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Analytical Variance – A Major Source of Uncertainty in Passive Sampling?

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Information from PT Schemes and Validation ILCs

- **Pharmaceuticals**
- **Polar Pesticides**
- **PBDEs**

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Pharmaceuticals in Water

- **Special Interlaboratory Comparison on Pharmaceuticals in „Raw Water“**
  - **Organiser**
    - *Behörde für Soziales, Familie, Gesundheit und Verbraucher-schutz (BSG), Institut für Hygiene und Umwelt, Bereich Umweltuntersuchungen, Marckmannstraße 129 b, D-20539 Hamburg, Germany*
  - **Target analytes**
    - *Phenazone, Propyphenazone, Ibuprofen, Diclofenac, Clofibric acid, Benzafibrate, Carbamazepine, Sotalol, Metoprolol, Sulfamethoxazole, Iopamidol, Amidotrizoic acid*
  - **Number of participants: 41**
  - **Report**

    http://www.hamburg.de/contentblob/2726378/data/ausw-sonder-luerv-03-2010.pdf

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Pharmaceuticals in Water

Anallyte	No of results	Level 1 µg/L	$SD_{robust, rel}$	No of results	Level 2 µg/L	$SD_{robust, rel}$
Phenazone	22	0,166	18,0	23	0,249	15,1
Propyphenazone	21	0,325	14,9	24	0,502	13,4
Ibuprofen	29	0,336	17,4	29	0,400	15,8
Diclofenac	29	0,478	18,8	30	0,105	22,7
Clofibric acid	25	0,109	21,0	27	0,344	13,1
Benzafibrate	24	0,204	18,1	24	0,323	13,1
Carbamazepine	29	0,456	12,6	28	0,096	14,8
Sotalol	20	0,389	31,2 (30,0)	22	0,186	34,9 (30,0)
Metoprolol	21	0,283	40,0 (30,0)	21	0,398	45,7 (30,0)
Sulfametoxazole	26	0,198	21,3	27	0,326	16,6
Iopamidol	16	0,379	12,9	18	0,144	23,2
Amidotrizoic acid	11	0,640	19,3	14	0,162	18,9

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WFD Pesticides in Surface Water

- **PT-WFD Proficiency test 5/2011 - Priority pesticides in surface water**
  - **Organiser:**
    - *AQS Baden-Württemberg at Institute for Sanitary Engineering, Water Quality and Solid Waste Management, University of Stuttgart Bandtäle 2, 70569 Stuttgart-Büsnau, Germany*
  - **Target analytes**
    - *Aclonifen, alachlor, atrazine, bifenox, chlorfenvinphos, chlorpyriphos, cybutryne, diuron, isoproturon, quinoxyfen, simazine, terbutryne, trifluralin*
  - **Number of participants: 33**
  - **Report**

    http://www.iswa.uni-stuttgart.de/ch/aqs/rv/index.en.html#rv_list

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WFD Pesticides in Water

Pesticide	Assigned Value [ng/L]	SD_{robust} [ng/L]	$SD_{robust, rel}$	No of results
Aclonifen	0.0713	0.0231	32.4%	22
Alachlor	0.0694	0.0111	16.0%	29
Atrazine	0.0781	0.0174	22.3%	32
Bifenox	0.0723	0.0149	20.6%	23
Chlorfenvinphos	0.0635	0.0133	20.9%	26
Chlorpyriphos	0.0606	0.0212	35.0%	25
Cybutryne	0.0648	0.0100	15.4%	24
Diuron	0.0810	0.0169	20.9%	28
Isoprturon	0.0772	0.0108	14.0%	29
Quinoxyfen	0.0635	0.0225	35.4%	21
Simazine	0.0704	0.0191	27.1%	32
Terbutryne	0.0622	0.0130	20.9%	30
Trifluralin	0.0678	0.0169	24.9%	23

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Validation Interlaboratory Study

DIN 38407-35: 2010; Determination of selected phenoxyalkyl carboxylic acids and other acidic pesticides - Method using high performance liquid chromatography and mass spectrometric detection (HPLC-MS/MS)

Wirkstoff	*l*	*n*	n_{AP}	$\bar{x}$	x_{soll}	η	s_R	CV_R	s_r	CV_r
2,4-D	18	54	0,0	0,200	0,188	106,6	0,0262	13,1	0,0094	4,7
2,4-DB	17	51	0,0	0,217	0,225	96,6	0,0362	16,6	0,0116	5,3
2,4,5-T	17	51	5,6	0,230	0,225	102,0	0,0487	21,2	0,0080	3,5
Bentazon	16	48	0,0	0,210	0,187	112,3	0,0396	18,9	0,0086	4,1
Bromoxynil	16	48	5,9	0,198	0,188	105,5	0,0225	11,3	0,0083	4,2
Clopyralid	12	36	0,0	0,216	0,225	96,2	0,0407	18,8	0,0120	5,5
Dicamba	14	42	6,7	0,197	0,187	105,4	0,0354	18,0	0,0098	5,0
Dichlorprop	17	51	5,6	0,190	0,188	101,3	0,0232	12,2	0,0064	3,4
Dinoterb	14	42	6,7	0,239	0,250	95,5	0,0440	18,4	0,0148	6,2
DNOC	16	48	0,0	0,244	0,250	97,6	0,0331	13,6	0,0122	5,0
Fenoxaprop	14	42	6,7	0,182	0,187	97,1	0,0393	21,6	0,0068	3,7
Fluazifop	15	45	6,3	0,193	0,188	102,7	0,0260	13,5	0,0054	2,8
Fluroxypyr	14	42	12,5	0,182	0,188	96,8	0,0388	21,3	0,0084	4,6
Haloxyfop	16	48	0,0	0,184	0,188	97,9	0,0302	16,4	0,0078	4,2
Ioxynil	13	39	18,8	0,221	0,225	98,2	0,0308	13,9	0,0062	2,8
MCPA	18	54	0,0	0,199	0,188	105,9	0,0268	13,5	0,0096	4,8
MCPB	17	51	0,0	0,230	0,250	92,0	0,0227	9,8	0,0134	5,8
Mecoprop	16	48	11,1	0,204	0,187	109,2	0,0136	6,6	0,0072	3,5
Mesotrion	15	45	6,3	0,230	0,249	92,5	0,0268	11,6	0,0083	3,6
Nicosulfuron	13	39	18,8	0,249	0,250	99,8	0,0270	10,8	0,0061	2,4
Quinmerac	16	48	0,0	0,189	0,188	100,5	0,0259	13,7	0,0079	4,2
Sulcotrion	15	45	6,3	0,297	0,225	132,2	0,0305	10,2	0,0087	2,9

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PBDE in Surface Water

- **PT-WFD Proficiency Test 6/2010 – Polybrominated diphenyl ethers in surface water**
  - **Target Analytes**
    - *BDE 28, BDE 47, BDE 99, BDE 100, BDE 153, BDE 154*
  - **Organiser:**
    - *AQS Baden-Württemberg at Institute for Sanitary Engineering, Water Quality and Solid Waste Management, University of Stuttgart Bandtäle 2, 70569 Stuttgart-Büsnau, Germany*
  - **Number of participants: 28**
  - **Report**

    http://www.iswa.uni-stuttgart.de/ch/aqs/rv/index.en.html#rv_list

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PBDE in Water

BDE Congener	Assigned Value [ng/L]	SD_{robust} [ng/L]	$SD_{robust, rel}$ [%]	No of results
BDE 28	0,7877	0,2047	26%	19
BDE 47	1,172	0,3227	28%	20
BDE99	0,9902	0,4249	43%	20
BDE100	0,9249	0,2449	26%	20
BDE153	1,106	0,3718	34%	20
BDE 154	1,207	0,2964	25%	22

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Uncertainty of Measurement

- **Hypothesis**
  - **Analytical variance is the main contributor to overall uncertainty in passive sampling**

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Uncertainty Budget - Example

- **Assumptions**
  - Uncertainty of analysis: 30%
  - Total uncertainty: 100%

$$u = \sqrt{u_1^2 + u_2^2 + u_3^2 + ... + u_n^2}$$

$$100\% = \sqrt{u_1^2 + u_2^2 + ... + u_{n-1}^2 + 30^2}$$

$$100\% = \sqrt{9100 + 900}$$

Contribution to overall uncertainty $u_{PS} = 95\%$

Contribution to overall uncertainty $u_{Analysis} = 5\%$