New developments in high resolution water quality sensor technologies and their application

University of ULSTER

teagasc
Agriculture and Food Development Authority

AGRICULTURAL CATCHMENTS PROGRAMME

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Synchronous and continuous nutrient concentration and discharge measurements in rivers

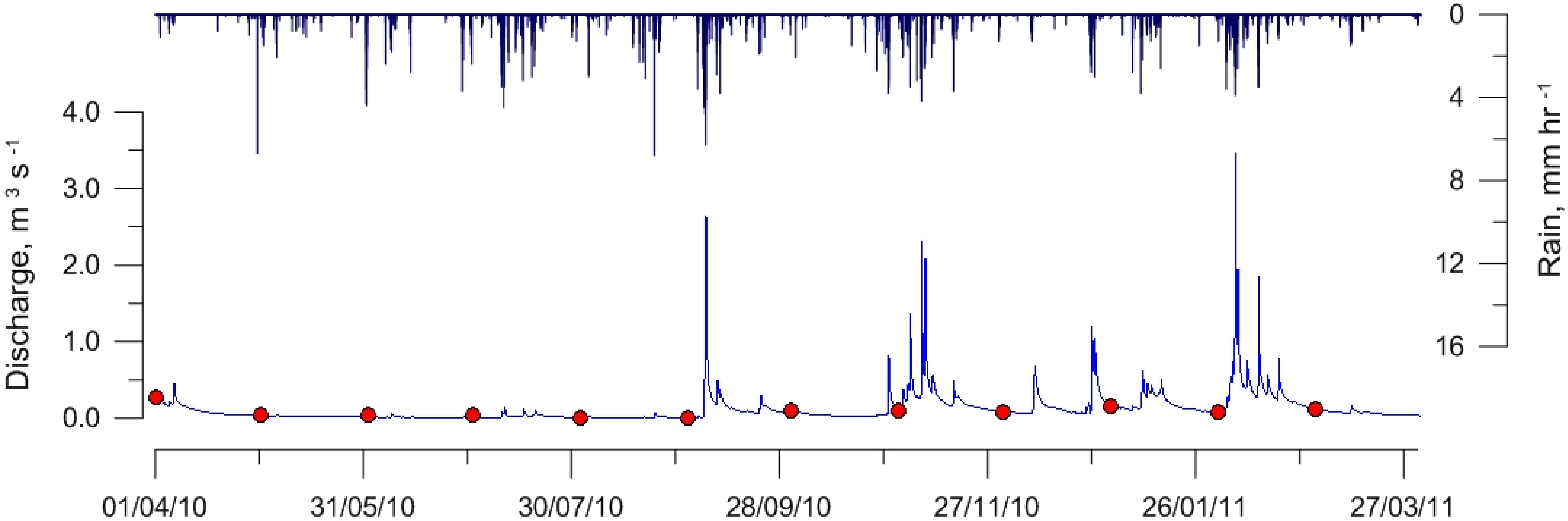
- Precision and bias
- Methods testing
- Resources and commitment
- Catchment applications

Sub-hourly

- P fractions
- N fractions
- Turbidity
- Conductivity
- Temperature
- Telemetry etc

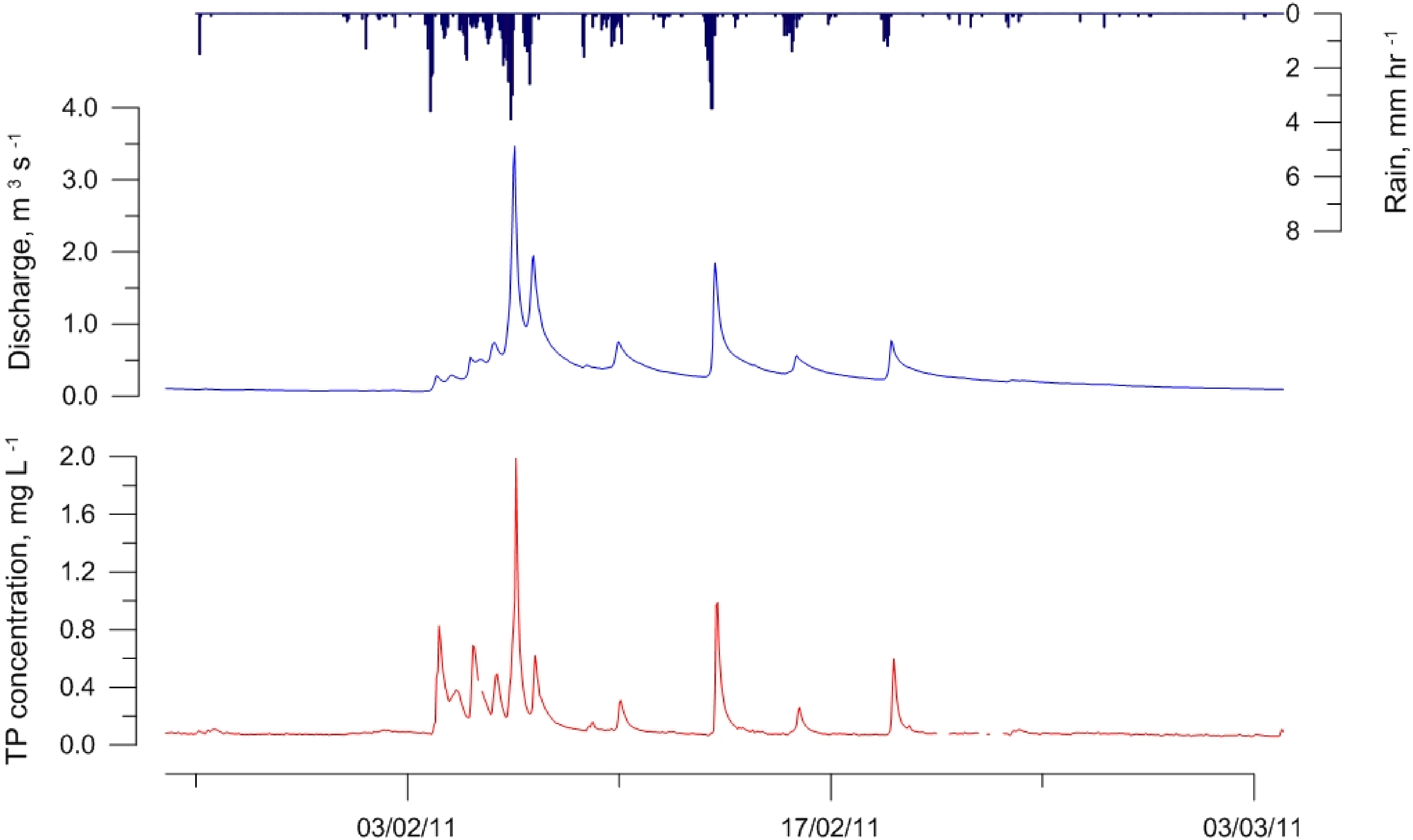
Arnscheidt et al. (2007)
Cassidy and Jordan (2011)
Jordan and Cassidy (2011)
Jordan et al. (2005, 2007, 2012, 2014)
Macintosh et al. (2011)
Melland et al., (2012)
Mellander et al. (2012, 2013, 2014)
Wall et al. (2011)
Withers et al. (2012, 2014)

Dynamic river flow



Mandatory up to 12 grab samples per year

- associate with ecology metrics
- low probability of capturing ‘diffuse events’

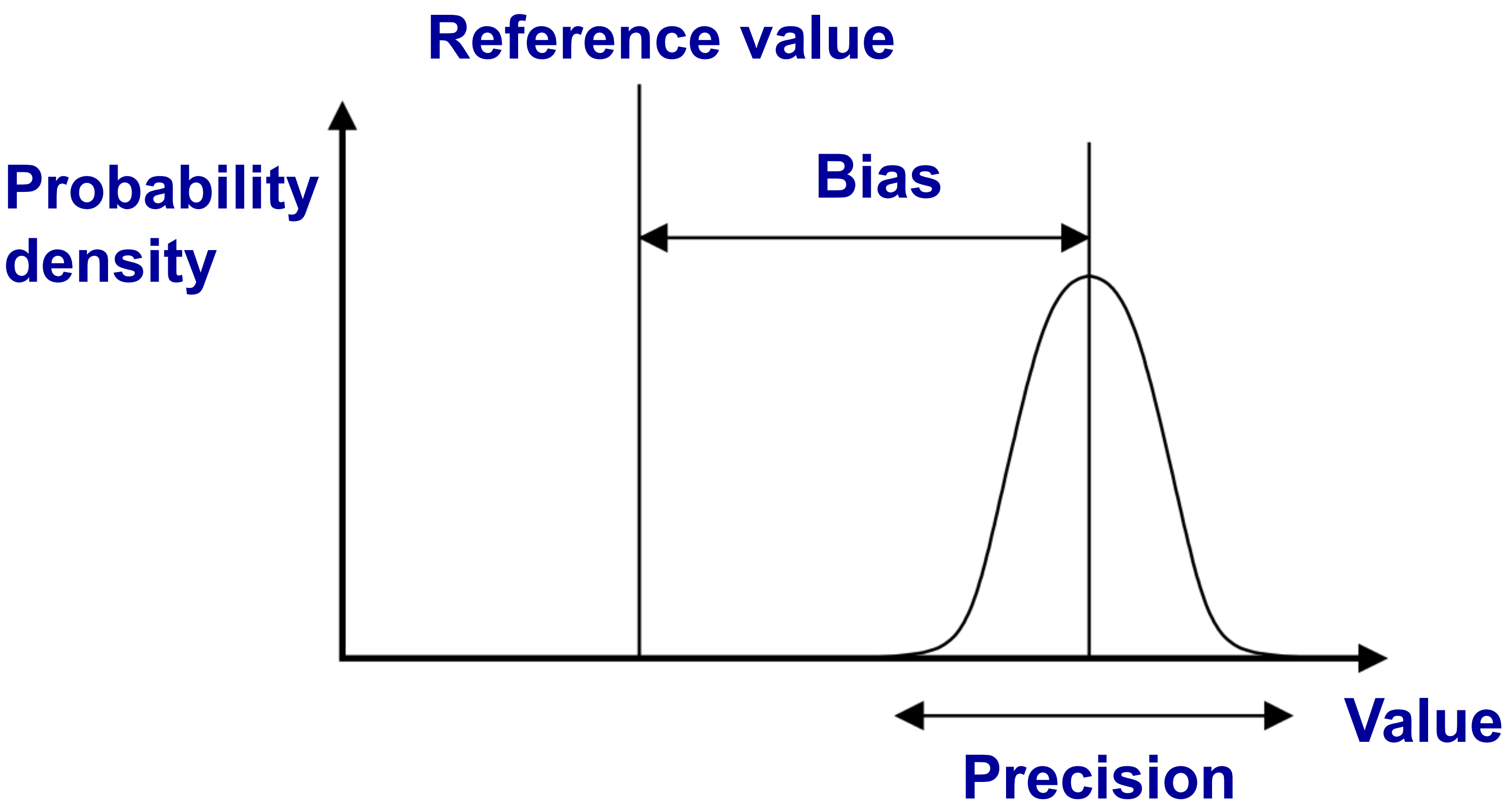


Rain, mm hr $^{-1}$
0
2
4
6
8
Discharge, m ^{3} s $^{-1}$
4.0
3.0
2.0
1.0
0.0
TP concentration, mg L $^{-1}$
2.0
1.6
1.2
0.8
0.4
0.0
03/02/11
17/02/11
03/03/11

Hach-Lange Phosphax Sigma

- TP and TRP on alternate cycles
- ~6 measurements per hour
- Rate controlled by Sigmatax
- Time stamp set to 10mins
- Reagents, etc. last for 3 months

Precision and bias



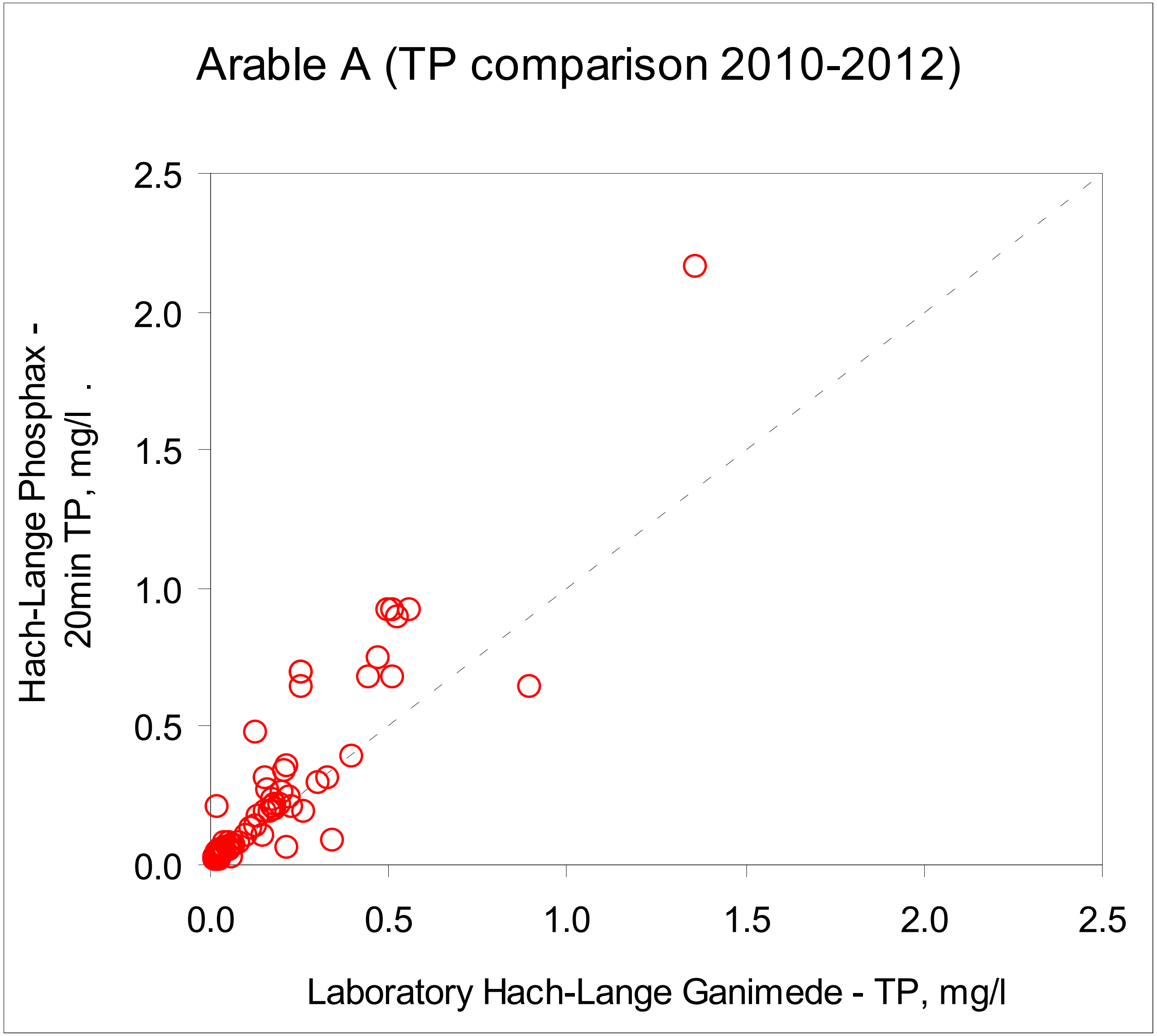
Precision and bias

TP standard 0.2 mg/l

Arable A			Grassland B		
Time	**TP, mg/l**		**Time**	**TP, mg/l**	
16:10	0.180		14:10	0.171	
16:30	0.182		14:50	0.178	
16:50	0.182		15:20	0.179	
17:10	0.183		15:40	0.178	
17:30	0.183		16:10	0.178	
17:50	0.181				
18:10	0.182				
Mean	0.182		**Mean**	0.177	
MDL	0.003		**MDL**	0.010	
Precision	0.001	0.5%	**Precision**	0.003	1.8%
Bias	-0.018		**Bias**	-0.023	

David Ryan, Teagasc

Phosphax (un)certainty – sampling ‘packets’ of water



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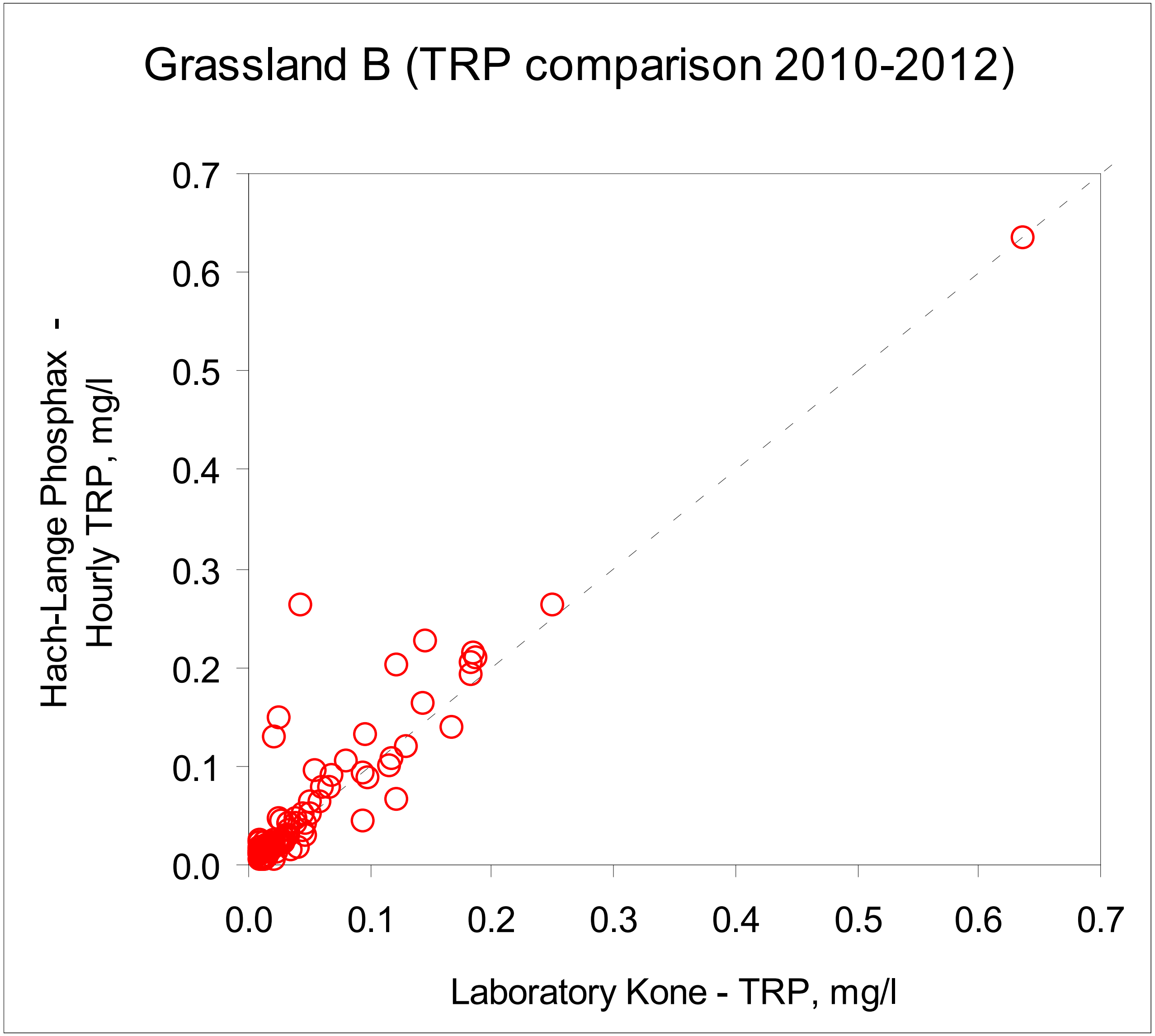
Phosphax (un)certainty – sampling ‘packets’ of water



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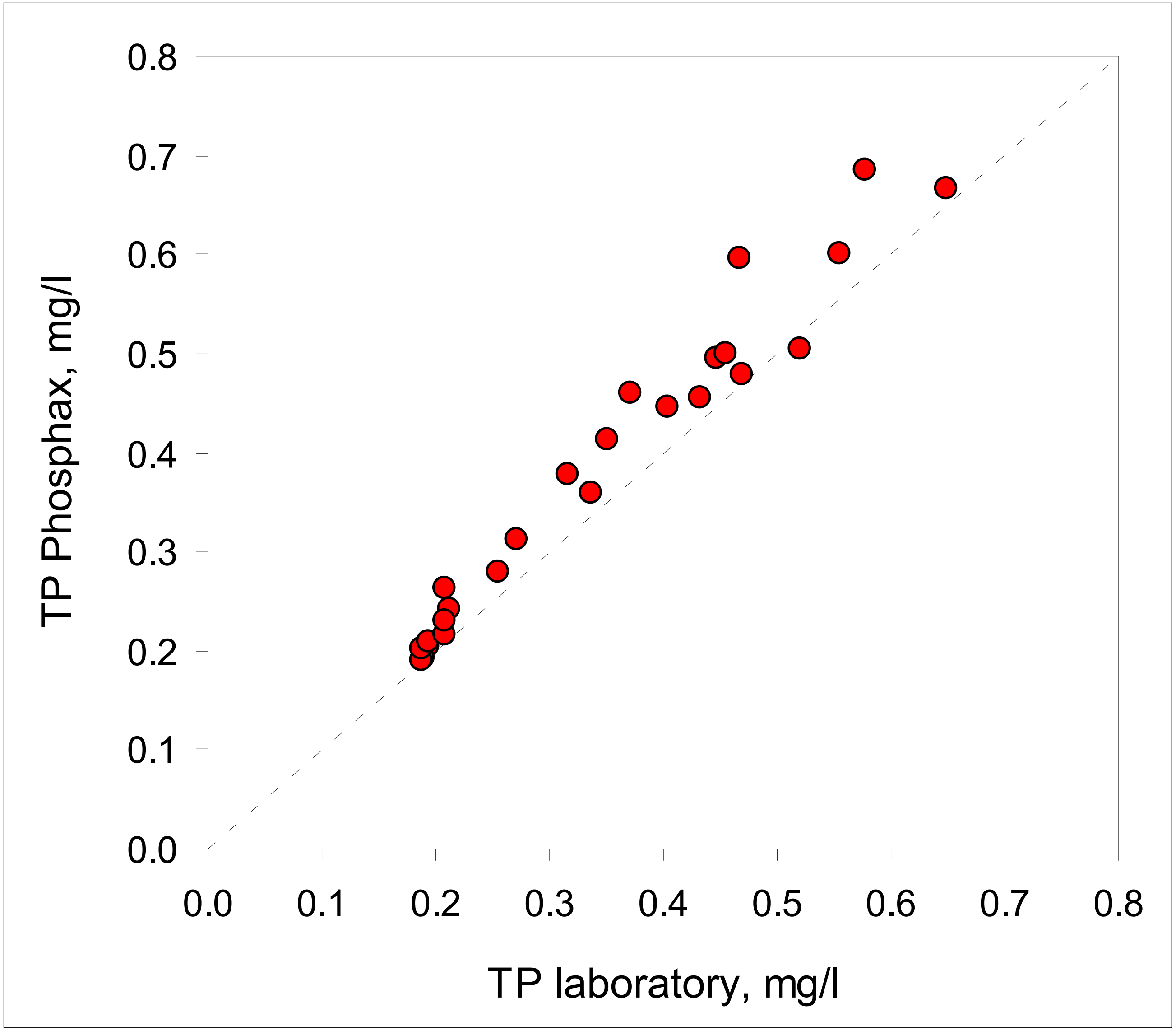
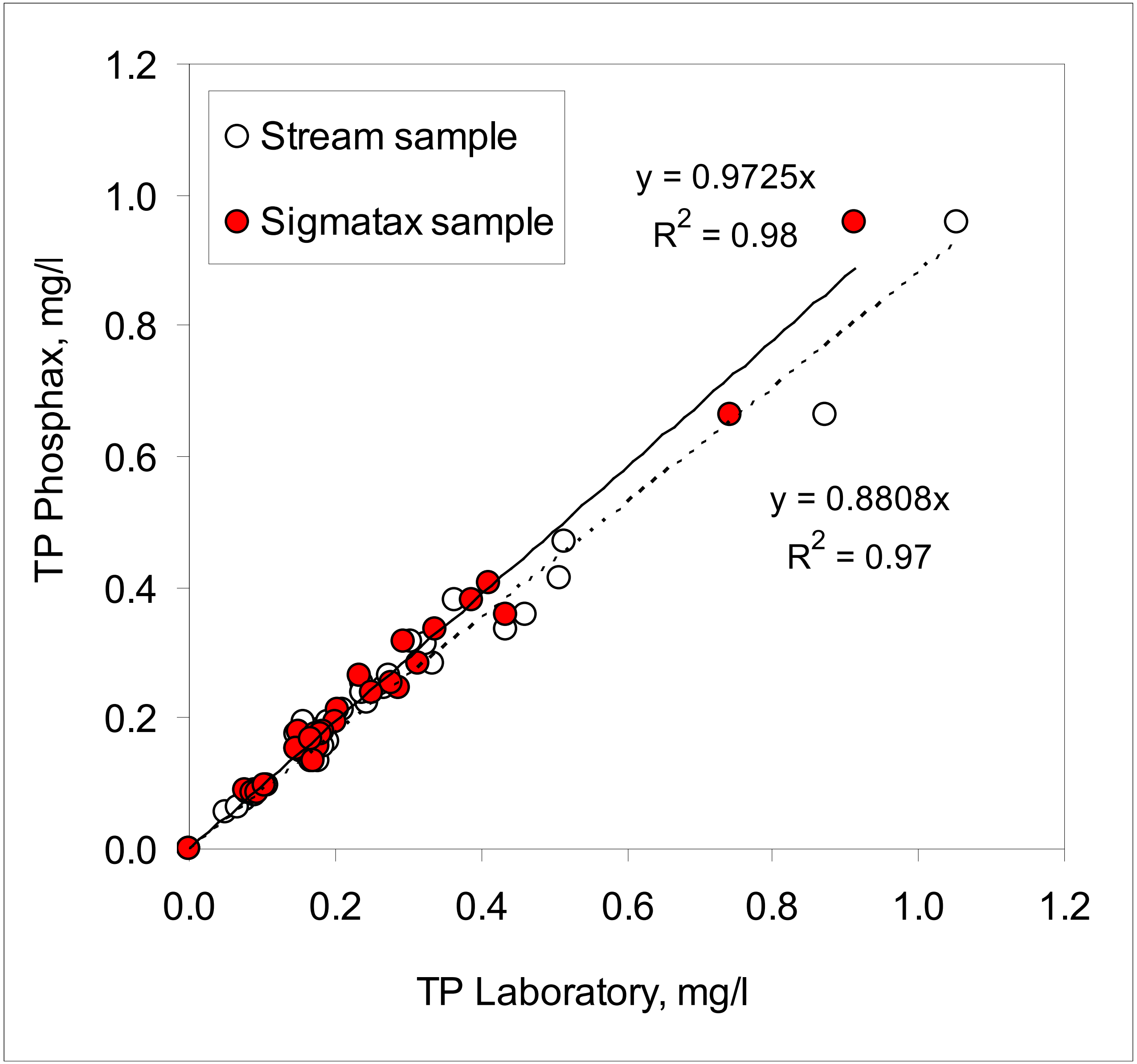
Phosphax (un)certainty – more precisely sampling ‘packets’ of water



Dr Joerg Arnscheidt, Ulster

Sigmatax – homogenisation jar

Phosphax (un)certainty – even more precisely sampling ‘packets’ of water



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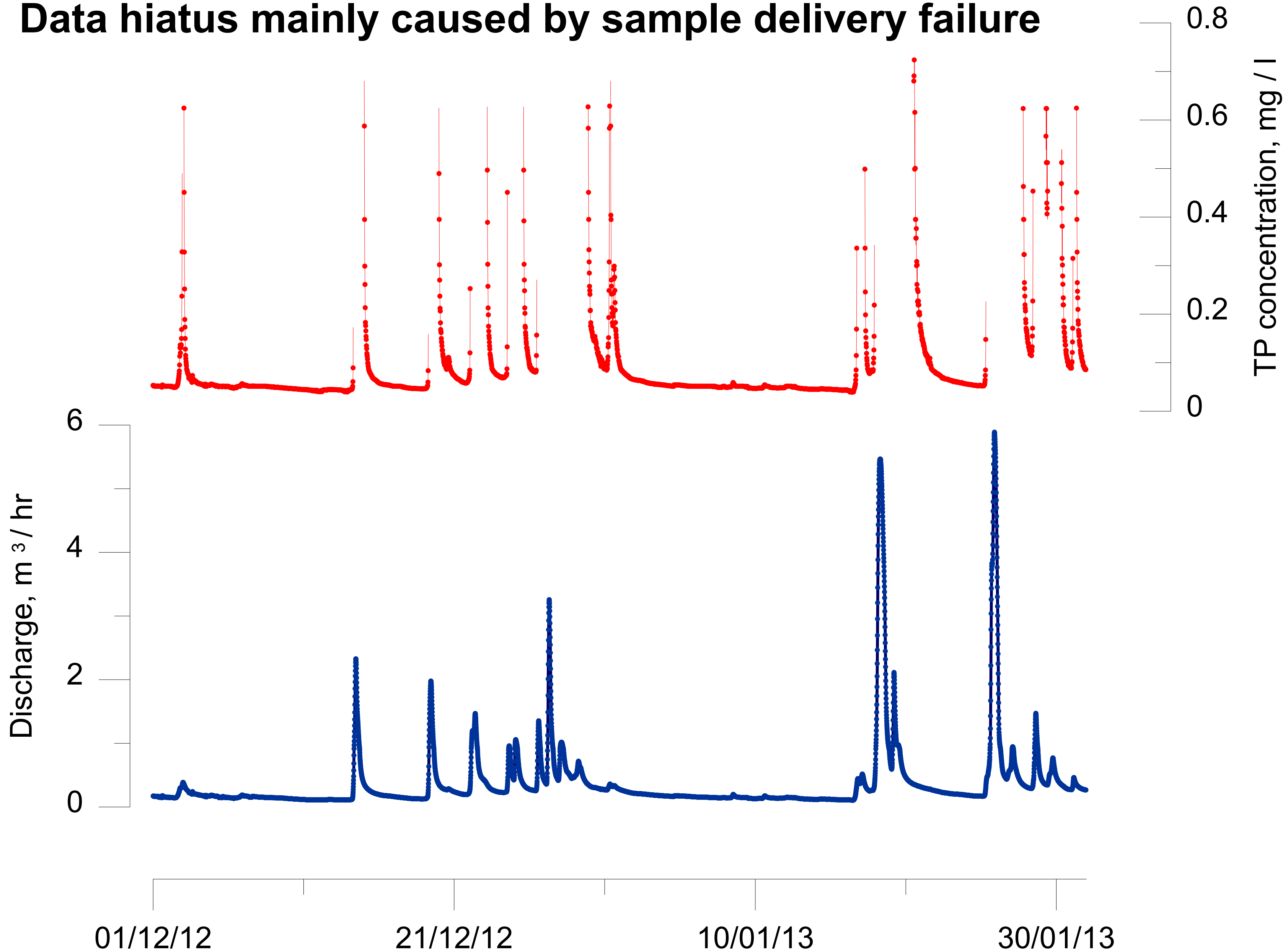
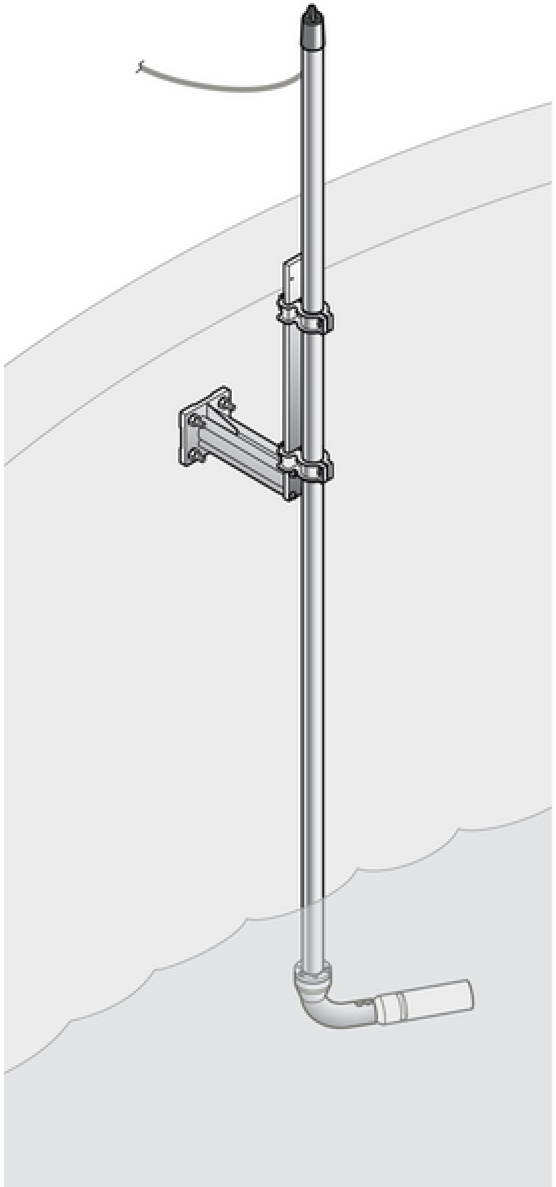
Sigmatax – and delivery

Data hiatus mainly caused by sample delivery failure

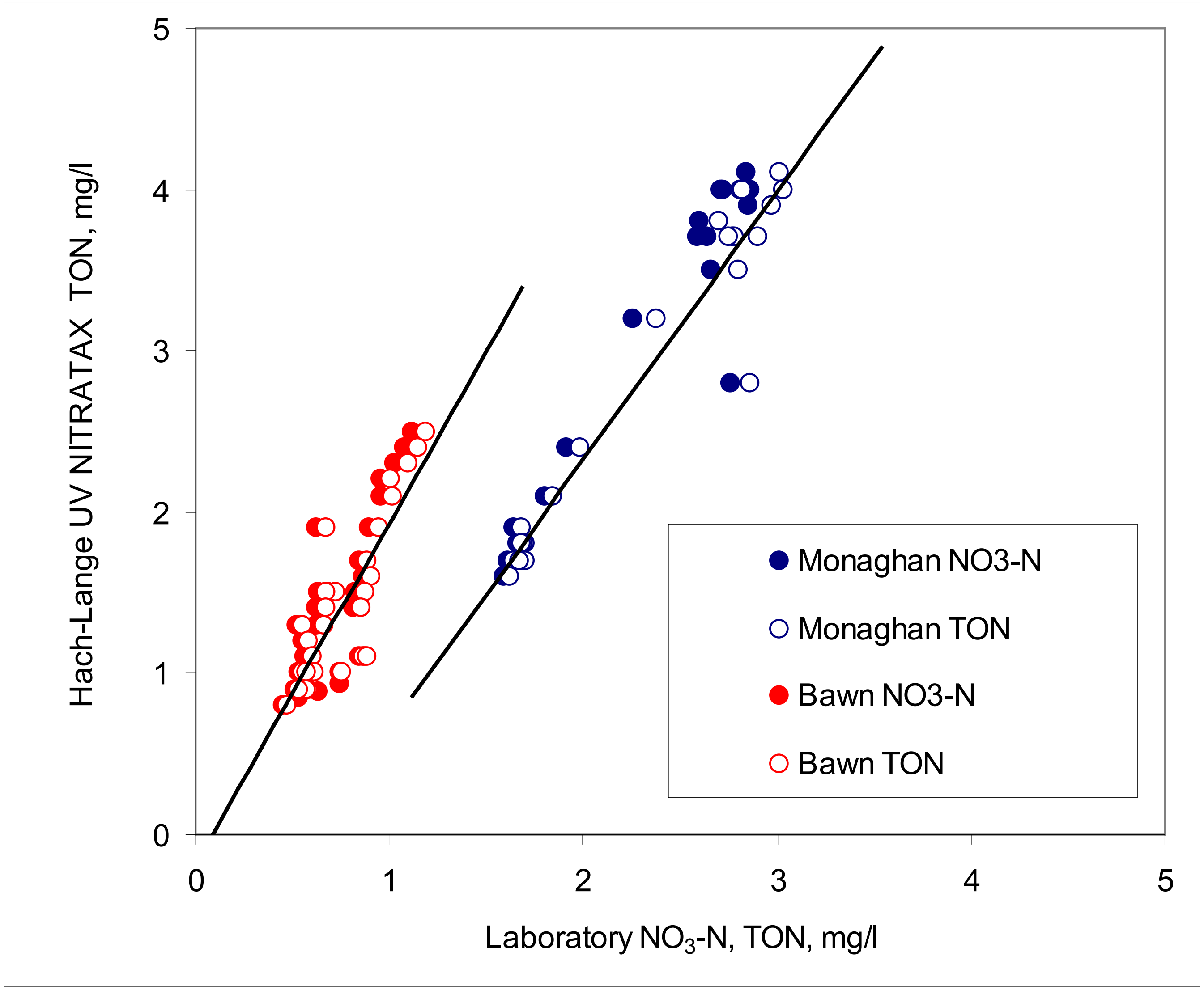




Hach-Lange
Nitratax SCplus
TON-N (0-25 or 0-50 mg/l)

Solitax SC
Turbidity
(0.001 – 4000 NTU)

TON probe – DOM interference (not turbidity)



Macintosh et al. 2011 – "EPA STRIVE report 81"

Testing established methods of load estimation

- Scandinavian methods using flow-proportional composite sampling
- Slightly different approaches in each country (DK, SE, NO)
- Based on calculation of flow constant to take a sub-sample:

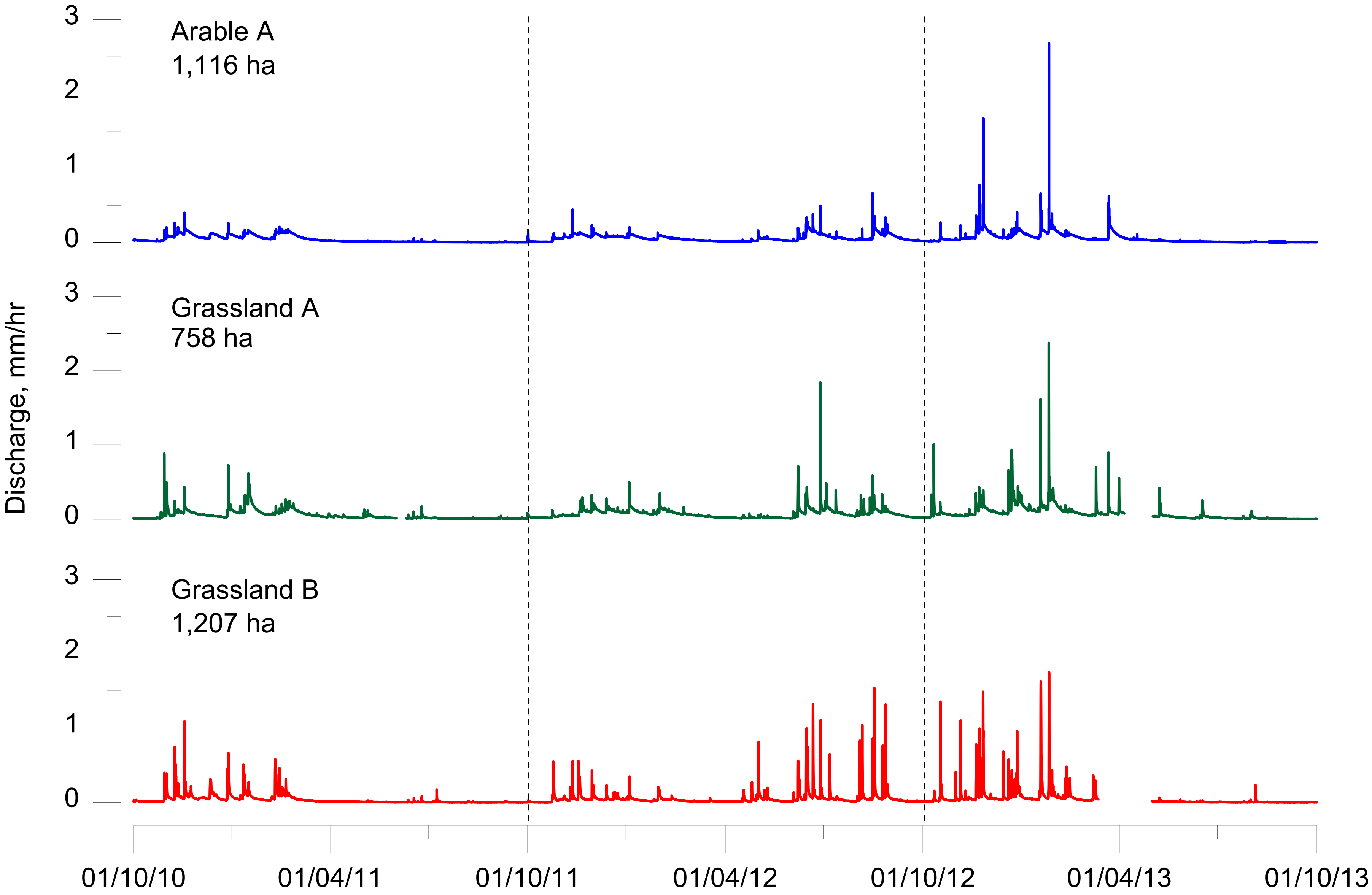
Denmark
Median monthly flow rate from long term record applied weekly as a volume

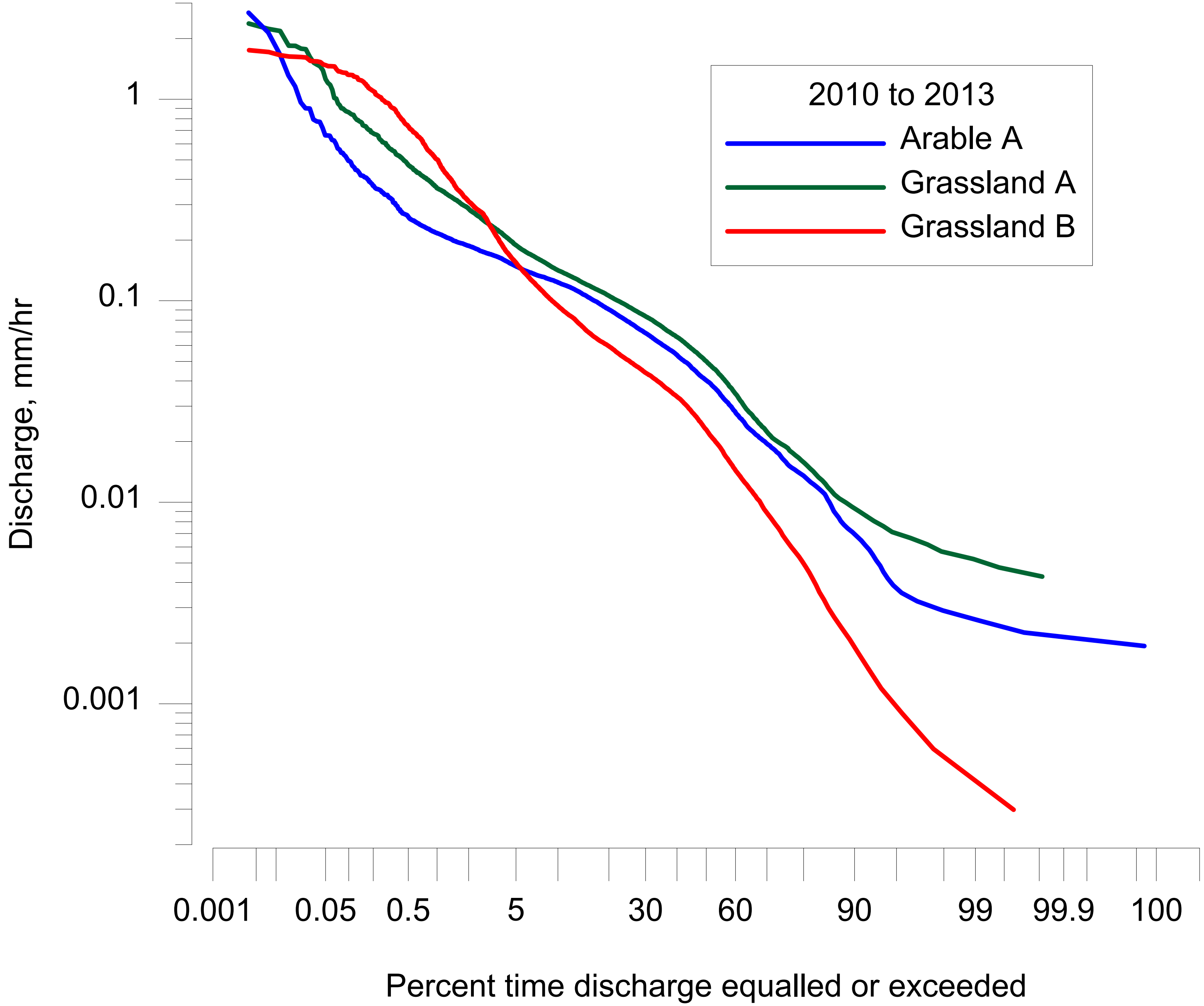
Sweden
Maximum flow volume recorded in two weeks from long term record

Norway
Flow constant forecast every two weeks from meteorological forecast

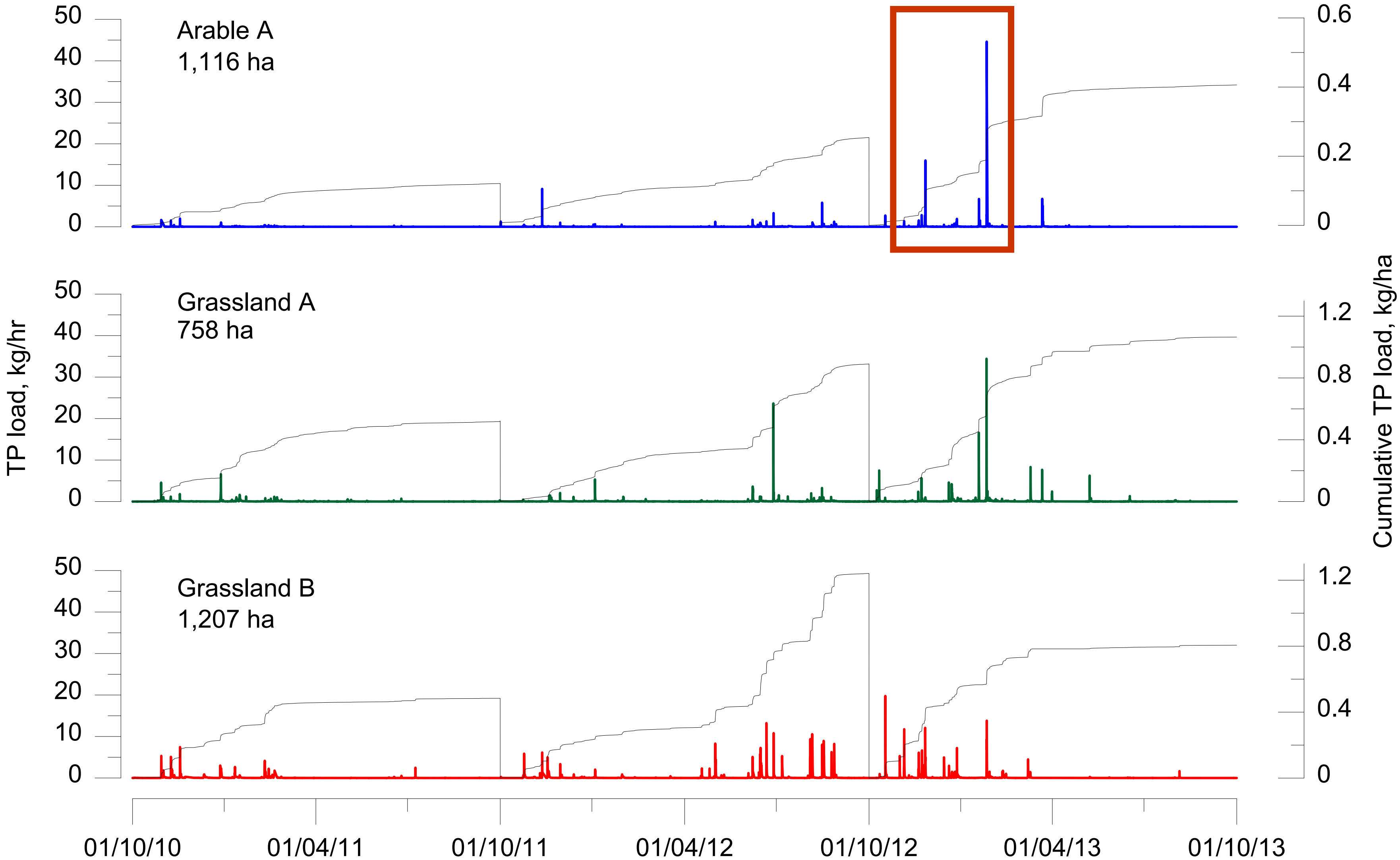
Testing established methods of load estimation

- Use three year discharge record from three Irish catchments
- Calculate flow constants for each Scandinavian method (plus 24/7)
- Use with 10min discharge record and accumulate flow
- Take virtual samples from synchronous TP concentration dataset
- Calculate average concentration for accumulated flow period
- Use different starting points to gauge variance (168 starting points)
- Bottle of Bushmills whiskey for the winner

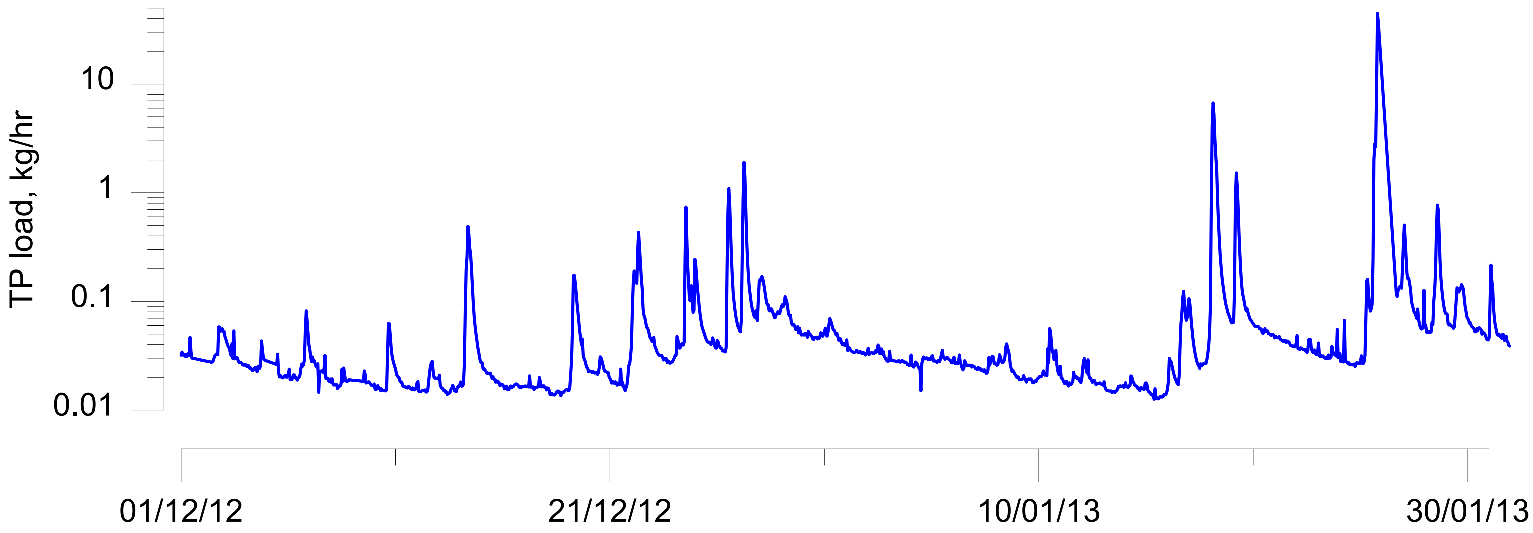

Arable A
1,116 ha
Grassland A
758 ha
Grassland B
1,207 ha
Discharge, mm/hr
0
1
2
3
01/10/10
01/04/11
01/10/11
01/04/12
01/10/12
01/04/13
01/10/13



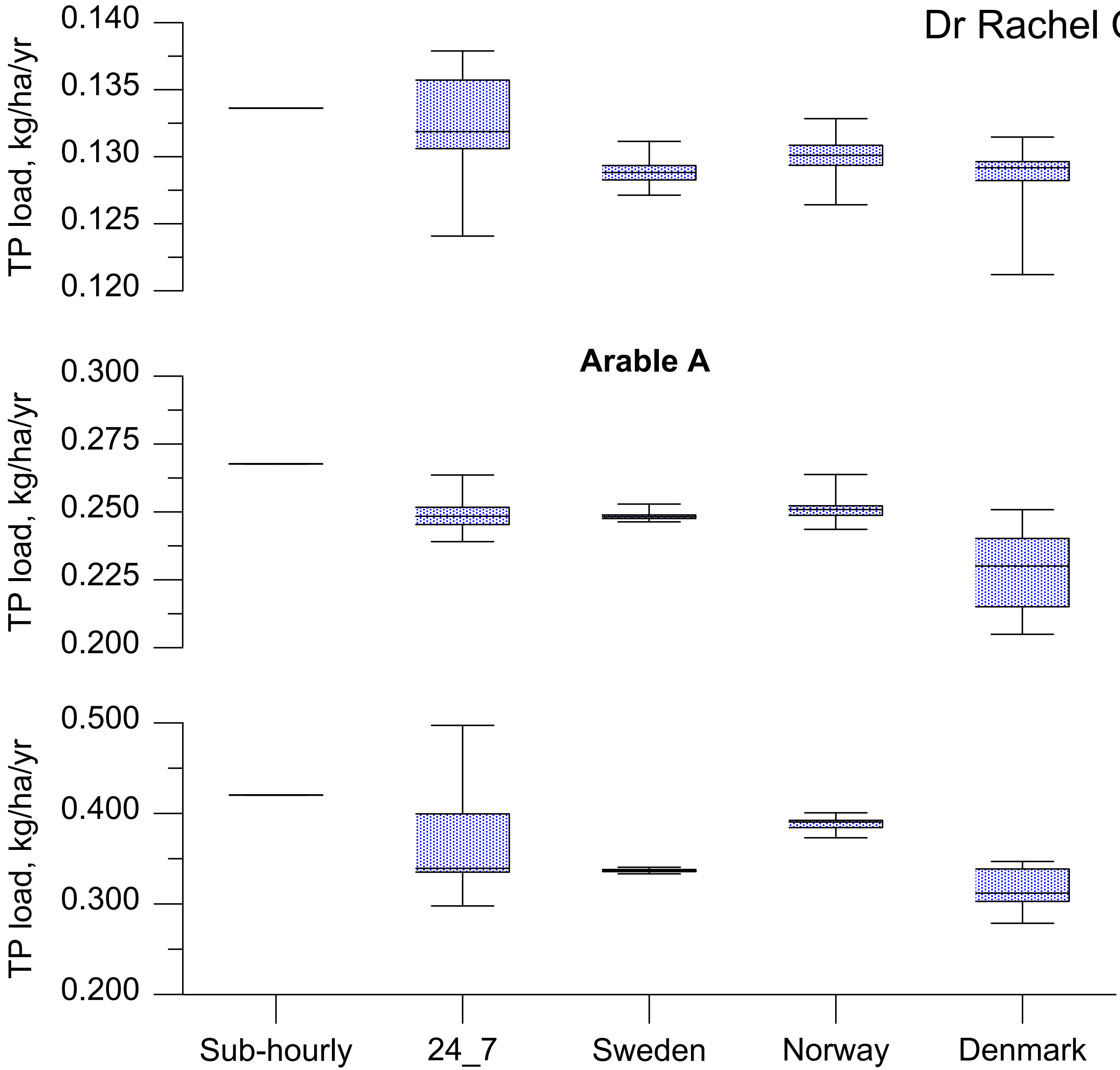
2010 to 2013
Arable A
Grassland A
Grassland B
Discharge, mm/hr
1
0.1
0.01
0.001
0.001
0.05
0.5
5
30
60
90
99
99.9
100
Percent time discharge equalled or exceeded



Arable A
1,116 ha
Grassland A
758 ha
Grassland B
1,207 ha
TP load, kg/hr
Cumulative TP load, kg/ha
50
40
30
20
10
0
0.6
0.4
0.2
0
1.2
0.8
0.4
0
01/10/10
01/04/11
01/10/11
01/04/12
01/10/12
01/04/13
01/10/13


TP load, kg/hr
10
1
0.1
0.01
01/12/12
21/12/12
10/01/13
30/01/13

Dr Rachel Cassidy, QUB



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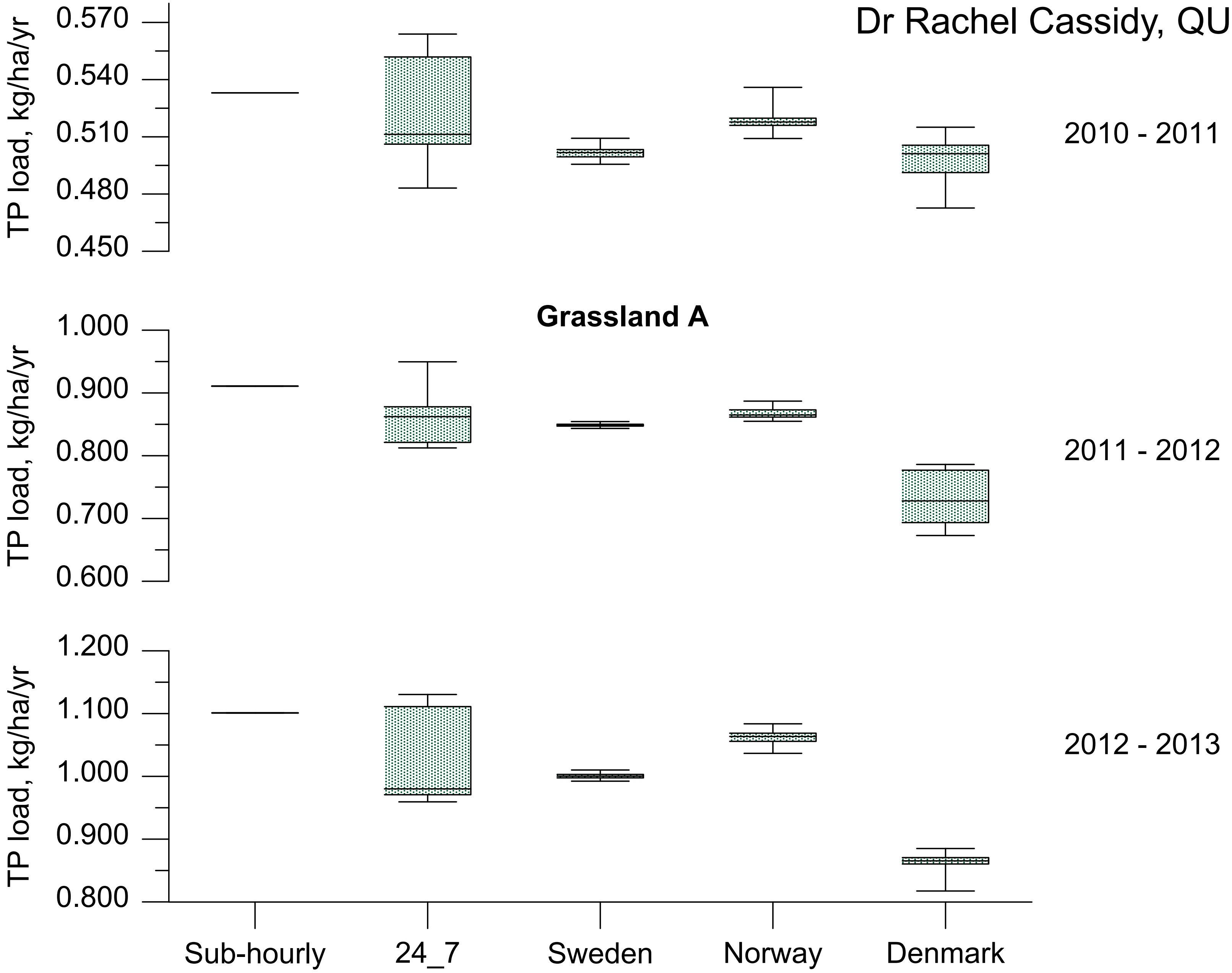
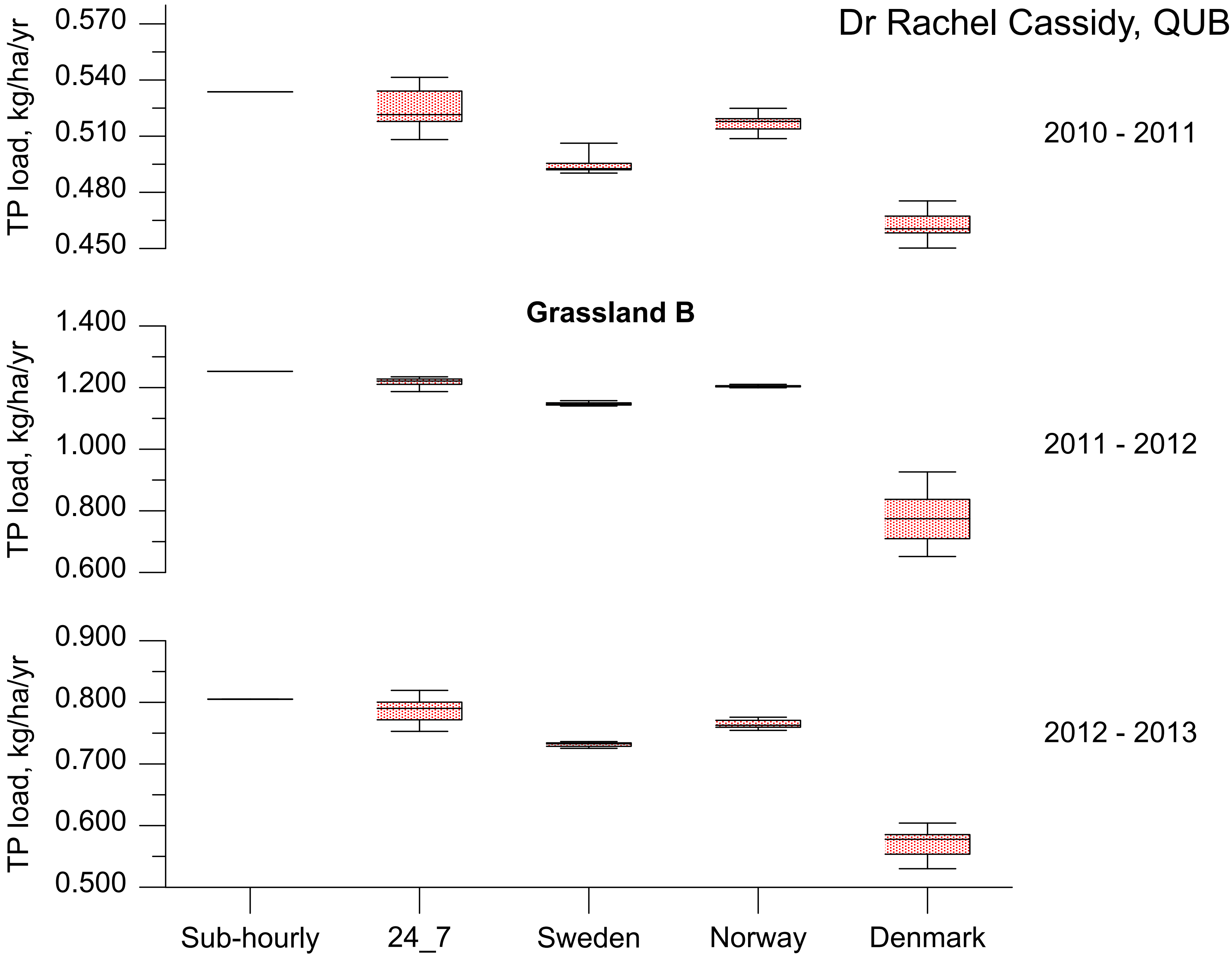




Dr Rachel Cassidy, QUB
Grassland B
TP load, kg/ha/yr
0.570
0.540
0.510
0.480
0.450
2010 - 2011
TP load, kg/ha/yr
1.400
1.200
1.000
0.800
0.600
2011 - 2012
TP load, kg/ha/yr
0.900
0.800
0.700
0.600
0.500
2012 - 2013
Sub-hourly
24_7
Sweden
Norway
Denmark

Grassland B

2010 - 2011	**24_7**	**Sweden**	**Norway**	**Denmark**
Precision, kg/ha	0.009	0.004	0.004	0.006
Precision, %	1.8	**0.7**	0.7	1.4
Bias, kg/ha	-0.010	-0.040	-0.017	-0.071
Bias, %	**98.2**	92.6	96.9	86.6
2011 - 2012				
Precision, kg/ha	0.012	0.004	0.003	0.085
Precision, %	1.0	**0.4**	0.3	11.0
Bias, kg/ha	-0.034	-0.106	-0.048	-0.476
Bias, %	**97.2**	91.6	96.2	62.0
2012 - 2013				
Precision, kg/ha	0.018	0.003	0.031	0.020
Precision, %	2.3	**0.4**	0.8	3.6
Bias, kg/ha	-0.019	-0.074	-0.041	-0.234
Bias, %	**97.7**	90.9	94.9	71.0

Annual TP loads
24/7 less bias, slightly less precise

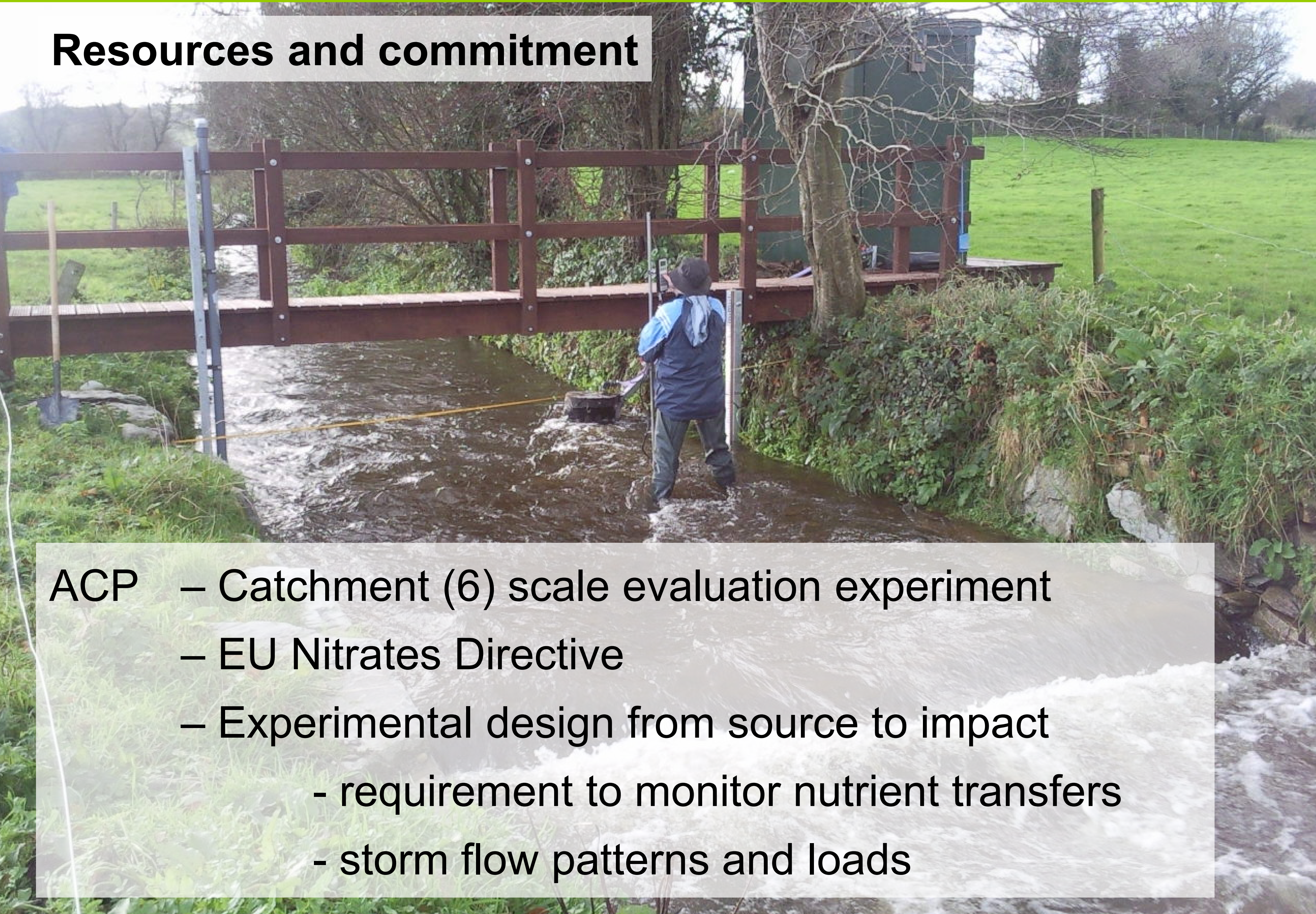
Swedish method more precise, slightly more bias

Tradeoffs
24/7 requires the analysis of 168 samples per year and weekly resources
– gives process information

Swedish method requires 28 samples per year and fortnightly resources
– no process information

Both – total chemistry only

Resources and commitment



ACP – Catchment (6) scale evaluation experiment

– EU Nitrates Directive

– Experimental design from source to impact

- requirement to monitor nutrient transfers
- storm flow patterns and loads

Resources and commitment

Cost comparison of bankside analysis versus 24/7 analysis* per station

*in situ 7 hourly sampling and ex situ analysis of TP, TRP, TON, EC and turbidity

Cost per catchment (rounded to nearest €1,000)	Bankside analysis	24/7 analysis
Year 1 capital maintenance and consumables, €	65,000	31,000
Year 2+ maintenance, €	18,000	18,000
Year 2+ consumables, €	4,000	9,000

David Ryan and Alice Melland

Resources and commitment

Cost comparison of bankside analysis – FTE

0.20 FTE/yr furthest and most problematic station
0.13 FTE/yr closest and least problematic station

Estimated cost of maintenance included two scheduled visits per week and five visits per year for specific issues

Similar amount estimated for 24/7 autosampler approach

Non-monetary benefits of bankside analysis include more complete data coverage; precision in load estimation; soluble fractions; revealing process patterns

Catchment applications – and finding out stuff

INVITED COMMENTARY

HP TODAY

HYDROLOGICAL PROCESSES
Hydrol. Process. **18**, 1353–1359 (2004)
Published online in Wiley InterScience (www.interscience.wiley.com). DOI: 10.1002/hyp.5537

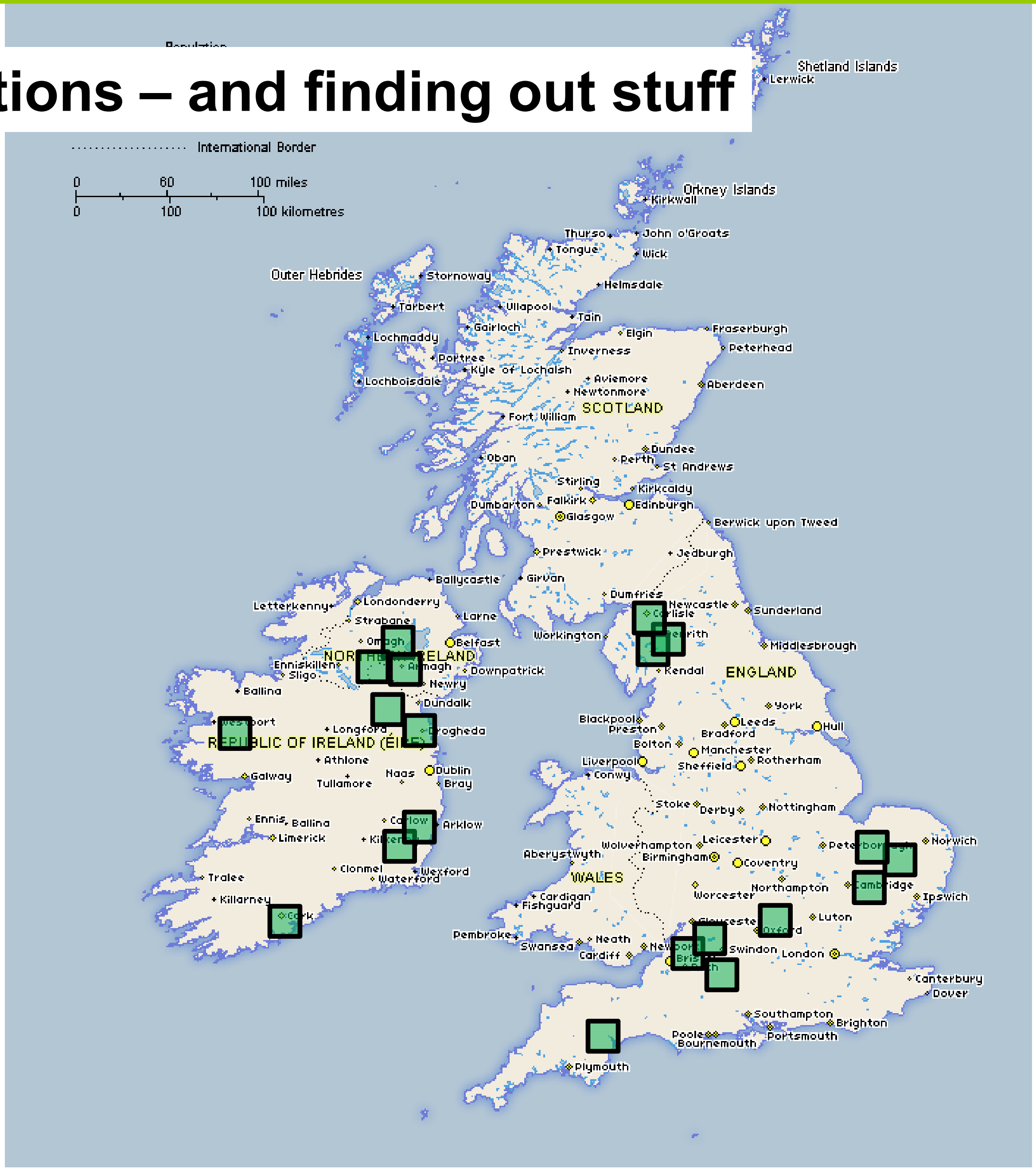
The fine structure of water-quality dynamics: the (high-frequency) wave of the future

James W. Kirchner[1]*
Xiahong Feng[2]
Colin Neal[3]
Alice J. Robson[3]

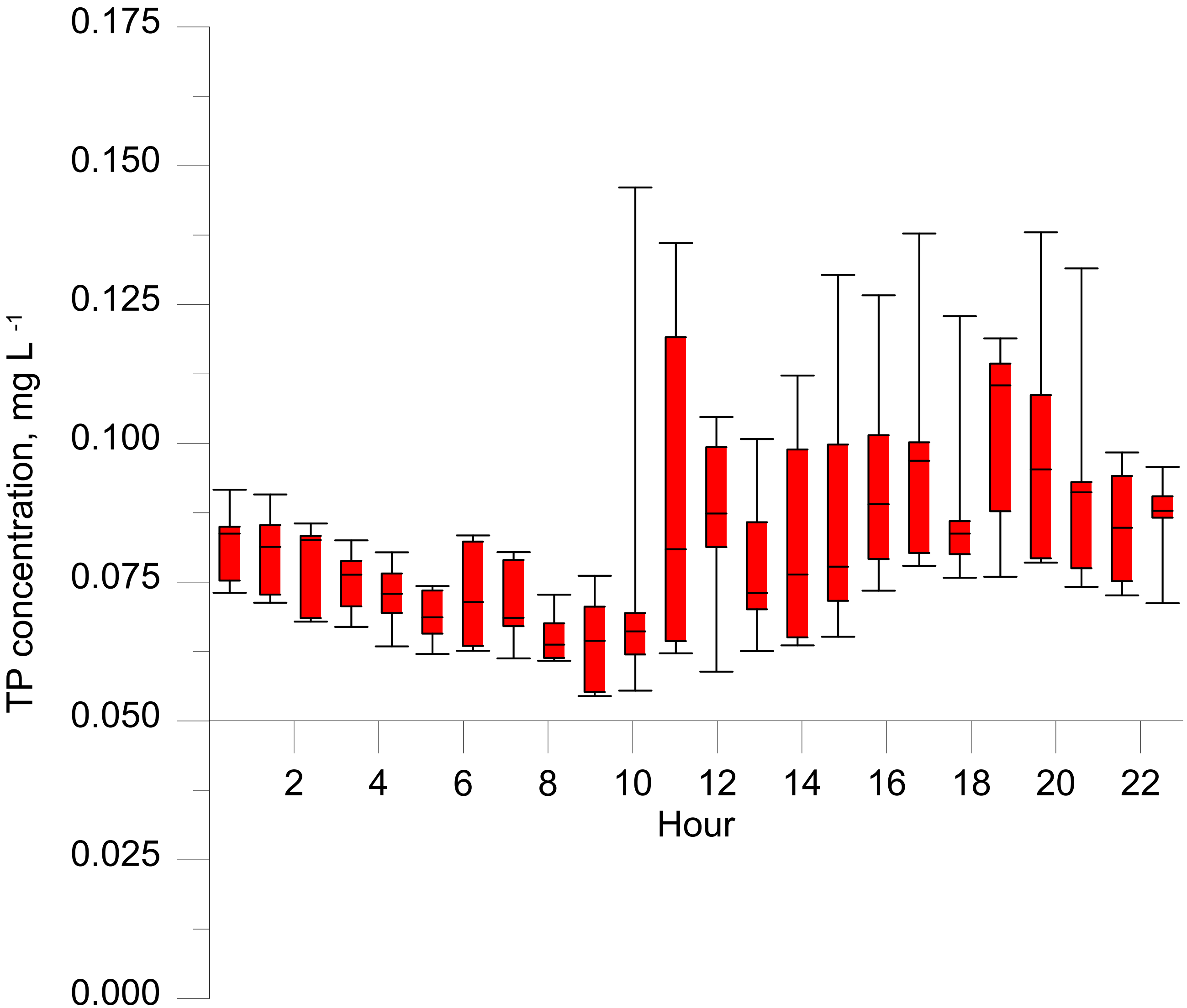
[1] *Department of Earth and Planetary Science, University of California, Berkeley, CA, USA*

Science is often driven forward by the emergence of new measurements. Whenever one makes observations at a scale, precision, or frequency that was previously unattainable, one is almost guaranteed to learn something new and interesting. Our purpose in this commentary is to argue that catchment hydrochemistry is on the verge of just such a major new advance, driven by automated, online continuous analysis for many chemical constituents in natural waters.

Catchment applications – and finding out stuff



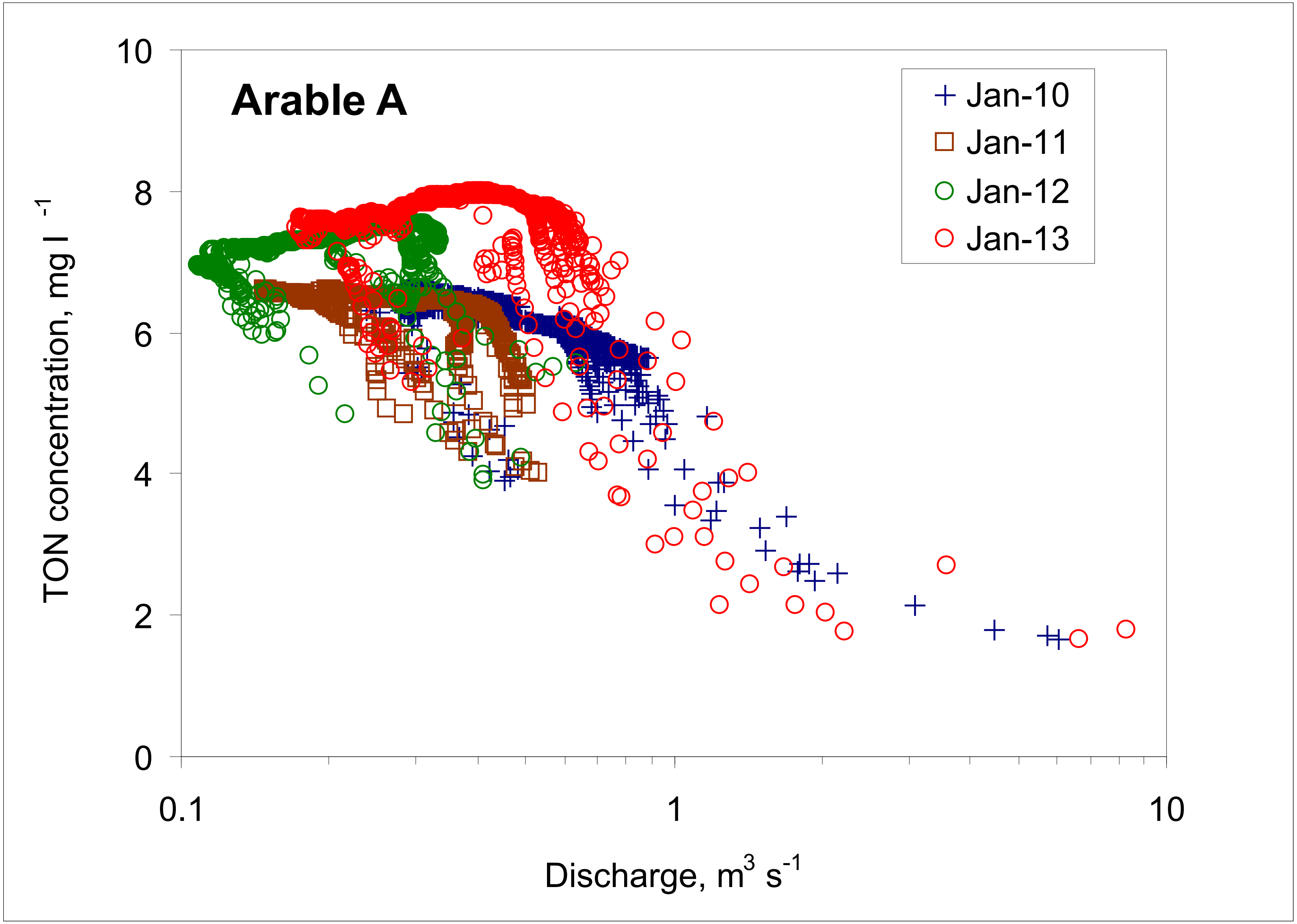
Diurnal P cycles – rural point sources WITH biogeochemical cycling



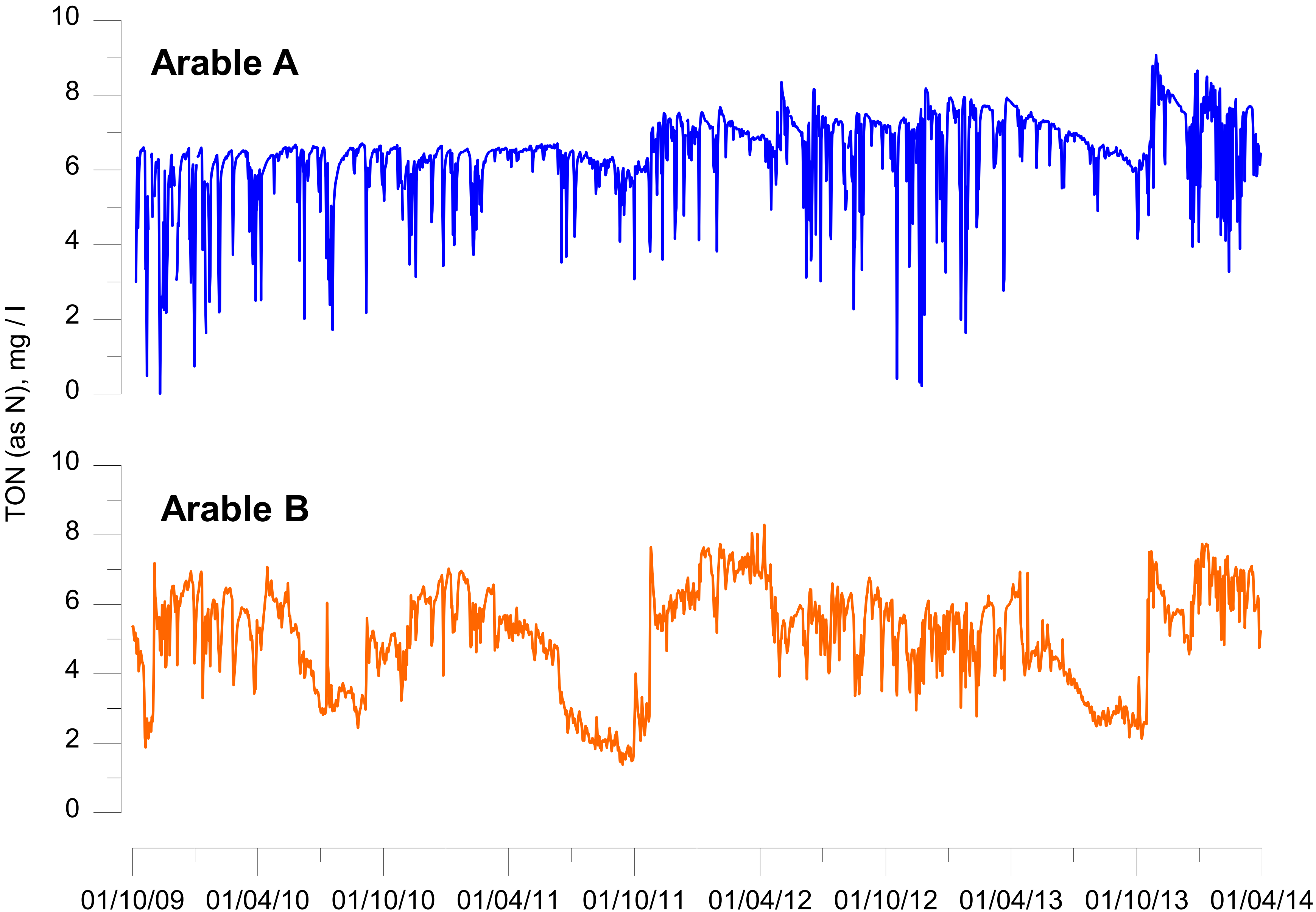
Halliday et al. 2013 – *Biogeosciences*

Sub-daily nitrate cycles in the uplands
(advection and dispersion processes)

Policy evaluation: climate and monitoring changing practice



Policy evaluation: climate and monitoring changing practice



Summary

Bankside technologies are robust and offer certainty with regard to bias and precision when maintained

Periods of data hiatus generally caused by sample delivery (several methods being used and adapted)

Set-up and maintenance costs are high - maybe

Trade-offs with more traditional methods can be quantified

Investment can yield deeper process understanding in the short to medium term and provide a framework for longer term monitoring