Article:
Comer-Warner, S, Knapp, JLA, Blaen, P et al. (19 more authors) (2020) The method controls the story - Sampling method impacts on the detection of pore-water nitrogen concentrations in streambeds. Science of The Total Environment, 709. 136075. ISSN 0048-9697

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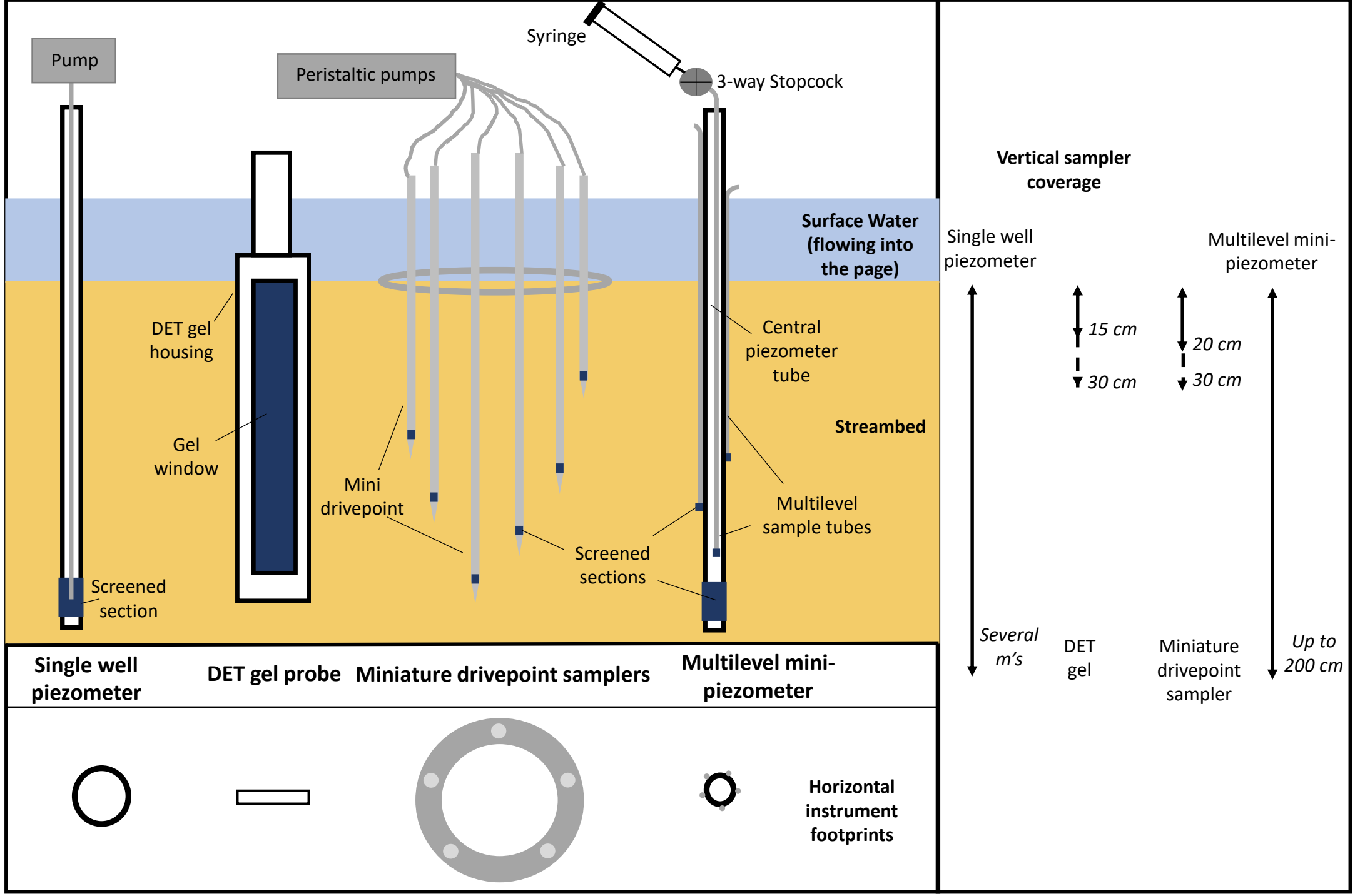
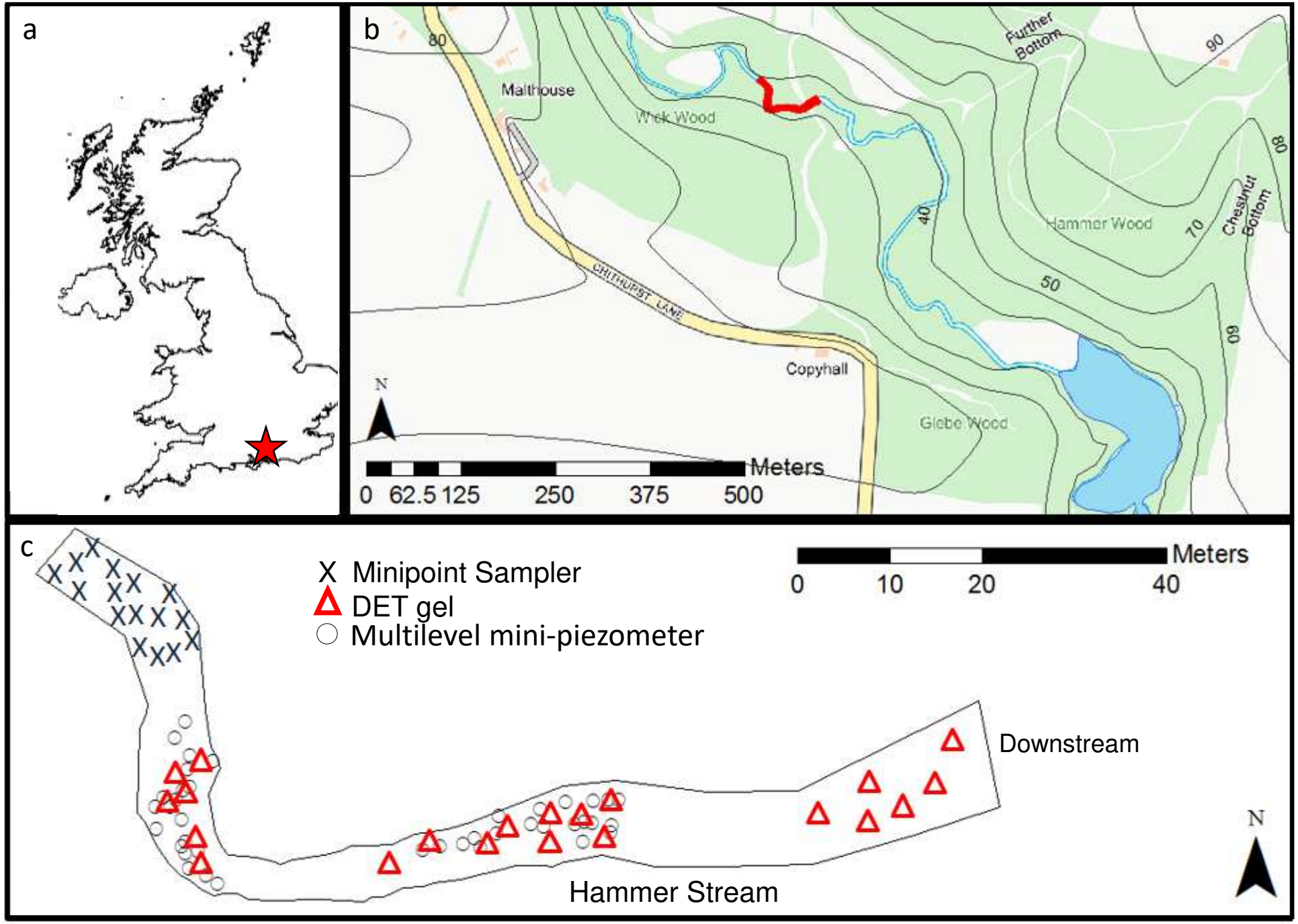
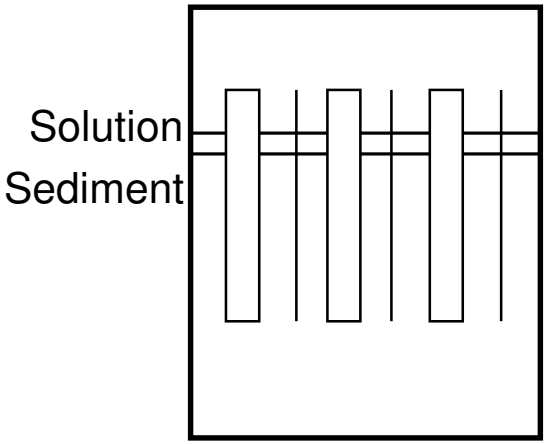
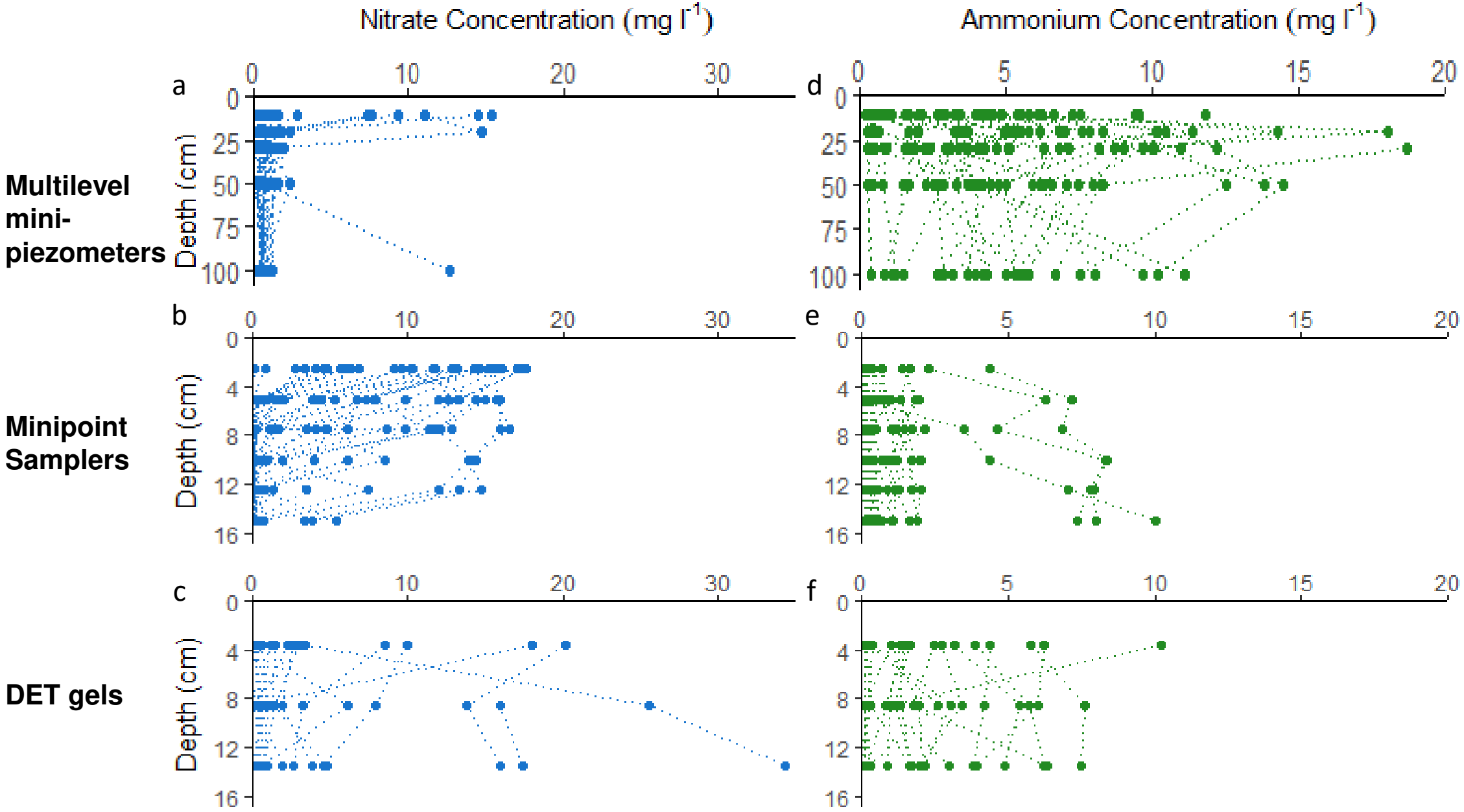

Pump
Peristaltic pumps
Syringe
3-way Stopcock
Surface Water (flowing into the page)
DET gel housing
Gel window
Mini drivepoint
Central piezometer tube
Streambed
Multilevel sample tubes
Screened sections
Screened section
Single well piezometer
DET gel probe
Miniature drivepoint samplers
Multilevel mini-piezometer
Horizontal instrument footprints
Vertical sampler coverage
Single well piezometer
Several m's
15 cm
30 cm
DET gel
20 cm
30 cm
Miniature drivepoint sampler
Multilevel mini-piezometer
Up to 200 cm


a
b
80
Malthouse
Wet Wood
Further Bottom
90
80
40
Hammer Wood
70
Chestnut Bottom
50
60
CHITHURST LANE
Copyhall
Glebe Wood
N
Meters
0 62.5 125 250 375 500
c
X Minipoint Sampler
DET gel
Multilevel mini-piezometer
Meters
0 10 20 40
Downstream
Hammer Stream
N

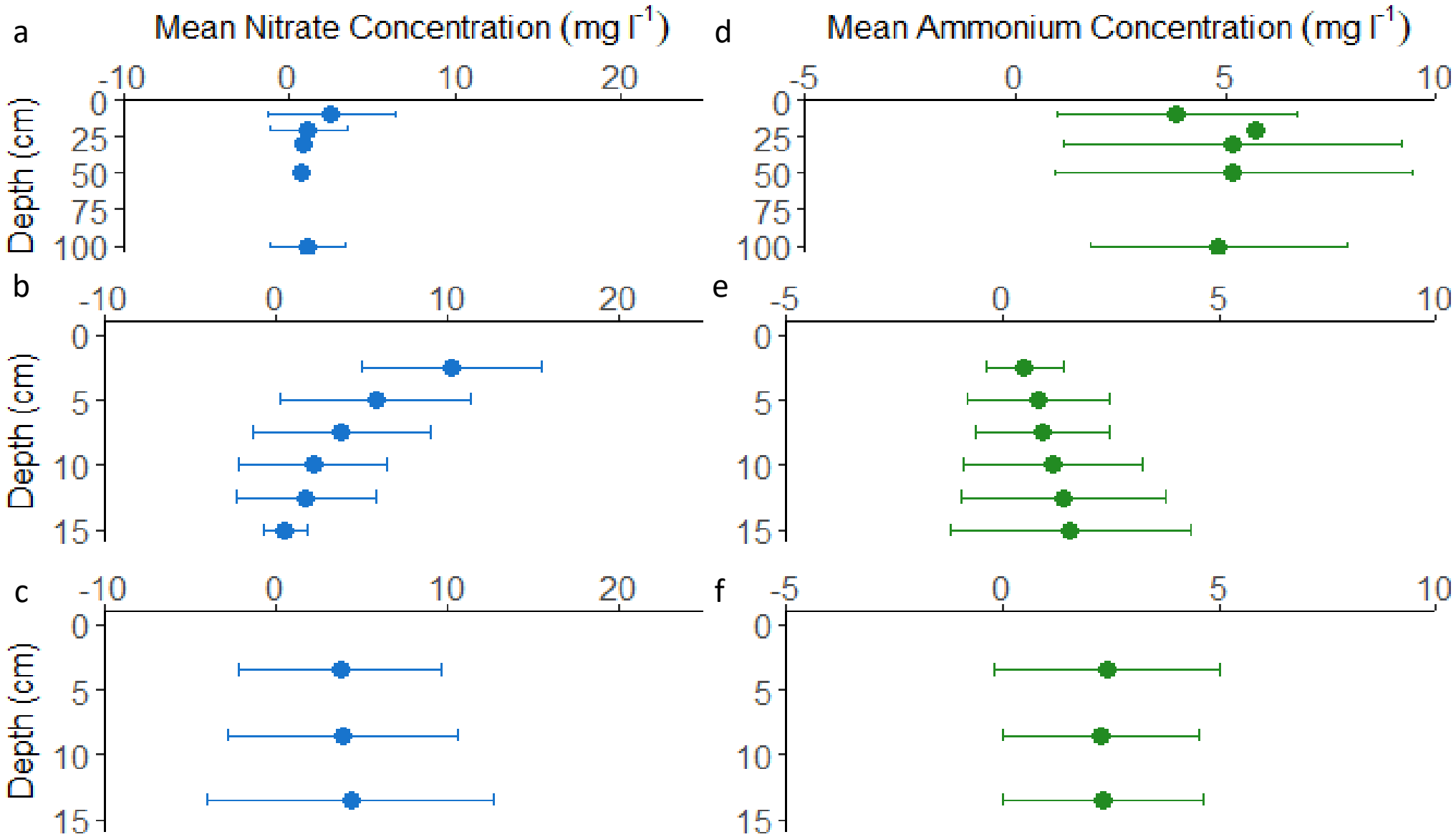

Solution
Sediment

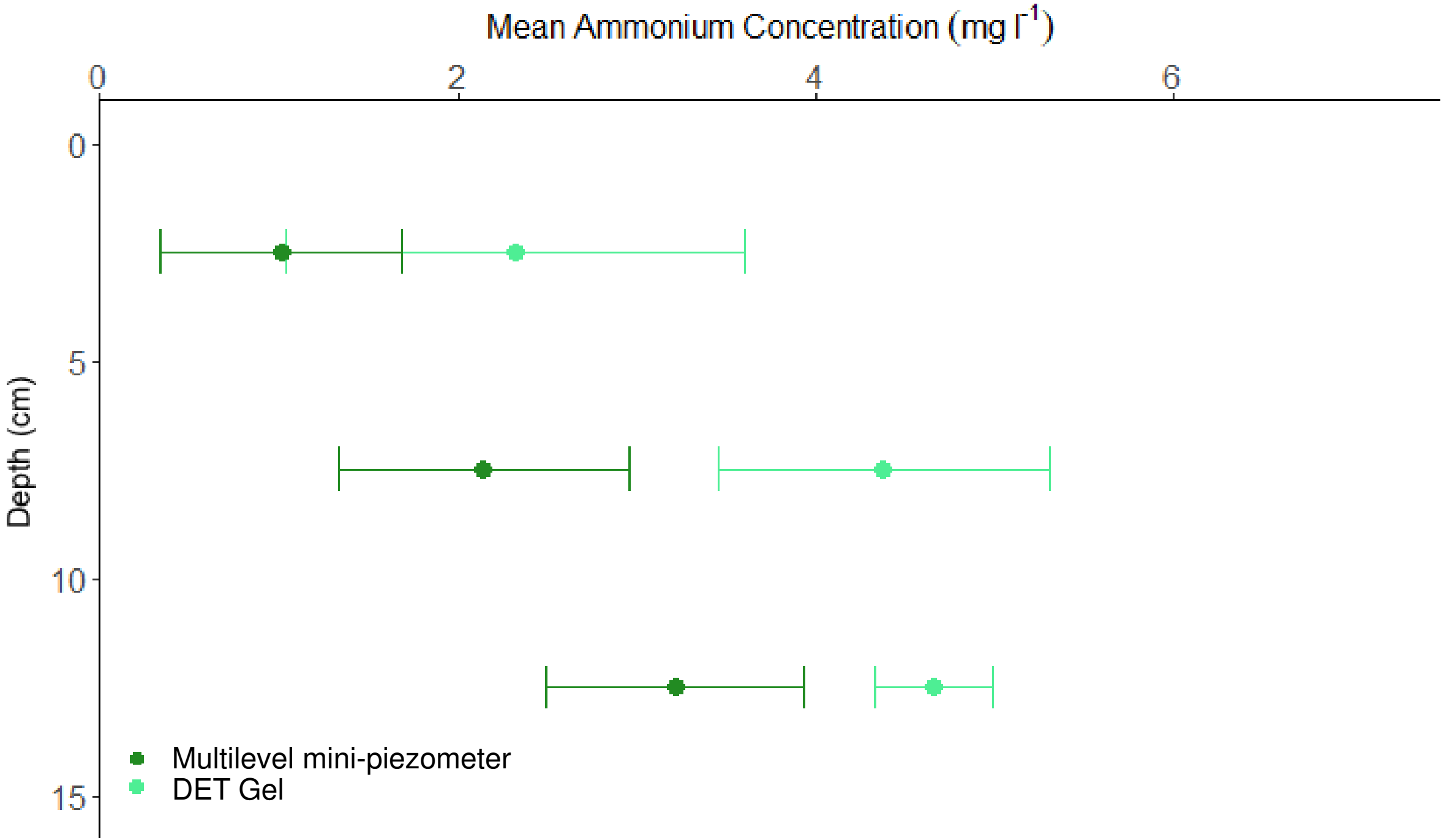

Nitrate Concentration (mg l-1)
Ammonium Concentration (mg l-1)
Multilevel mini-piezometers
Minipoint Samplers
DET gels
Depth (cm)
a
b
c
d
e
f
0
10
20
30
5
15
25
50
75
100
4
8
12
16

Multilevel mini-piezometers

Minipoint Samplers

DET gels




Mean Ammonium Concentration (mg l-1)
0
2
4
6
0
5
10
15
Depth (cm)
Multilevel mini-piezometer
DET Gel

Sampling Methodology	Active or Passive Sampling	Sampling Technique	Sampling Depth	Horizontal Instrument Footprint	Vertical Resolution	Temporal Resolution	Deployment Time	Advantages	Limitations
Single-depth piezometers	Active	Porewater extraction	Up to several m's	10-50 mm	> 100 mm's	Snapshot during time of sampling	Days to years	- Hydrological information at location of chemical sampling - Large sample volume - Easy installation in sandy and silt sediments - Permanent logger installation	- Must be installed prior to sampling (hours to days before) - Substantial hammering or pre-drilling is required in gravel and clay sediments - Time to refill after purging can be long, preventing sampling or exposing sample to the atmosphere - Large horizontal instrument footprint - Low vertical resolution - Although hyporheic fluxes can be estimated, this assumes vertical flow is present, which is not always the case - The larger piezometer design may alter hyporheic flow
Multilevel mini-piezometers	Active	Porewater extraction	0.1 to 2 m	30 mm	50-100 mm	Snapshot during time of sampling	Days to years	- Hydrological information obtained in central tube - Hyporheic fluxes and reaction rates can be determined at all depths - Porewater extraction from discrete, user-defined depths - Easy installation in soft sediments - Small sampling diameter due to small horizontal instrument footprint - Flexible, more storm-resilient piezometer, less prone to vandalism - Sampling via a closed loop when syringes are used	- Hydrological information gained via hydraulic gradients is not possible to determine in the multilevel sampling tubes, so information is only attainable from the depth of the central piezometer - The central piezometer is typically too small for permanent loggers - The vertical solute profile may be disrupted if sampling occurs too rapidly - Coarse sampling interval - Installment a few days prior to sampling is required - Installation is difficult in gravel or clay sediments, and may require substantial pre-drilling or hammering - Although hyporheic fluxes can be estimated, this assumes vertical flow is present, which is not always the case
Miniature drivepoint samplers	Active	Porewater extraction	up to 0.4 m	50-100 mm	10-30 mm	Snapshot during time of sampling	Hours to days	- Hydrological information and reaction rates can be determined at all depths - Small diameter allows easy and rapid installation with minimal disturbance, allowing use as roaming samplers and to sample unstable sediments - Porewater samples can be pre-filtered at the sampler tip or in line during pumping - High resolution porewater extraction	- The temporary nature of installation prevents longer temporal studies in the same location and the samplers may be easily disturbed - Installation success may be affected by sediment type, gravel, cobble or clay-rich can be problematic - The horizontal instrument footprint is relatively large, resulting in lateral spacing of the vertical solute profiles - The vertical solute profile may be disrupted if sampling does not occur at low flow rates - The screening or filter at the base of the drivepoint is prone to clogging - Information on hydraulic gradients can not be determined from these samplers - Although hyporheic fluxes can be estimated, this assumes vertical flow is present, which is not always the case
Diffusive equilibrium in thin-film (DET) gels	Passive	Solute equilibration	0.15-0.3 m	18-20 mm	10 mm (1 mm is theoretically possible)	Integrated over time of diffusive equilibration	At least 72 hours	- The nature of passive sampling prevents disturbance of the vertical solute profile as long as diffusion within the gel is minimal - Quick and easy installation in soft sediments - High vertical resolution - Small horizontal instrument footprint	- Installation is difficult in gravel sediments - No hydrological infromation can be determined from the DET gel - The gel requires installation at least 72 hours ahead of sampling - Vertical diffusion may occur within the gel, which can reduce profile fidelity, both during deployment and after removal - The 40 mm wide plastic frame may alter hyporheic flow

Groups	p-value	d.f.	Test
Nitrate	0.54	2	Kruskal-Wallis rank sum
Ammonium	**<0.01**	2	Kruskal-Wallis rank sum
DET-Minipoint	**<0.01**	-	Dunn Test
DET-Piezometer	**<0.01**	-	Dunn Test
Minipoint-Piezometer	**<0.01**	-	Dunn Test
Nitrate (15 cm)	0.27	2	Kruskal-Wallis rank sum
Ammonium (15 cm)	**<0.01**	2	Kruskal-Wallis rank sum
DET-Minipoint (15 cm)	**<0.01**	-	Dunn Test
DET-Piezometer (15 cm)	**<0.01**	-	Dunn Test
Minipoint-Piezometer (15 cm)	**<0.01**	-	Dunn Test

	Nitrate (mg l^{-1})			Ammonium (mg l^{-1})		
Method	**Mean**	**CV**	**Range**	**Mean**	**CV**	**Range**
Multilevel mini-piezometer	2.53	151.78	15.00	3.83	74.67	11.64
Minipoint Sampler	4.08	135.05	17.62	1.05	188.57	10.02
DET gel	4.02	173.36	34.23	2.32	101.52	10.18

Groups	p-value	d.f.	Test
DET gel v piezometer 2.5 cm	**0.02**	-	Wilcoxon signed rank
DET gel v piezometer 7.5 cm	**0.02**	-	Wilcoxon signed rank
DET gel v piezometer 12.5 cm	**<0.01**	8	Paired t-test

Sampling methodology	Nitrate	Vertical nitrate profile	Ammonium	Vertical ammonium profile	Streambed redox conditions	Applications
Multilevel mini-piezometers	Low	Decrease with depth, although not very pronounced	High	Maxima at 0.2 m	Reduced	- Coarser investigation of exchange processes and biogeochemical activity within the wider streambed - Determination of hydrological characteristics and reaction rates a wide range of depths (up to a few metres) - Investigation of coarser resolution (50 - 100 mm) nutrient and contaminant dynamics throughout the streambed - Detection and investigation of groundwater and associated contaminants
USGS Minipoint Samplers	Low-high	Non-linear decrease with depth	Low with some high	Linear increase with depth	Oxidised	- Fine scale investigation of exchange processes and biogeochemical activity within the hyporheic zone - Determination of hydrological characteristics and reaction rates within the top 0.4 m of the streambed - Investigation of high resolution (10-30 mm) nutrient and contaminant dynamics in the top 0.4 m of the streambed
DET gels	Low with some high	No obvious shape to the profile	Intermediate	No obvious shape to the profile	Reduced with oxic zones	- Fine scale investigation of biogeochemical processes within the hyporheic zone - Investigation of very high resolution (1 mm-10 mm) nutrient and contaminant dynamics in the top 0.15 m of the streambed