Electronic Supplementary Material (ESI) for Environmental Science: Processes & Impacts

Evaluation of DGT as a long-term water quality monitoring tool in natural waters; uranium as a case study

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Supplementary Information

Materials and methods

Water chemistry

Spot water samples were taken at weekly interval from the main flow of the river at each monitoring site. Sub-samples were filtered immediately (0.45 μm cellulose nitrate membrane, WCN grade: Whatman Ltd., Maidstone, UK) for subsequent analysis of dissolved determinants. Unfiltered sub-samples were taken for the determination of chlorophyll-*a*, total phosphorus and suspended particulate matter. Samples for chlorophyll-*a* were filtered and processed within 24 h. Water samples (0.5 L) were passed through a GF/F grade filter paper (Whatman Ltd.) and pigment extracted overnight using 90% acetone. The concentration of chlorophyll-*a* of the extract was determined spectrophotometrically.[1] Total phosphorus (TP) was determined by digesting an unfiltered water sample with acidified potassium persulphate in an autoclave at 121°C for 40 min, then reacting with acid ammonium molybdate reagent to produce a molybdenum-phosphorus complex, which was quantified spectrophotometrically.[2] Soluble reactive phosphorus (SRP) was determined on a filtered sample, using the phosphomolybdenum blue colorimetry method of Murphy and Riley,[3] as modified by Neal *et al.*[4] Dissolved reactive silicon was determined by reaction with acid ammonium molybdate, to form yellow molybdosilicic acids. These were then reduced using an acidified tin (II) chloride solution to form intensely coloured silicomolybdenum blues, which were quantified spectrophotometrically using a Discrete Analyser (Auto Analyser 2; Seal Analytical, Fareham, UK).[5]

Total dissolved nitrogen and dissolved organic carbon were determined by thermal oxidation, (Elementar Isoprime). Nitrate, nitrite and major anion concentrations were analysed by ion chromatography (Dionex DX500). Major cations were analysed by ICP-MS (Perkin Elmer Optima 2100DV).

Table S1. Water quality parameters measured as part of the CEH Boxford Observatory Project and Thames Initiative.

Anions	**Cations**	**Particulates and organics**
Soluble reactive phosphate (SRP)	Sodium (Na^+)	Chlorophyll-*a* (Chl *a*)
Total dissolved phosphate (TDP)	Potassium (K^+)	Dissolved organic carbon (DOC)
Total phosphate (TP)	Calcium (Ca^+)	Suspended particulate material (SPM)
Ammonia (NH_4)	Magnesium (Mg^+)	
Dissolved reactive silicon (Si)	Boron (B^+)	
Total dissolved nitrate (TDN)	Iron (Fe^+)	
Nitrate (NO_3^-)	Manganese (Mn^{2+})	
Nitrite (NO_2^-)	Zinc (Zn^{2+})	
Sulphate (SO_4^{2-})	Copper (Cu^{2+})	
Fluoride (F^-)	Aluminium (Al^{3+})	
Chloride (Cl^-)		
Bromide (Br^-)		

Results

Flow rate data

No direct flow rate (m s^{-1}) data was available from the National Rivers Flow Archive for either of the deployment sites. This was calculated using Q = FA (where Q is discharge, m^3 s^{-1}, F is flow, m s^{-1} and A is cross-sectional area of the weir, m^2). Cross-section drawings of the weirs were provided by the Environment Agency for England and Wales. Discharge data (m^3 s^{-1}) has been used here to indicate each rivers response to precipitation events. An increase in rainfall may affect discharge through increased run off resulting in a higher volume of water passing through the sampling site, which in turn would increase the flow rate. Figure S1 shows that the River Enborne discharge is highly responsive to changing meteorological conditions, with short lag-times between peak rainfall and peak discharge.[6] Towards the winter months (December 2011 onwards) there was sustained precipitation which resulted in sustained higher flow conditions in the River Enborne. This can be attributed to the predominantly clay catchment area. The River Lambourn, which is a ground water fed chalk stream,[7] maintained a relatively constant flow over the deployment period, with a slight increase in December 2011. The porous chalk catchment of the River Lambourn attenuates any increase in surface run-off from increased precipitation that may affect discharge.

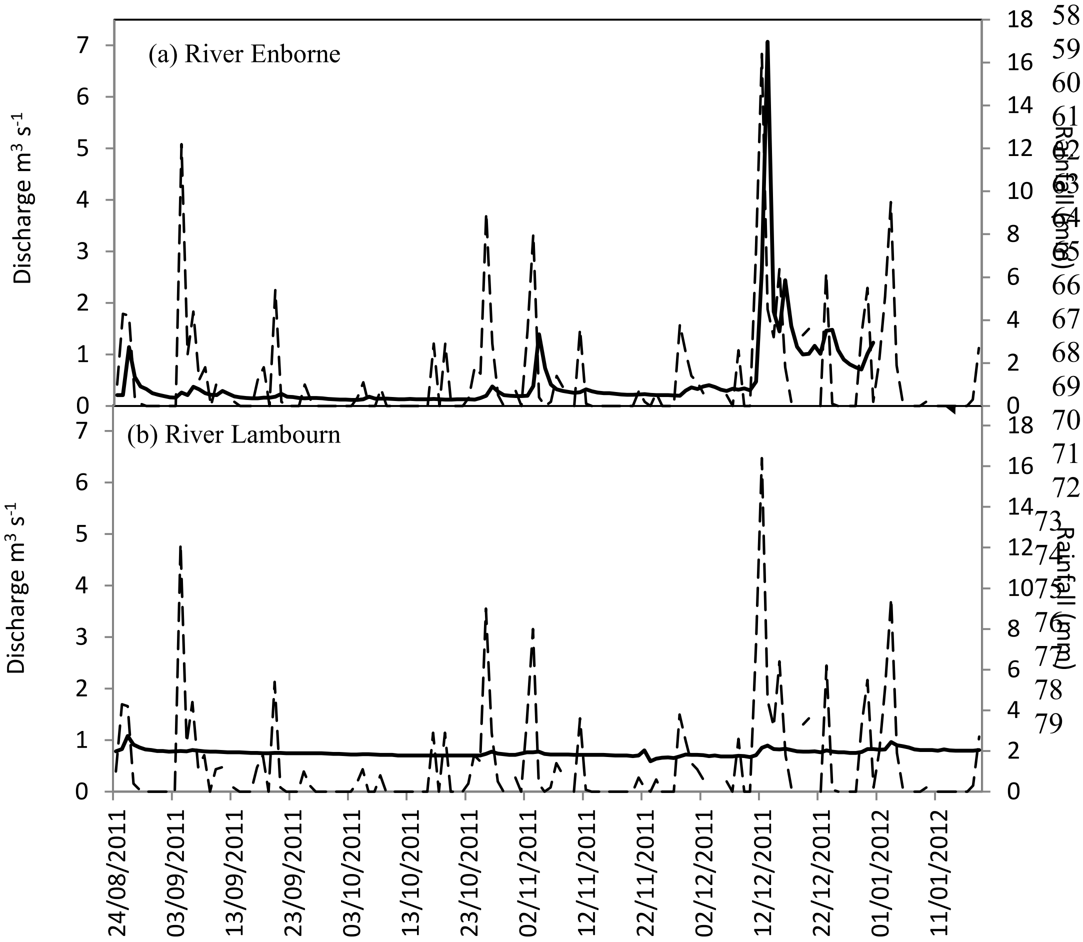

Figure S1. Regional rainfall data (dashed line) supplied by the CEH at the Wallingford Observatory (51.603166 N, -1.113393 W) using a groundflush type rain gauge, and river discharge data supplied by the Environment Agency for England and Wales National River Flow Archive, for the (a) River Enborne and (b) the River Lambourn. The discharge data (solid line) for the River Lambourn is from the crump weir monitoring station (51° 24 42.375 N, 1° 19 32.092 W) located 13 km downstream of the sampling site. At the River Enborne, the Agency's flow monitoring station is at the deployment site (*Contains Environment Agency information© Environment Agency and database right).*

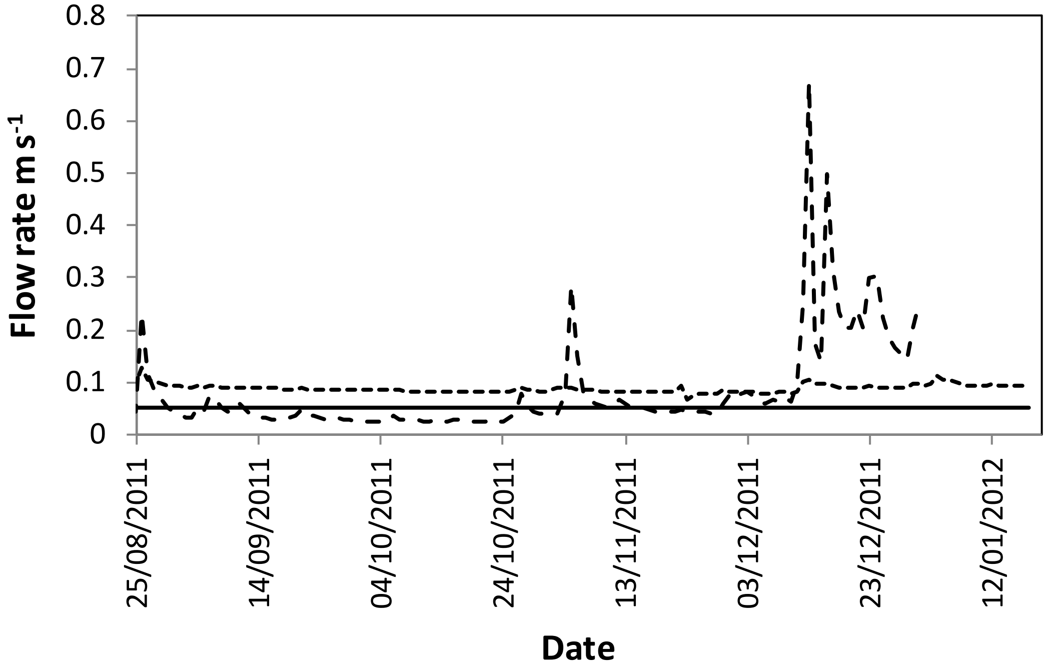

Figure S2. Flow rates (m s^{-1}) for the River Enborne (— —) and for the River Lambourn (-----) calculated from river discharge data supplied by the CEH National River Flow Archive. The crest widths for the River Enborne at Brimpton were 7.62 m (accounting for the width of both sluices and the concrete separator at the weir) and for the River Lambourn at Shaw, 10.67 m. The mean river height was used for each river to calculate the flow speed from the discharge (Q): Q = m x m s^{-1}. The average height for the River Lambourn at Shaw was 0.8 m (data supplied by the Environment Agency for England and Wales) and for the River Enborne at Brimpton, 0.35 m, except from the 12–15/12/2011, where a the bank-full level of 1.5 m was used due to exceptionally high flow. The solid line represents the minimum flow rate detectable by the flow meter used in this study. As the DGTs were situated out of the main flow channel in a low velocity pool to allow for ease of access, the flow measures recorded during the study were much less than those registered at the gauging station.

The lower discharge in the autumn months (September–November 2011) in the River Enborne, are directly related to the low rainfall experienced in the region. Table S2 shows that the rainfall experienced in the region was below average during this period of time. The impact of precipitation did not seem to affect flow rates in the Lambourn, which maintained a constant discharge.

Table S2. Regional rainfall data from the Benson Met Office Meteorological monitoring station (51.62 N, -1.097 W).

Year	Month	Rain (mm)	Monthly Average rain (mm) (1971-2000)
2011	August	65.6	50.0
2011	September	31.8	51.3
2011	October	26.3	65.7
2011	November	28.4	65.0
2011	December	71.2	57.2
2012	January	34.6	53.9

The river height (m) and flow rate (m s^{-1}) were also measured at each deployment site (Table S3). There was little variation in flow conditions and river height at the River Lambourn site, which fits with the discharge and rainfall data in Figure S1. The River Enborne deployment site was generally very low flow, with a low height, but with increasing discharge and precipitation (Figure S1) the river was inaccessible (14/12/2011) or fast moving with a high discharge (21/12/2011).

Table S3. Flow rates at the River Lambourn and River Enborne sites measure using a hydro-prop type flow meter. Each measurement was undertaken in triplicate, at 66% water column depth. The lowest flow detectable by the instrument was 5 cm s^{-1}. Where there is '< 5' the data is below the flow rate detectable by the meter used. Very heavy rain was experienced across the region on 11/12/2011 to 17/12,2011. This resulted in the River Enborne becoming too high to enter to take a reading on 14/12/2011, with the 21/12/2011 the only date that the flow meter registered a flow at the River Enborne.

	Flow rate (cm s^{-1})		Approximate depth (m)	
Date	River Lambourn	River Enborne	River Lambourn	River Enborne
24/08/2011	10	< 5	0.4	0.5
05/10/2011	7	< 5	0.4	0.5
12/10/2011	8	< 5	0.5	0.4
19/10/2011	11	< 5	0.5	0.4
24/10/2011	8	< 5	0.5	0.3
02/11/2011	1	< 5	0.5	0.4
09/11/2011	7	< 5	0.5	0.4
16/11/2011	6	< 5	0.5	0.4
23/11/2011	7	< 5	0.5	0.6
30/11/2011	8	< 5	0.5	0.6
07/12/2011	7	< 5	0.6	0.7
14/12/2011	9	No data	0.6	1.5
21/12/2011	6	12	0.6	1.2
28/12/2011	8	< 5	0.6	1
05/01/2012	8	< 5	0.5	0.8
11/01/2012	7	< 5	0.5	0.8
18/01/2012	8	< 5	0.5	0.8

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Figure S3a and b show the difference in the river conditions during high (Figure S3a) and low (Figure S3b) precipitation and discharge.

Figure S3a. Photograph of high flow conditions (date 14/12/2011) River Enborne. The circle shows the location of the float which is in this instance completely submerged. The conditions were judged too hazardous to retrieve the samplers on this sample date. Picture taken looking towards weir.

Figure S3b. Photograph of very low flow conditions, River Enborne (12/10/2011). Location chosen for ease of access. Picture taken looking away from weir.

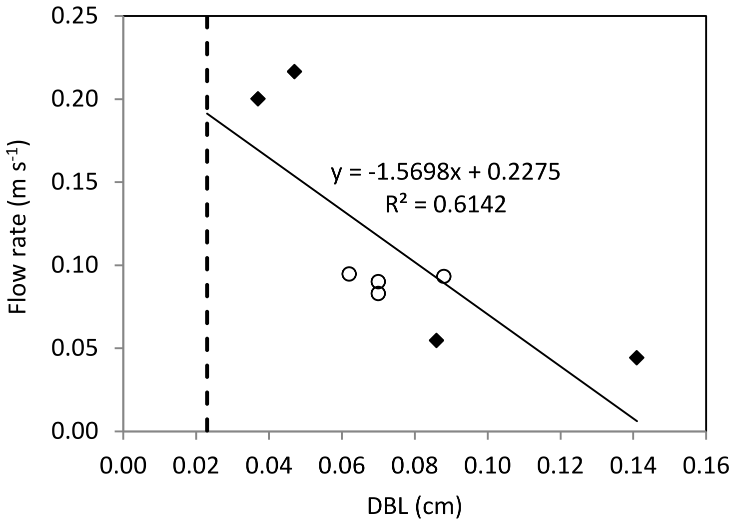

Figure S4. Graph showing the correlation with the flow rate (m s^{-1}) of the river and the size of the DBL (cm). The black diamonds represent data from the River Enborne and the open circles are data from the River Lambourn. The linear regression (black line) includes both data sets. The black dashed line represents the theoretical minimum DBL from laboratory measurements as found by Warnken *et al.*[8]

Diffusive boundary layer

The DBL was calculated by deploying devices in triplicate with the following diffusive layer thicknesses 0.015, 0.055, 0.095 and 0.135 cm after Warnken *et al*.[9] and plotting the reciprocal of the mass of uranium accumulated (ng) ion each receiving disk against the diffusive layer thickness. This was undertaken periodically throughout the deployment to assess any seasonal effects on the size of the DBL. The high error bars are as a result of the length of time the devices were deployed and represent the standard error of the mean (of triplicate measurements). Previous studies have shown increasing errors with the time the devices remain in the water due to for instance bio-fouling or sedimentation or variations in flow rates.[10]

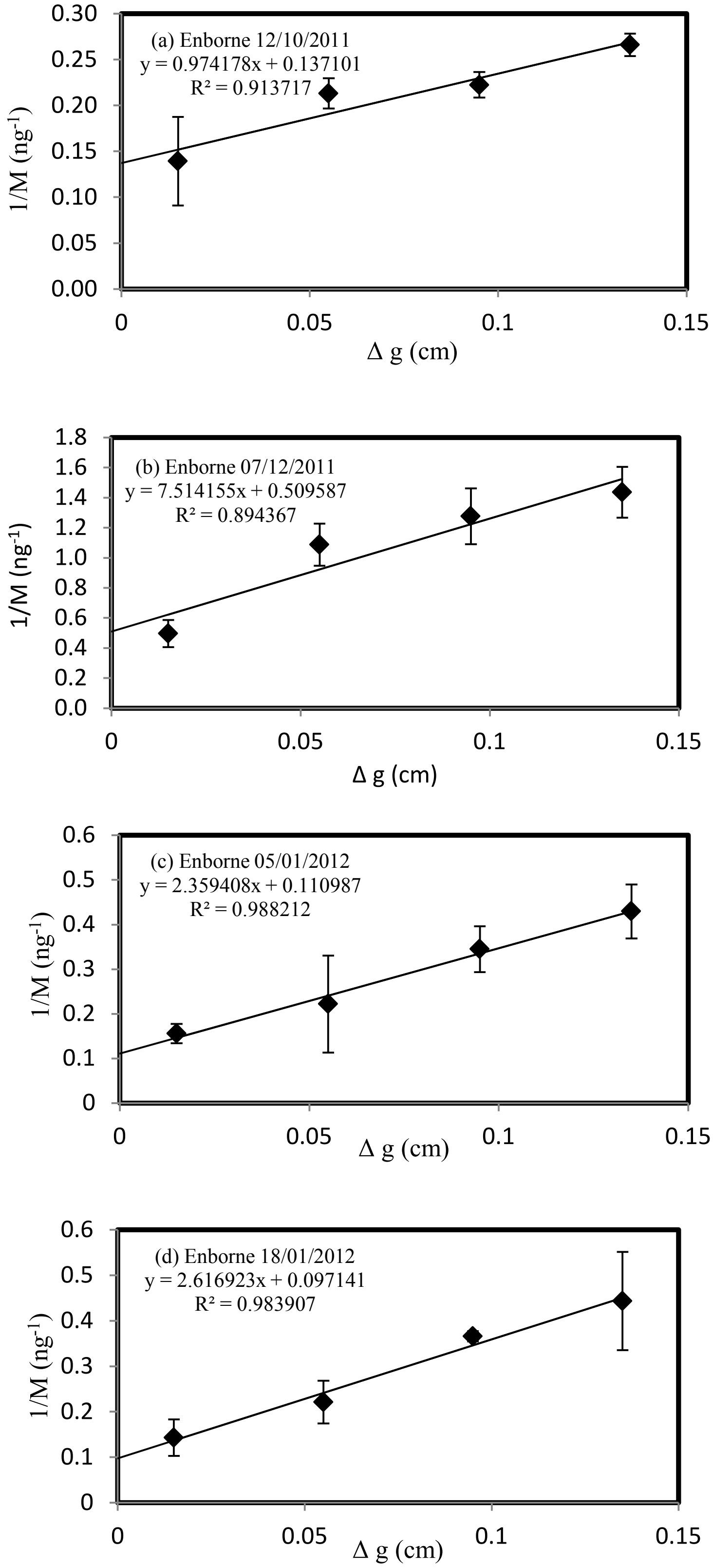

Figure S5. Reciprocal of the mass of uranium accumulated (in triplicate) plotted against the thickness of the diffusion layer used to calculate the thickness of the diffusive boundary layer (DBL) for the River Enborne on the following dates a) 12/10/2011 b) 07/12/2011 c) 05/01/2012 d) 18/01/2012. Error bars represent the standard deviation of triplicate values of *1/M*.

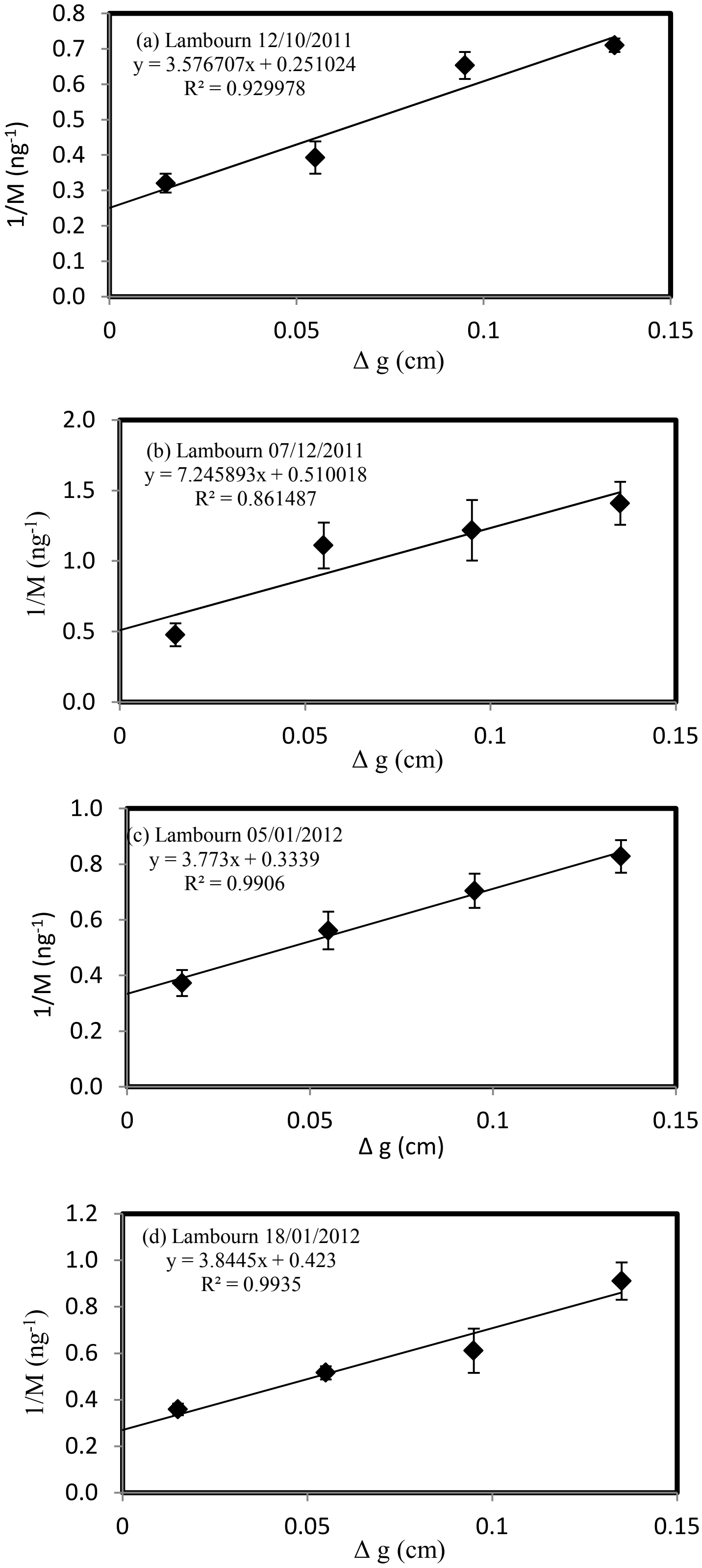

Figure S6. Reciprocal of the mass of uranium accumulated (in triplicate) plotted against the thickness of the diffusion layer used to calculate the thickness of the diffusive boundary layer (DBL) for the River Lambourn on the following dates a) 12/10/2011 b) 07/12/2011 c) 05/01/12 d) 18/01/2012. Error bars represent the standard error of triplicate values of *1/M*.

Effect of particulate matter and bio-fouling on DBL

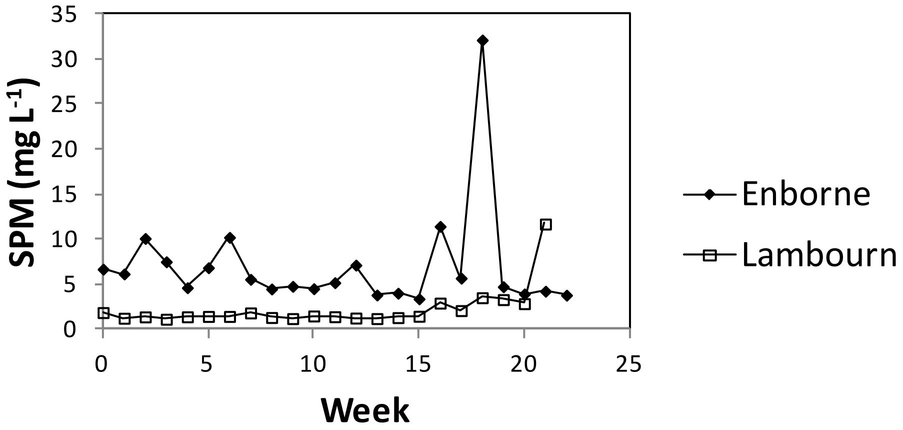

Figure S7. Suspended particulate material (SPM) (mg L^{-1}) measured at the River Lambourn and the River Enborne over the deployment period. Data provided by the CEH as part of the Boxford Observatory Project and Thames Initiative.

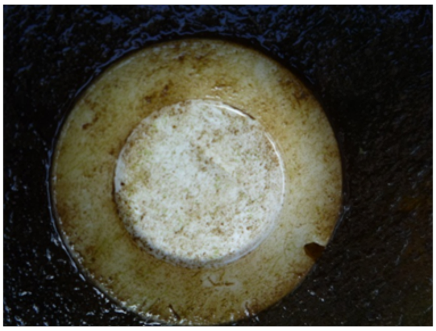

Figure S8. Typical image of DGT device after a 7-day deployment in the River Enborne.

Figure S9a. Devices at the beginning of each weekly deployment after vegetation has been cleared, River Lambourn. Figure S9b. Devices after 7-d deployment. Image shows accumulation of algae, River Lambourn. Figure S9c. Devices after 7-d deployment. Image shows accumulation of sub-surface macro-fauna around the devices, River Lambourn.

Effects of dissolved organics on the DBL

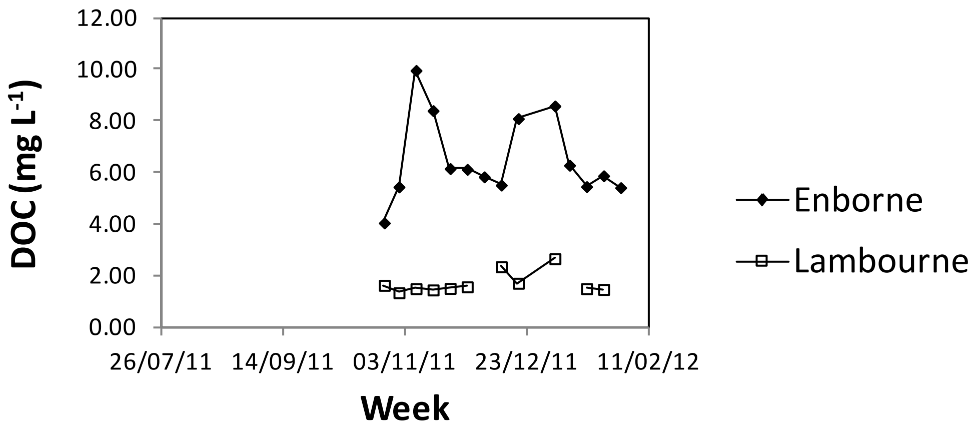

Figure S10. Dissolved organic carbon (DOC) (mg L^{-1}) measured at the River Lambourn and the River Enborne over the deployment period. Data provided by the CEH as part of the Boxford Observatory Project and Thames Initiative.

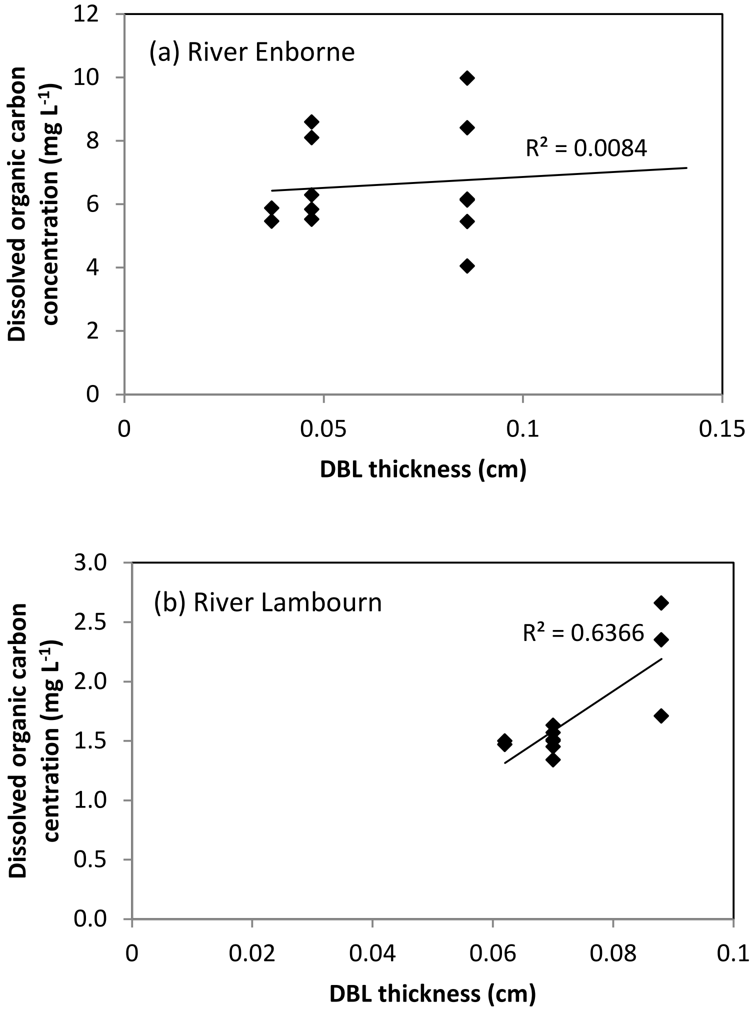

Figure S11. Dissolved organic carbon (DOC) plotted against the DBL thickness for (a) the River Enborne and (b) the River Lambourn. DOC data provided by the CEH as part of the Boxford Observatory Project and Thames Initiative.

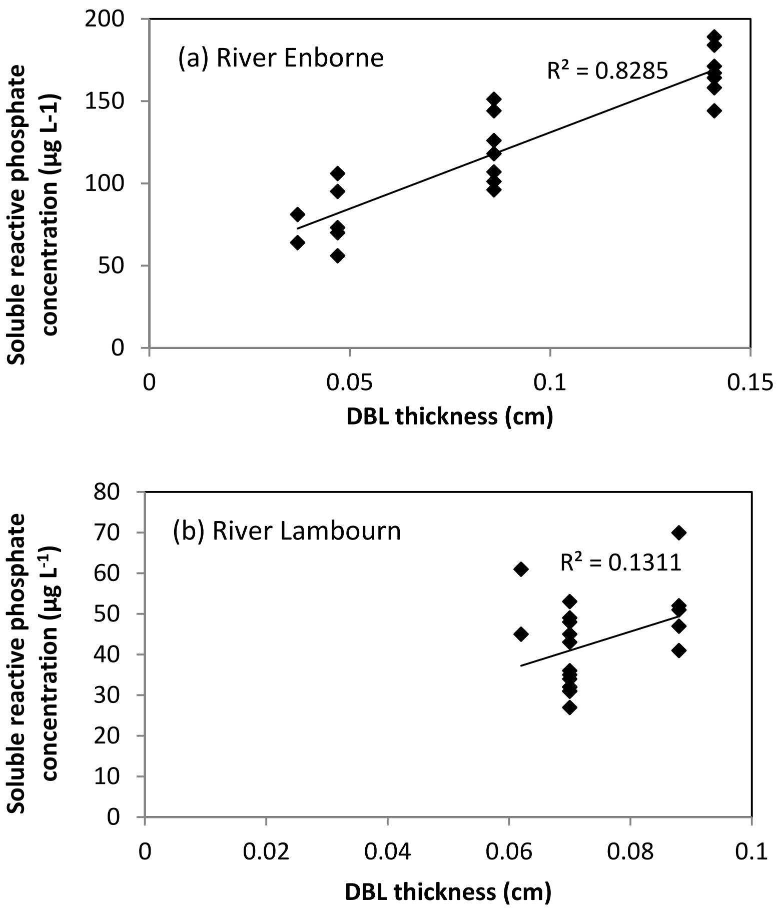

Figure S12. Soluble reactive phosphate (SRP) plotted against the DBL thickness for (a) the River Enborne and (b) the River Lambourn. SRP data provided by the CEH as part of the Boxford Observatory Project and Thames Initiative.

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Time weighted averaged concentrations

Table S4. Diffusion coefficients over the deployment period, using diffusion coefficient data from Hutchins *et al.*[11] and corrected using the Stokes Einstein equation (Equation 3).

Week	Date	River Lambourn		River Enborne	
		Temperature (^{o}C)	Diffusion coefficient (x 10^{-6} cm^{-2} s^{-1})	Temperature (^{o}C)	Diffusion coefficient (x 10^{-6} cm^{-2} s^{-1})
0	24/08/2011	15	1.99	15	2.08
1	31/08/2011	14	1.87	14	1.92
2	07/09/2011	14	1.76	14	1.92
3	14/09/2011	14	1.87	14	1.92
4	23/09/2011	14	1.83	14	1.92
5	28/09/2011	15	1.96	14	2.09
6	05/10/2011	16	2.10	15	2.24
7	12/10/2011	11	1.37	16	1.43
8	19/10/2011	10	1.28	11	1.28
9	24/10/2011	12	1.57	10	1.61
10	02/11/2011	11	1.42	11	1.28
11	09/11/2011	10	1.22	11	1.35
12	16/11/2011	9	1.05	11	1.08
13	23/11/2011	7	0.78	9	1.02
14	30/11/2011	8	0.93	9	0.93
15	07/12/2011	8	0.90	8	0.61
16	14/12/2011	7	0.76	6	0.66
17	21/12/2011	9	1.01	6	0.73
18	28/12/2011	8	0.97	7	1.09
19	05/01/2012	9	1.01	9	0.89
20	11/01/2012	10	1.23	8	0.95
21	18/01/2012	10	1.23	8	0.95

Table S5. Values (average of triplicate readings) for the TWA (DGT) concentrations of uranium and spot water sample concentrations of uranium, with error (standard error of triplicate measurements) for the River Enborne. DGT: weekly averaged ratio is also shown for comparison of the two measurements. The measurements shown were calculated using the changing DBL values over the deployment period. No data shown for weeks 0 and 15 for the DGT uranium concentrations (Week 0 is the deployment week and time 0, so no samplers to remove. Week 15 was during a period of very high flow making sampler retrieval dangerous).

Week Number	Date	Concentration of uranium, C_{DGT} (µg L^{-1})		Concentration of uranium in spot water samples (µg L^{-1})		Weekly averaged concentration of uranium in spot water samples (µg L^{-1})	Ratio of the averaged concentration of uranium in spot water samples: concentration of uranium C_{DGT}
		Average	±	Average	±		
0	24/08/2011	Deployment Week		0.87	0.02	-	-
1	31/08/2011	0.41	0.02	1.11	0.01	1.02	0.40
2	07/09/2011	1.06	0.38	0.92	0.10	0.95	1.11
3	14/09/2011	0.25	0.04	0.25	0.02	0.22	1.13
4	23/09/2011	0.12	0.01	0.18	0.00	0.21	0.57
5	28/09/2011	0.23	0.06	0.25	0.00	0.41	0.56
6	05/10/2011	0.34	0.07	0.58	0.10	0.40	0.85
7	12/10/2011	0.22	0.04	0.21	0.00	0.23	0.96
8	19/10/2011	0.26	0.14	0.26	0.02	0.26	1.00
9	24/10/2011	0.21	0.02	0.27	0.01	0.20	1.05
10	02/11/2011	0.19	0.08	0.13	0.00	0.24	0.79
11	09/11/2011	0.21	0.03	0.36	0.02	0.33	0.64
12	16/11/2011	0.23	0.03	0.30	0.01	0.27	0.85
13	23/11/2011	0.39	0.03	0.24	0.00	0.19	2.05
14	30/11/2011	0.15	0.01	0.14	0.00	0.14	1.07
15	07/12/2011	No Data		0.15	0.05	0.18	-
16	14/12/2011	0.30	0.04	0.21	0.00	0.25	1.20
17	21/12/2011	0.09	0.01	0.29	0.01	0.24	0.38
18	28/12/2011	0.31	0.08	0.18	0.01	0.21	1.48
19	05/01/2012	0.31	0.03	0.24	0.05	0.30	1.03
20	11/01/2012	0.34	0.07	0.36	0.07	0.36	0.94
21	18/01/2012	0.30	0.04	0.36	0.01	0.39	0.77

Table S6. Values (average of triplicate readings) for the TWA (DGT) concentrations of uranium and spot water sample concentrations of uranium, with error (standard error of triplicate measurements) for the River Lambourn. DGT: weekly averaged ratio is also shown for comparison of the two measurements. The measurements shown were calculated using the continuously measured DBL values over the deployment period. No data shown for week 0 (Week 0 is the deployment week and time 0, so there no samplers to remove)

Week number	**Date**	**Concentration of uranium, C_{DGT} (µg L^{-1})**		**Concentration of uranium in spot water samples (µg L^{-1})**		**Weekly averaged concentration of uranium in spot water samples (µg L^{-1})**	**Ratio of the averaged concentration of uranium in spot water samples: concentration of uranium C_{DGT}**
		Average	±	Average	±		
0	24/08/2011	Deployment Week		0.87	0.04	-	-
1	31/08/2011	0.25	0.04	0.99	0.05	0.93	0.27
2	07/09/2011	0.77	0.09	0.91	0.09	0.95	0.81
3	14/09/2011	0.25	0.04	0.11	0.01	0.51	0.49
4	23/09/2011	0.14	0.01	0.27	0.03	0.19	0.74
5	28/09/2011	0.26	0.02	0.24	0.01	0.25	1.04
6	05/10/2011	0.19	0.08	0.94	0.08	0.59	0.32
7	12/10/2011	0.68	0.17	0.22	0.01	0.58	1.17
8	19/10/2011	0.32	0.06	0.26	0.00	0.24	1.33
9	24/10/2011	0.21	0.02	0.36	0.01	0.31	0.68
10	02/11/2011	0.11	0.01	0.18	0.02	0.27	0.41
11	09/11/2011	0.15	0.02	0.33	0.06	0.25	0.60
12	16/11/2011	0.10	0.02	0.27	0.07	0.30	0.33
13	23/11/2011	0.22	0.04	0.25	0.01	0.26	0.85
14	30/11/2011	0.13	0.01	0.21	0.01	0.23	0.57
15	07/12/2011	0.11	0.04	0.16	0.01	0.18	0.61
16	14/12/2011	0.29	0.02	0.26	0.03	0.21	1.38
17	21/12/2011	0.30	0.04	0.17	0.01	0.22	1.36
18	28/12/2011	0.14	0.02	0.12	0.01	0.15	0.93
19	05/01/2012	0.12	0.02	0.20	0.03	0.16	0.75
20	11/01/2012	0.16	0.02	0.19	0.01	0.20	0.80
21	18/01/2012	0.16	0.01	0.19	0.01	0.19	0.84

Water quality data

Table S7a. Concentrations of 0.45 μm filtered major cations in the River Enborne over the deployment period. The data has been averaged over each deployment week (average of data points taken closest to day 1 and day 7 of each week). Data provided by the CEH as part of the Boxford Observatory Project and Thames Initiative.

Week	**Date**	**Na^+**	**K^+**	**Ca^{2+}**	**Mg^{2+}**	**B^+**	**Fe^{2+}**	**Mn^{2+}**	**Zn^{2+}**	**Cu^+**	**Al^{3+}**
		$mg\ L^{-1}$	$mg\ L^{-1}$	$mg\ L^{-1}$	$mg\ L^{-1}$	$\mu g\ L^{-1}$	$\mu g\ L^{-1}$	$\mu g\ L^{-1}$	$\mu g\ L^{-1}$	$\mu g\ L^{-1}$	$\mu g\ L^{-1}$
		LOD = 0.01 $mg\ L^{-1}$					LOD = 0.5 $\mu g\ L^{-1}$				
1	31/08/2011	20.54	4.12	58.42	4.32	29.83	221.37	24.80	3.02	1.99	21.82
2	07/09/2011	20.97	4.19	63.64	4.47	29.68	212.92	27.80	2.90	2.11	19.96
3	14/09/2011	22.37	4.64	65.93	4.63	29.67	174.32	31.83	3.09	2.07	15.06
4	23/09/2011	23.03	4.71	68.02	4.63	29.67	133.10	30.85	3.51	1.78	10.24
5	28/09/2011	22.98	4.57	74.59	4.50	29.19	96.69	28.65	3.97	2.00	7.50
6	05/10/2011	24.09	4.66	77.74	4.53	29.36	68.39	32.04	4.53	2.63	8.19
7	12/10/2011	26.73	5.17	79.75	4.55	30.23	70.27	36.21	4.27	2.38	10.44
8	19/10/2011	26.95	5.39	77.32	4.57	30.24	82.13	32.63	3.55	2.17	10.99
9	24/10/2011	27.22	5.39	78.74	4.73	29.67	85.90	27.05	3.32	2.60	9.95
10	02/11/2011	24.74	5.35	70.33	4.86	29.32	100.10	25.21	3.13	2.19	8.18
11	09/11/2011	19.74	5.22	59.25	5.31	29.28	163.08	23.84	3.32	2.35	14.38
12	16/11/2011	20.00	5.19	59.20	5.62	29.43	208.57	24.65	4.68	3.85	21.85
13	23/11/2011	21.82	4.83	62.55	5.52	28.50	173.06	26.03	5.01	4.10	15.21
14	30/11/2011	22.08	4.64	65.33	5.58	26.74	131.00	22.91	3.76	2.83	9.09
15	07/12/2011	21.73	4.73	63.32	5.70	25.83	139.25	18.03	7.31	3.06	12.34
16	14/12/2011	22.68	4.68	59.48	5.76	24.95	159.93	14.24	11.36	4.65	17.25
17	21/12/2011	20.96	4.16	57.84	5.55	23.90	174.34	14.53	7.32	4.33	31.39
18	28/12/2011	16.47	3.72	55.01	5.39	24.06	219.40	17.99	3.19	2.43	69.39
19	05/01/2012	16.07	3.55	60.05	5.36	24.47	226.18	19.03	2.87	1.51	83.82
20	11/01/2012	15.78	3.32	64.44	5.22	24.42	165.69	17.40	2.68	1.73	47.88
21	18/01/2012	16.10	3.38	63.79	5.30	24.48	151.91	15.47	3.02	1.74	26.30

Table S7b. Concentrations of major anions in the River Enborne over the deployment period. The data has been averaged over each deployment week (average of data points taken closest to day 1 and day 7 of each week). Data provided by the CEH as part of the Boxford Observatory Project and Thames Initiative. Greyed out boxes indicate no data available.

Week	**Date**	**SRP**	**TDP**	**TP**	**NH_4**	**Si**	**DOC**	**TDN**	**F^-**	**Cl^-**	**NO_2^-**	**NO_3^-**	**$SO4^{2-}$**
		µg L^{-1}	µg L^{-1}	µg L^{-1}	mg L^{-1}	mg L^{-1}	mg L^{-1}	mg L^{-1}	mg L^{-1}	mg L^{-1}	mg L^{-1}	mg L^{-1}	mg L^{-1}
1	31/08/2011	163.00	196.50	237.00	0.09	7.39		1.72	0.15	39.895	0.01	15.21	27.87
2	07/09/2011	157.50	199.50	249.00	0.07	7.48			0.08	20.662		7.86	13.66
3	14/09/2011	177.50	210.50	256.00	0.09	7.96			0.07	20.954		6.84	12.82
4	23/09/2011	186.50	208.50	251.00	0.06	8.23			0.14	42.863	0.01	17.40	25.91
5	28/09/2011	173.50	205.00	246.50	0.05	8.42			0.14	42.377	0.01	19.03	25.15
6	05/10/2011	161.00	197.50	249.50	0.05	8.66			0.14	43.891	0.09	17.52	24.61
7	12/10/2011	165.50	197.50	248.00	0.03	8.95			0.14	48.678	0.10	19.29	24.66
8	19/10/2011	159.00	193.00	227.50	0.04	8.95		2.79	0.11	49.187	0.02	19.92	24.50
9	24/10/2011	138.50	173.00	207.50	0.04	8.74	2.03	3.97	0.10	47.928	0.00	21.36	24.84
10	02/11/2011	135.00	164.50	194.50	0.05	8.23	4.75	2.86	0.12	42.923	0.26	17.22	24.53
11	09/11/2011	120.00	145.00	172.00	0.06	7.66	7.71	3.26	0.11	36.413	0.39	13.35	28.37
12	16/11/2011	107.00	127.00	157.50	0.06	7.92	9.19	3.30	0.11	38.092	0.18	14.57	30.03
13	23/11/2011	109.50	126.50	161.50	0.06	8.63	7.29	3.74	0.11	42.747	0.05	14.92	28.10
14	30/11/2011	104.00	123.50	151.50	0.06	8.87	6.15	2.02	0.11	44.019	0.18	16.79	27.86
15	07/12/2011	101.00	123.00	143.50	0.05	8.34	5.99		0.12	41.581	0.18	15.76	28.07
16	14/12/2011	100.50	118.50	147.50	0.07	7.61	5.68	2.02	0.19	44.037	0.01	15.71	29.23
17	21/12/2011	81.00	91.50	120.50	0.13	6.80	6.81	3.66	0.11	41.909	0.05	18.54	30.79
18	28/12/2011	64.50	75.00	140.50	0.12	6.06	8.35	1.64	0.12	33.300	0.04	17.91	30.09
19	05/01/2012	71.50	76.50	143.50	0.08	6.45	7.44		0.07	15.726	0.01	7.94	13.95
20	11/01/2012	67.00	70.00	94.50	0.10	7.13	5.88						
21	18/01/2012	72.50	79.00	107.50	0.09	7.33	5.67	1.09	0.06	17.114	0.07	8.47	14.83

Table S7c Concentration of particulates, pH and alkalinity in the River Enborne over the deployment period. The data has been averaged over each deployment week (average of data points taken closest to day 1 and day 7 of each week). Data provided by the CEH as part of the Boxford Observatory Project and Thames Initiative

Week	**Date**	**pH**	**Alkalinity**	**Suspended material**	
				Chl *a*	**SPM**
			μequiv L^{-1}	μg L^{-1}	mg L^{-1}
1	31/08/2011	7.62	2494.00	2.61	6.43
2	07/09/2011	7.66	2666.50	2.06	8.13
3	14/09/2011	7.67	2833.50	1.95	8.81
4	23/09/2011	7.74	2915.50	1.47	6.07
5	28/09/2011	7.69	3131.00	1.12	5.74
6	05/10/2011	7.60	3252.00	1.60	8.54
7	12/10/2011	7.63	3364.00	1.59	7.89
8	19/10/2011	7.65	3245.50	1.26	5.03
9	24/10/2011	7.71	3257.50	1.18	4.64
10	02/11/2011	7.62	2946.50	1.26	4.65
11	09/11/2011	7.47	2434.50	1.57	4.86
12	16/11/2011	7.43	2430.00	1.37	6.17
13	23/11/2011	7.48	2695.00	0.81	5.48
14	30/11/2011	7.57	2780.00	0.67	3.92
15	07/12/2011	7.64	2598.00	0.44	3.71
16	14/12/2011	7.64	2446.50	0.89	7.42
17	21/12/2011	7.54	2278.50	1.11	8.57
18	28/12/2011	7.50	2080.00	1.92	18.92
19	05/01/2012	7.52	2216.50	1.94	18.44
20	11/01/2012	7.63	2585.50	0.68	4.34
21	18/01/2012	7.72	2709.00	0.53	4.09

Table S8a. Concentrations of 0.45 μm filtered cations in the River Lambourn over the deployment period. The data has been averaged over each deployment week (average of data points taken closest to day 1 and day 7 of each week). Data provided by the CEH as part of the Boxford Observatory Project and Thames Initiative.

Week	Date	Na^+	K^+	Ca^{2+}	Mg^{2+}	B^+	Fe^{2+}	Mn^{2+}	Zn^{2+}	Cu^+	Al^{3+}
		mg L^{-1}	mg L^{-1}	mg L^{-1}	mg L^{-1}	μg L^{-1}	μg L^{-1}	μg L^{-1}	μg L^{-1}	μg L^{-1}	μg L^{-1}
		LOD = 0.01 mg L^{-1}					LOD = 0.5 μg L^{-1}				
1	31/08/2011	9.56	1.69	108.91	1.77	14.96	4.10	1.07	6.48	0.30	<0.5
2	07/09/2011	9.45	1.74	108.15	1.75	14.77	4.25	0.77	5.66	<0.5	<0.5
3	14/09/2011	9.05	1.67	105.69	1.68	13.13	6.53	0.46	3.32	0.38	7.52
4	23/09/2011	9.27	1.77	105.43	1.68	13.48	6.60	0.48	2.17	<0.5	0.11
5	28/09/2011	9.30	1.80	105.87	1.68	13.41	3.93	0.49	2.66	1.63	-8.35
6	05/10/2011	9.34	1.67	107.43	1.71	13.31	3.74	0.41	2.34	1.98	1.94
7	12/10/2011	9.53	1.66	108.44	1.73	13.46	4.12	0.64	1.97	0.23	3.92
8	19/10/2011	9.39	1.77	107.39	1.71	13.13	4.75	0.82	2.83	0.03	0.21
9	24/10/2011	9.32	1.89	108.19	1.73	13.32	4.42	0.69	3.18	0.12	<0.5
10	02/11/2011	9.26	1.91	108.32	1.74	13.43	3.75	0.51	2.72	0.10	<0.5
11	09/11/2011	9.22	1.88	107.48	1.71	13.28	3.77	0.52	2.84	0.30	3.83
12	16/11/2011	9.33	1.88	106.66	1.72	13.11	3.18	0.52	3.17	0.64	0.86
13	23/11/2011	9.65	1.91	105.78	1.72	12.46	3.18	<0.5	2.92	0.53	<0.5
14	30/11/2011	9.95	1.94	106.76	1.74	12.20	4.08	<0.5	3.73	5.41	<0.5
15	07/12/2011	9.94	1.87	107.44	1.75	12.63	4.13	0.55	3.55	5.64	2.52
16	14/12/2011	12.63	2.34	105.86	1.76	13.78	4.64	0.84	4.13	4.37	2.40
17	21/12/2011	12.75	2.35	107.03	1.77	14.84	4.18	1.05	6.90	11.89	<0.5
18	28/12/2011	9.72	1.79	109.51	1.75	14.72	2.61	1.15	4.92	7.96	<0.5
19	05/01/2012	9.38	1.75	108.10	1.71	14.02	2.48	1.13	2.50	0.85	<0.5
20	11/01/2012	9.41	1.69	107.41	1.71	14.21	2.45	0.88	2.58	1.03	<0.5
21	18/01/2012	9.83	1.67	105.82	1.68	14.25	4.68	1.34	2.38	0.23	0.56

Table S8b. Concentrations of major anions in the River Lambourn over the deployment period. The data has been averaged over each deployment week (average of data points taken closest to day 1 and day 7 of each week). Data provided by the CEH as part of the Boxford Observatory Project and Thames Initiative. Greyed out boxes indicate no data available.

Week	**Date**	**SRP**	**TDP**	**TP**	**NH_4**	**Si**	**DOC**	**TDN**	**F^-**	**Cl^-**	**NO_2^-**	**NO_3^-**	**SO_4^{2-}**
		µg L^{-1}	µg L-1	µg L-1	mg L-1	mg L^{-1}	mg L^{-1}	mg L^{-1}	mg L^{-1}	mg L^{-1}	mg L^{-1}	mg L^{-1}	mg L^{-1}
1	31/08/2011	26.0	39.0	41.0	0.06	7.66		4.07	0.13	18.02	0.06	33.89	12.35
2	07/09/2011	29.0	38.5	44.0	0.02	7.57			0.12	18.00	0.06	34.10	12.20
3	14/09/2011	31.5	37.0	46.5	0.08	7.50			0.12	17.47	0.06	33.39	12.16
4	23/09/2011	31.5	39.0	49.5	0.08	7.63			0.12	17.68	0.04	34.19	12.63
5	28/09/2011	33.0	38.0	53.5	0.03	7.81			0.19	43.85	0.01	17.93	16.58
6	05/10/2011	34.5	43.0	55.0	0.04	7.81			0.19	43.63	0.02	17.36	16.36
7	12/10/2011	35.0	45.5	51.5	0.03	7.89			0.06	8.94	0.02	17.07	6.26
8	19/10/2011	34.0	35.5	40.0	0.05	7.91							
9	24/10/2011	32.0	36.0	42.0	0.06	7.84	0.82	4.41	0.04	8.85	0.00	17.07	6.28
10	02/11/2011	37.5	46.5	50.0	0.04	7.88	1.49	8.69	0.09	17.58	0.02	34.22	12.46
11	09/11/2011	44.0	50.0	54.0	0.03	8.02	1.42	8.72	0.09	17.56	0.04	34.71	12.74
12	16/11/2011	49.0	55.0	61.0	0.03	8.08	1.48	8.80	0.10	17.37	0.04	34.23	13.02
13	23/11/2011	50.5	55.5	60.0	0.02	8.04	1.48	8.98	0.11	17.58	0.02	34.37	12.99
14	30/11/2011	48.5	51.0	57.0	0.04	8.00	1.54	9.15	0.12	18.10	0.00	35.49	13.34
15	07/12/2011	45.0	49.0	59.0	0.04	8.03	0.79	4.54	0.12	18.41	0.02	36.09	13.72
16	14/12/2011	55.5	66.0	73.0	0.13	7.95	1.18		0.11	22.73	0.16	37.12	14.63
17	21/12/2011	58.5	62.5	67.5	0.14	7.87	2.03	4.34	0.11	22.71	0.20	36.78	14.43
18	28/12/2011	49.0	50.0	80.5	0.08	8.02	2.19	8.57	0.11	18.39	0.12	34.95	13.00
19	05/01/2012	51.5	55.5	86.0	0.08	8.14	1.33	4.23	0.12	18.32	0.10	34.49	12.68
20	11/01/2012	48.5	70.0	80.0	0.05	8.10	0.75		0.12	18.33	0.08	35.61	12.79
21	18/01/2012	53.0	66.0	92.5	0.04	7.84	1.49		0.11	19.37	0.06	33.95	12.23

Table S8b. Concentration of particulates, pH and alkalinity in the River Lambourn over the deployment period. The data has been averaged over each deployment week (average of data points taken closest to day 1 and day 7 of each week). Data provided by the CEH as part of the Boxford Observatory Project and Thames Initiative

Week	**Date**	**pH**	**Alkalinity**	**Suspended material**	
				Chl *a*	**SPM**
			μequiv L^{-1}	μg L^{-1}	mg L^{-1}
1	31/08/2011	7.95	4509	1.99	1.56
2	07/09/2011	7.89	4479	1.93	1.32
3	14/09/2011	7.98	4392	1.21	1.26
4	23/09/2011	7.98	4468	1.31	1.27
5	28/09/2011	7.86	4461	1.21	1.42
6	05/10/2011	7.93	4396	0.88	1.44
7	12/10/2011	7.92	4406	1.11	1.64
8	19/10/2011	7.87	4384	1.06	1.58
9	24/10/2011	7.78	4502	0.93	1.26
10	02/11/2011	7.68	4416	1.2	1.35
11	09/11/2011	7.76	4379	1.48	1.45
12	16/11/2011	7.78	4461	1.35	1.34
13	23/11/2011	7.77	4550	0.84	1.23
14	30/11/2011	7.80	4553	0.75	1.26
15	07/12/2011	7.74	4481	0.93	1.39
16	14/12/2011	7.82	4346	1.18	2.19
17	21/12/2011	7.81	4343	0.83	2.51
18	28/12/2011	7.67	4497	0.52	2.81
19	05/01/2012	7.70	4411	0.71	3.42
20	11/01/2012	7.75	4571	0.88	3.09
21	18/01/2012	7.76	4492	1.51	7.28

Table S9. Results of Spearman's rank correlation coefficient for the River Enborne and River Lambourn using monitoring data that was averaged over each deployment week to make it comparable with TWA (DGT) concentrations for uranium. Many of the distributions were found not to be normally distributed so the Spearman's (which is non-parametric test) was used in place of the Pearson's coefficient (a parametric test that requires normally distributed data). The 99% confidence limit (0.01) for a two tailed test was used, with a sample size of 21. The significance figure used was $r_s = 0.548$. If the test value was equal to or above this figure then the null hypothesis of no correlation was rejected (**correlation is significant at the 0.01 level (2-tailed); *correlation is significant at the 0.05 level (2-tailed)).

	River Enborne				River Lambourn			
	C_{DGT} ($\mu g\ L^{-1}$)	C_{DGT} error ($\mu g\ L^{-1}$)	U spot ($\mu g\ L^{-1}$)	U:C_{DGT} ratio	C_{DGT} ($\mu g\ L^{-1}$)	C_{DGT} error ($\mu g\ L^{-1}$)	U spot ($\mu g\ L^{-1}$)	U:C_{DGT} ratio
C_{DGT} ($\mu g\ L^{-1}$)	1.000	0.268	0.745**	0.489*	1.000	0.399	0.270	0.501*
C_{DGT} error ($\mu g\ L^{-1}$)	0.268	1.000	0.181	0.299	0.399	1.000	-0.197	0.370
U soot ($\mu g\ L^{-1}$)	0.745**	0.181	1.000	0.076	0.270	-0.197	1.000	-0.613**
U:DGT ratio	0.489*	0.299	0.076	1.000	0.501*	0.370	-0.613**	1.000
pH	-0.044	0.142	0.115	0.045	0.217	-0.274	0.573**	-0.381
Alkalinity (μequiv L^{-1})	0.186	0.002	0.517*	-0.272	-0.053	-0.090	-0.078	-0.071
Chl-*a* ($\mu g\ L^{-1}$)	0.206	0.201	0.347	-0.158	0.123	-0.031	0.445*	-0.400
SPM ($mg\ L^{-1}$)	0.086	0.325	0.296	-0.157	0.068	0.340	-0.462*	0.424
SRP ($\mu g\ L^{-1}$)	0.106	0.265	0.334	-0.156	-0.027	0.205	-0.608**	0.628**
TDP ($\mu g\ L^{-1}$)	0.088	0.182	0.353	-0.200	-0.076	0.213	-0.523*	0.434*
TP ($\mu g\ L^{-1}$)	-0.165	0.247	-0.116	0.035	-0.221	0.233	-0.669**	0.455*
NH_4 ($mg\ L^{-1}$)	-0.268	-0.055	-0.335	0.110	-0.142	0.010	-0.497*	0.312
Si ($mg\ L^{-1}$)	0.003	0.311	-0.126	0.168	-0.171	0.204	-0.514*	0.396
DOC ($mg\ L^{-1}$)	-0.303	0.062	-0.167	-0.475*	-0.157	0.085	-0.477*	0.389
TDN ($mg\ L^{-1}$)	-0.271	0.244	-0.300	-0.126	-0.257	-0.112	-0.106	-0.022
F^- ($mg\ L^{-1}$)	-0.354	0.333	-0.411	0.055	-0.309	-0.348	0.029	-0.379
Cl^- ($mg\ L^{-1}$)	-0.332	0.035	-0.270	-0.089	-0.163	0.067	-0.392	0.238
NO_2^- ($mg\ L^{-1}$)	-0.360	0.232	-0.283	-0.051	-0.005	0.297	-0.369	0.230
NO_3^- ($mg\ L^{-1}$)	-0.314	0.225	-0.313	-0.241	-0.151	0.326	-0.591**	0.381
SO_4^{2-} ($mg\ L^{-1}$)	-0.215	0.190	-0.135	-0.141	-0.337	-0.032	-0.305	0.161
Na^+ ($mg\ L^{-1}$)	-0.347	0.196	-0.232	-0.077	0.374	0.281	-0.338	0.564**
K^+ ($mg\ L^{-1}$)	-0.111	0.065	0.034	0.105	0.021	0.044	-0.244	0.398
Ca^{2+} ($mg\ L^{-1}$)	-0.391	-0.078	-0.550**	-0.077	0.046	0.315	0.201	-0.202
Mg^{2+} ($mg\ L^{-1}$)	0.163	0.200	0.511*	-0.172	0.270	0.312	0.146	0.086
B^+ ($\mu g\ L^{-1}$)	0.111	-0.175	0.144	-0.191	0.223	0.319	-0.088	0.106
Fe^{2+} ($\mu g\ L^{-1}$)	0.172	0.313	0.496*	0.012	0.326	0.030	0.103	0.077
Mn^{2+} ($\mu g\ L^{-1}$)	-0.102	0.362	-0.140	-0.203	0.243	0.443*	-0.372	0.414
Zn^{2+} ($\mu g\ L^{-1}$)	0.166	0.385	-0.123	0.135	0.278	0.179	0.086	0.128
Cu^+ ($\mu g\ L^{-1}$)	0.161	-0.141	0.185	-0.055	-0.221	0.109	-0.426	0.305
Al^{3+} ($\mu g\ L^{-1}$)	0.092	-0.118	-0.005	-0.115	-0.063	0.266	0.022	-0.053

Water quality

Speciation distributions for uranium were made (Visual Minteq, version 3, beta (© 2010 KTH, Department of Land and Water Resources Engineering, Stockholm, Sweden) for each river for each week over the deployment. Uranium is highly soluble in aqueous environments, readily forming the uranyl ion (UO_2^{2+}) at pH < 4 to 5; at pH > 7 occurring as the stable uranyl carbonates $UO_2(CO_3)_2^{2-}$, $UO_2(CO_3)_3^{4}$- or its complexes; and under reducing conditions as U(IV)[12]. Aqueous chemistry and speciation is complex and is defined by the pH, Eh, ionic strength and the presence of organic and inorganic ligands.[13] Uranium was used in this study due to its complex physico-chemistry and susceptibility to changes in water chemistry. In order to show the effectiveness of passive samplers in fluctuating environments, it was helpful to compare the DGT data against water quality data.

Uranium has a high reactivity with complexing ligands ($OH^- > CO_3^{2-} > HPO_4^{2-} > H_2PO_4^- > F^- > SO_4^{2-} > Cl^-$), surfactants or flocculating agents.[13] These could potentially influence the oxidation states of the radionuclide with changing aqueous concentrations potentially affecting uptake by the DGT. In the River Enborne, over 90% of the dissolved uranium (depending on the ratio of U:DOC) was modelled to be complexed to DOC, with other uranium complexes including < 2% $Ca_2UO_2(CO_3)^{2-}$ and 1-4% $Ca_2UO_2(CO_3)^3$. The River Lambourn due to the higher alkalinity and lower DOC concentrations had a lower quantity of humate bound uranium, with an approximately even split between DOC and the calcium carbonate complexes $Ca_2UO_2(CO_3)^{2-}$ and $Ca_2UO_2(CO_3)^3$.

The measured water quality data was averaged over each week of deployment (i.e. an average reading of day 1 and day 7 for the deployment week) (Tables S7–S8) and tested for any relationship against the DGT data (Table S9). Turner *et al.*[10] showed that calcium carbonate complexes do not inhibit the uptake of uranium using the Metsorb™ DGT except at extremely high Ca^{2+} concentrations. However, uranium DOC complexes may affect the uptake by these devices as they are less labile.[14] At U:HA ratios below 0.1, as with the rivers in this study, it has been found that humic acids can suppress hydrolysis of U(VI) to promote formation of the U:HA complex with a larger portion of the uranium binding sites resulting in an increased in the non-labile fraction.[14,15] Algae can take up uranium and has been trialled as a removal technique for this element in dilute mine waste waters.[16] However, uranium bound to algae has been shown to be susceptible to changing physical conditions (such as on the surface of the devices where a diffusion gradient exists) and desorb.[17] No relationship between the Chl-*a* and the C_{DGT} for uranium was observed, however, further investigations are required into the effects of periphyton accumulation on DGT devices and the accuracy and precision of this technique. No relationships were found between the C_{DGT} uranium and water quality of the rivers, showing that the DGT technique for uranium operates independently from fluctuating water quality conditions.

Table S10. Results of speciation modelling for the River Enborne, with CO_2 at atmospheric partial pressure, using Visual Minteq. The modelling data has been shown for all instances a DBL was measured, plus a deployment average. $FA2UO_{2(aq)}$ and $FAUO_2^+{}_{(aq)}$ represent mono- and bi-dentate uranium bonds to fulvic acid respectively.

	Date				
Species	**12/10/2011**	**07/12/2011**	**05/01/2012**	**18/01/2012**	**Deployment Average**
UO_2OH^+	0.013	0.018		0.013	0.024
$UO_2(OH)_3^-$	0.023	0.045		0.035	0.039
$UO_2(OH)_{2\,(aq)}$	0.063	0.106	0.035	0.078	0.113
$Ca_2UO_2(CO_3)_{3\,(aq)}$	29.92	59.751	1.718	28.8	27.535
$CaUO_2(CO_3)_3^{2-}$	10.462	25.899	0.82	11.979	10.936
$UO_2CO_{3\,(aq)}$	0.176	0.295	0.081	0.159	0.287
$UO_2(CO_3)_2^{2-}$	0.407	0.924	0.076	0.336	0.512
$UO_2(CO_3)_3^{4-}$	0.203	0.599	0.031	0.54	0.299
$/FA2UO_{2(aq)}$	58.663	12.3	97.106	58.006	60.119
$/FAUO_2^+{}_{(aq)}$	0.068	0.061	0.114	0.052	0.132

Table S11. Results of speciation modelling for the River Lambourn, with CO2 at atmospheric partial pressure, using Visual Minteq. The modelling data has been shown for all instances a DBL was measured, plus a deployment average. $FA2UO_{2(aq)}$ and $FAUO_2^+{}_{(aq)}$ represent mono- and bi-dentate uranium bonds to fulvic acid respectively.

	Date				
Species	**12/10/2011**	**07/12/2011**	**05/01/2012**	**18/01/2012**	**Deployment Average**
UO_2OH^+				0.012	
$UO_2(OH)_3^-$	0.01	0.021		0.026	0.01
$UO_2(OH)_{2\,(aq)}$	0.015	0.048		0.064	0.019
$Ca_2UO_2(CO_3)_{3\,(aq)}$	79.043	73.819	79.099	75.098	79.462
$CaUO_2(CO_3)_3^{2-}$	18.92	17.899	19.182	18.349	19.415
$UO_2CO_{3\,(aq)}$	0.03	0.115	0.021	0.162	0.047
$UO_2(CO_3)_2^{2-}$	0.135	0.309	0.139	0.391	0.217
$UO_2(CO_3)_3^{4-}$	0.563	0.353	0.357	0.324	0.343
$/FA2UO_{2(aq)}$	1.282	7.418	1.186	5.563	0.481
$/FAUO_2^+{}_{(aq)}$*					

*Model shows no bi-dentate bonds form in this system, most likely as a function of carbonate concentration.

Electronic Supplementary Material (ESI) for Environmental Science: Processes & Impacts

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