg**	**MeHg/fom**	**%MeHg/%**	**MeHg/fH2(**	**THg Ratio P2/P1**	**MeHg**	**%MeHg**
Worm THg	-0.180	0.333	**0.714**	**0.857**	-0.405	**0.714**	0.333	0.476	0.452
Worm MeHg	-0.319	0.268	**0.756**	**0.830**	-0.488	**0.781**	0.073	0.683	0.659
Worm %MeHg	**-0.802**	-0.381	0.119	0.310	-0.643	0.167	-0.167	0.690	0.667
THg SBAF	-0.263	0.262	**0.810**	**0.905**	-0.405	**0.762**	0.095	0.524	0.548
MeHg SBAF	**-0.838**	-0.690	-0.071	0.190	**-0.857**	-0.143	-0.357	0.548	0.571
MeHg SBAFOM	-0.551	-0.619	-0.667	-0.524	-0.381	-0.619	0.000	0.071	-0.024
Ratio %MeHg	-0.575	**-0.714**	**-0.738**	-0.524	-0.476	-0.667	-0.119	0.000	-0.048

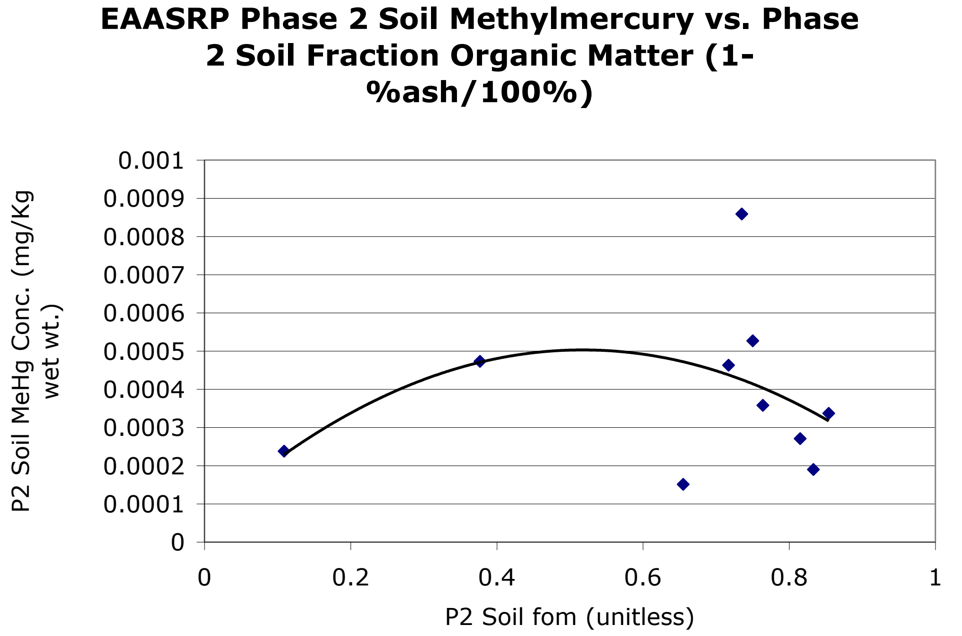
Spearman Correlation Analysis (bold = stat. sig. $p < 0.05$)

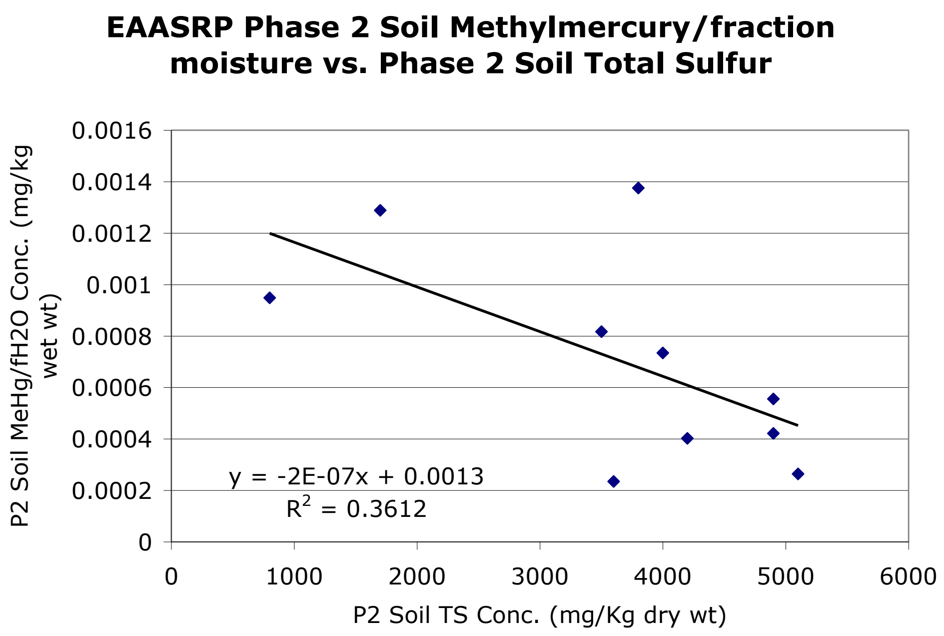
Results of Intercorrelation Analysis (Covariance Matrix): Worm vs. Soil

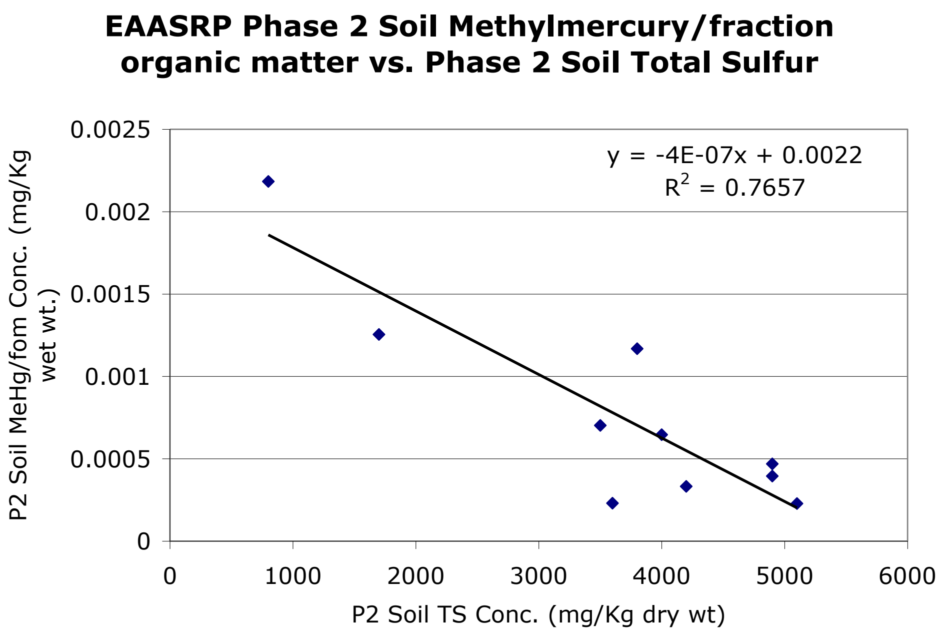
Spearman Covariance Matrix	**ASH**	**MOIST**	**TFE**	**TMN**	**TS**	**AVS**
Worm THg	**0.929**	**-0.833**	-0.452	**-0.892**	**-0.833**	-0.286
Worm MeHg	**0.878**	**-0.952**	-0.146	-0.704	-0.683	-0.439
Worm %MeHg	0.286	-0.381	-0.238	-0.253	-0.310	-0.238
THg SBAF	**0.976**	**-0.929**	-0.452	**-0.880**	**-0.833**	-0.429
MeHg SBAF	0.262	-0.286	-0.452	-0.229	-0.190	-0.071
MeHg SBAFOM	-0.405	0.405	-0.024	0.458	0.476	0.167
Ratio %MeHg	-0.452	0.429	0.071	0.446	0.429	0.357

Spearman Correlation Analysis (bold = stat. sig. $p < 0.05$)

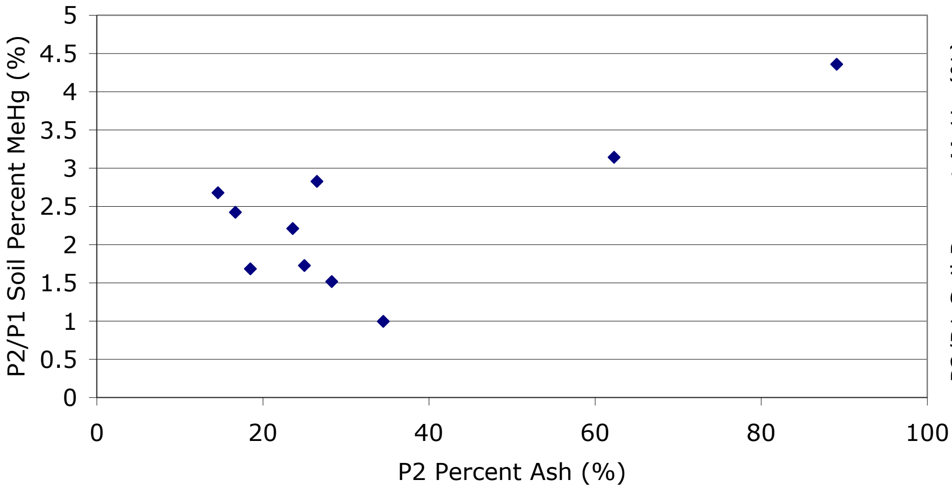

EAASRP Phase 2 Soil Methylmercury vs. Phase 2 Soil fraction mositure
P2 Soil MeHg Conc. (mg/Kg wet wt.)
P2 Soil fH2O (unitless)


EAASRP Phase 2 Soil Methylmercury vs. Phase 2 Soil Fraction Organic Matter (1-%ash/100%)
P2 Soil MeHg Conc. (mg/Kg wet wt.)
P2 Soil fom (unitless)

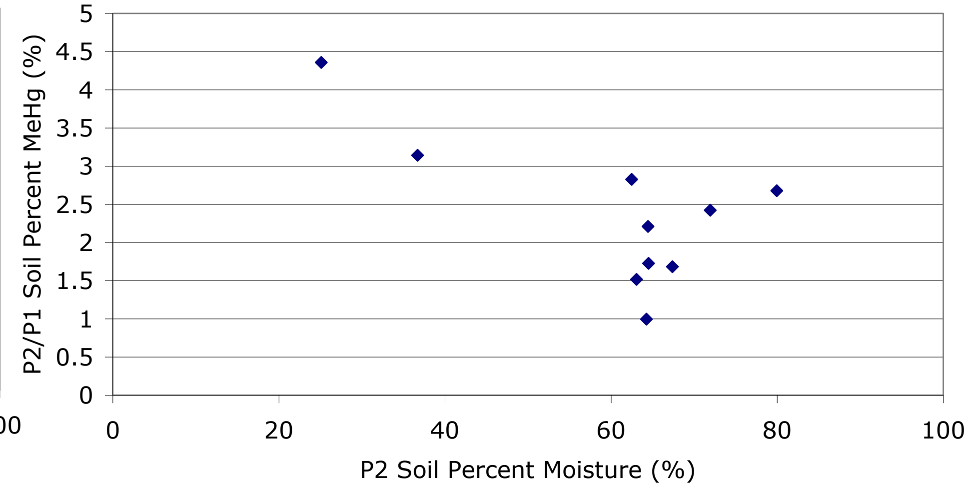

EAASRP Phase 2 Soil Methylmercury/fraction moisture vs. Phase 2 Soil Total Sulfur
P2 Soil MeHg/fH2O Conc. (mg/kg wet wt)
y = -2E-07x + 0.0013
R2 = 0.3612
P2 Soil TS Conc. (mg/Kg dry wt)


EAASRP Phase 2 Soil Methylmercury/fraction organic matter vs. Phase 2 Soil Total Sulfur
P2 Soil MeHg/fom Conc. (mg/Kg wet wt.)
y = -4E-07x + 0.0022
R2 = 0.7657
P2 Soil TS Conc. (mg/Kg dry wt)

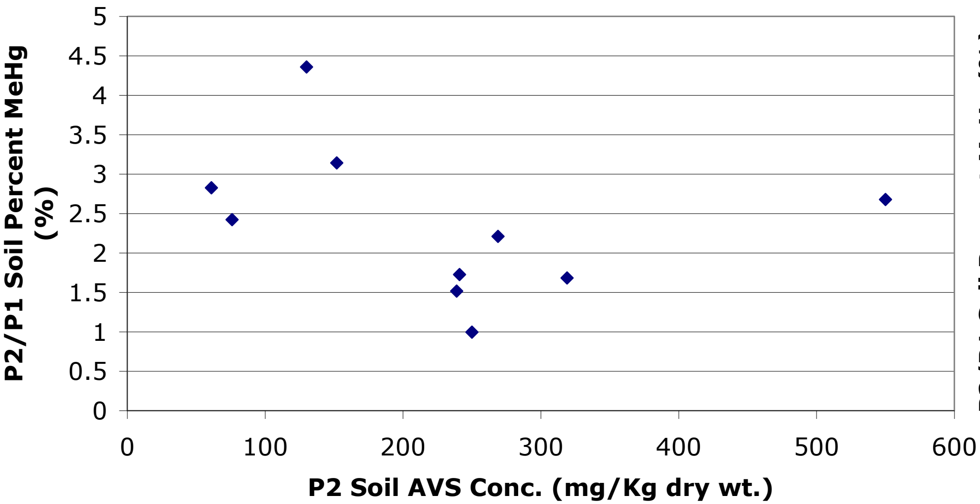
EAASRP Ratio Phase 2-to-1 Soil Percent Methylmercury vs. Phase 2 Soil Percent Ash



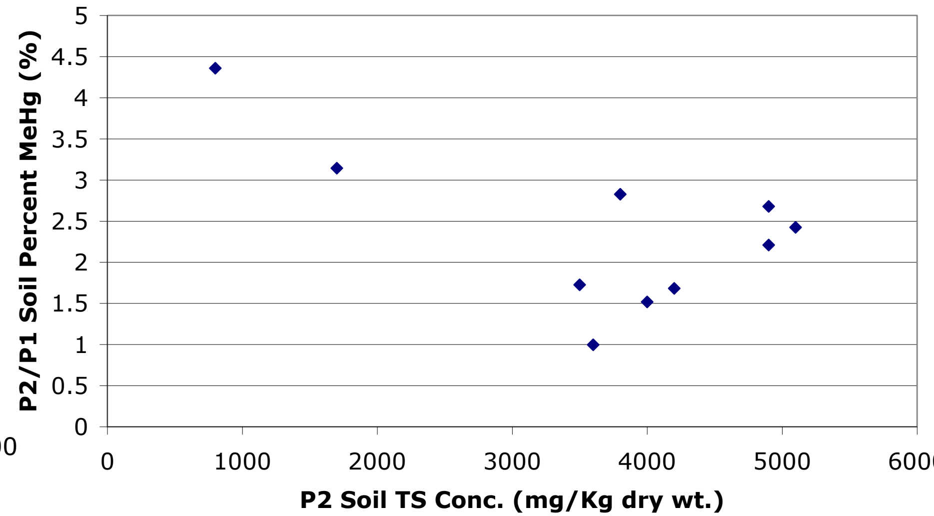
EAASRP Ratio Phase 2-to-1 Soil Percent Methylmercury vs. Phase 2 Soil Percent Moisture



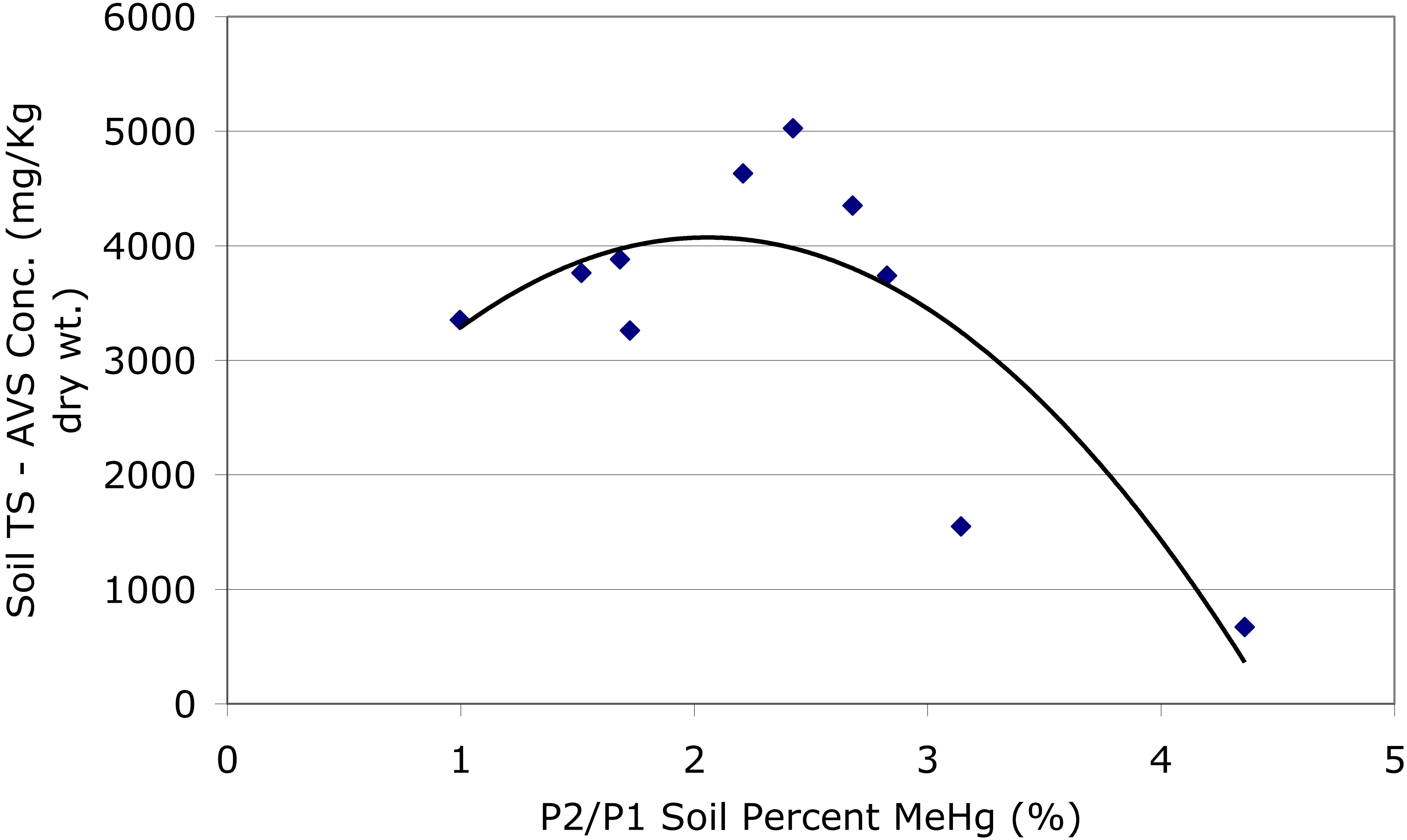
EAASRP Ratio Phase 2-to-1 Soil Percent Methylmercury vs. Phase 2 Acid Volatile Sulfide



EAASRP Ratio Phase 2-to-1 Soil Percent MeHg vs. Phase 2 Soil Total Sulfur



EAASRP Ratio Phase 2-to-1 Soil Percent MeHg vs. Phase 2 Soil Total Sulfur - Acid Volatile Sulfide ~ Total Organic Sulfur



Key Findings

- Neither soil MeHg nor LN MeHg conc. was strongly linearly correlated with any other absolute or normalized individual soil parameter except positively with THg.
- Conversely, soil %MeHg was very strongly inversely correlated with ash, moisture, TS and TMn, all of which strongly covary, but not AVS.
- P2/P1 & LN P2/P1 MeHg or %MeHg not statistically significantly linearly correlated with any individual soil parameter, but parabolic relationship vs. moisture and [TS-AVS] suggests more complex intxn. with/influence of soil TS species.

Key Findings

- Worm %MeHg & MeHg SBAF were most strongly inversely correlated with soil THg conc. but not positively with soil MeHg conc.

Key Conclusions

- The potential for a substantial first-flush MeHg anomaly during first flooding or reflooding of EAA Storage Reservoir soils appears to be low.
- The use of dry soil MeHg conc. or %MeHg conc. to infer corresponding post-flooding values is contraindicated for soils with low first-flush MeHg anomaly potential, but this limitation is of little consequence when determining whether to exclude an OU from a proposed treatment wetland or reservoir project footprint.

References

- USEPA (2000). Methods for Measuring the Toxicity and Bioaccumulation of Sediment-Associated Contaminants with Freshwater Invertebrates. EP/600/R-99/064. U.S. Environmental Protection Agency. Washington, DC.

Disclaimer

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- TetraTech, Inc. for its diligence in collecting and compositing multiple soil cores over 50,000 acres of actively and formerly farmed land, flexibility in adapting the sampling schedule to the accessibility of the sugar cane fields, delaying the mudworm bioassay to allow for depuration of the algae-fed mudworm, and most importantly carrying the work under contract to SFWMD with professionalism and alacrity.