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The rivers are alive: on the potential for diatoms as a tracer of water source and hydrological connectivity

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Introduction

Catchment hydrology is a field that is severely measurement-limited. While much progress is being made with new physical measurements—wireless sensor arrays (Estrin *et al.*, 2001), new geophysical approaches (Robinson *et al.*, 2008), new fibre-optic approaches (Selker *et al.*, 2006)—few advances have been made in water tracer studies. Some decades ago, geochemical and isotopic tracers qualitatively changed our understanding of the time- and geographic sources of water at the catchment scale. End-member mixing analysis (Hooper *et al.*, 1990) showed that streamwater could be apportioned into unique water signatures that mapped back to measurable water chemical concentrations in the landscape. Similarly, stable isotope tracing of water showed the importance of groundwater in the storm hydrograph (Sklash and Farvolden, 1979) and the old water paradox of rapid release of stored, old water during rain and snowmelt events (Martinec, 1975). However, since the first use of these tracer approaches, we now know better their limitations and related assumptions—things that have stymied further progress with the techniques: unstable end-member solutions (Elsenbeer *et al.*, 1995; Burns, 2002), temporally varying input concentrations (McDonnell *et al.*, 1990) and need for unrealistic mixing assumptions (McGuire and McDonnell, 2006).

So what are the possible new tracers that may be untapped and able to answer new questions of water source and, increasingly, hydrological connectivity (Bracken and Croke, 2007) between different landscape positions at different time and space scales? We seem to have exhausted the list of isotopes of the water molecule, geochemical constituents picked up along the flowpath and nutrients flushed from the soil profile. Here we ask: what about the mobilization of living organisms in the watershed? Specifically, we explore the possibility of diatoms as tracers during rainfall-runoff events.

What is a Diatom?

Diatoms are unicellular, eukaryotic algae and are one of the most common algal groups in freshwaters as well as in marine ecosystems (Round *et al.*, 1990). They are found in waters worldwide, and their photosynthesis in the sea is estimated to generate about as much organic carbon as all terrestrial rainforests combined (Armburst, 2009). A characteristic feature of diatoms is their highly differentiated cell wall (called frustule), which is heavily impregnated with silica (SiO_2). As suggested by their name (deviated from the Greek 'diatomos', meaning 'cut in half'), the diatom frustules consist of two valves and show an enormous diversity in form. These species-specific cell-wall ornamentations are the diagnostic features of diatoms and form the basis of diatom taxonomy and systematics. Detailed investigation of this siliceous exoskeleton is relatively straightforward with a light microscope and requires a preliminary removal of the protoplasm (e.g. using hydrogen peroxide).

In streams and rivers, diatoms are present in two main ecological niches: the benthos and the plankton. Benthic diatoms can be directly 'attached' to the substratum by one entire surface (type *Cocconeis*), 'stalked' including many species attached to the substratum by a branched or unbranched mucilaginous pedicel (type *Gomphonema*), or 'unattached' like many diatoms (type *Cyclotella* or *Navicula*) with no obvious method of attachment. These 'motile' diatoms, particularly for the biraphid diatom species (Yallop and Kelly, 2006), are adapted to gliding locomotion on the substrate. Planktonic diatoms are free-floating in water. The strongly diversified diatom species distributions are largely controlled by physiogeographical factors, as well as anthropogenic controls, e.g. organic pollution sources, acidification and eutrophication (Dixit *et al.*, 2002; Ector and Rimet, 2005). Diatoms are very sensitive to numerous environmental variables, including light, moisture conditions, temperature, current velocity, salinity, pH, oxygen, inorganic nutrients (carbon, phosphorous, nitrogen, silica), organic carbon and organic nitrogen. As such, they are frequently applied at various spatial and temporal scales to geological, archaeological and water quality research (Van Dam *et al.*, 1994; Stoermer and Smol, 1999). Most species are reported to measure 10–200 μm in their largest dimension (Mann, 2002), which causes them to be easily transported by flowing water and eventually to serve as a tracer in experimental hydrology.

On the Potential for Diatoms as a Tracer of Water Source and Hydrological Connectivity

While diatoms are a ubiquitous component of most aquatic ecosystems, they also occur in moist terrestrial habitats, such as soils, rock surfaces or epiphytes (Hoffmann, 1989; Round *et al.*, 1990; Ettl and Gärtner, 1995). As such, the so-called drift diatoms have the potential to link the terrestrial and aquatic worlds and trace water sources and hydrological connectivity at the watershed scale. Here we present a case for the use of drift diatoms for the identification and understanding of spatial patterns in runoff mechanisms. Our hypothesis is that since hydrological systems largely control species distribution, drift diatoms sampled in the stream during runoff events have the ability to record their geographical origins at the watershed scale. More specifically, we expect drift diatoms to have the potential for providing information on surface runoff processes that could extend considerably the insights given by existing isotope and geochemical tracers. Given that hydrological connectivity between upland, riparian and aquatic zones largely determines the spatio-temporal variability of storm-flow generation in a catchment, certain diatom species could be highly diagnostic of connectivity. Diatoms have their abundance tightly constrained by the moisture conditions prevailing in these terrestrial zones. Their mobilization during surface runoff phases (via saturation excess overland flow or infiltration excess overland flow) constitutes an identification opportunity of both the onset and cessation of these processes as expressed in the stream.

Diatom Proof of Concept

In our previous research in the Attert river basin (310 km^2) in Luxembourg, we have demonstrated that the regional distribution of benthic diatom assemblages found during low flow conditions in the headwater streams is strongly influenced by geology (Rimet *et al.*, 2004; Dohet *et al.*, 2008). Here we present the first data to determine whether drift diatoms might be a possible new tracer for storm-event analysis (in terms of hydrological connectivity and water source identification). We sampled two sub-watersheds of the Attert (Figure 1)—the forested Huewelerbach catchment (2·7 km^2, dominated by sandstone and marls) and the Weierbach catchment (0·45 km^2, dominated by schists). The geology of the Huewelerbach catchment is representative of most right bank tributaries of the Attert river (dominated by sandstone and marls), while the Weierbach catchment is very similar to most left bank tributaries (dominated by schists and sandstone). We located a third sampling point on the main branch of the Attert near the town of Useldange, downstream of the confluences of the tributaries that include the Weierbach and Huewelerbach (Figure 1). At this location the basin covers a total area of 245 km^2, and integrates all typical physiographical features of the region.

Since routine diatom-based bioindicator applications rely almost exclusively on base flow sampling, we have used our pilot data to assess whether drift diatoms can be sampled and identified in sufficient quantities throughout the different stages of a flood hydrograph. Two distinct rainfall–runoff events were investigated between 23 January (rain) and 12 February (rain-on-snow), 2009. We collected samples before the storm, on the early rising limb of the hydrograph and at peak flow. A total of seven water samples were selected and prepared for diatom species identification. Given the fact that the analysis of complex aquatic and terrestrial diatom species assemblages from flood-event samples is highly time consuming at this preliminary stage, the total number of samples was deliberately kept small.

Diatom valves were identified and counted on microscopic slides with a light microscope (Leica DM-RX). Our preliminary investigations presented here rely on the Denys (1991) diatom ecological classification system refined by Van Dam *et al.* (1994). We assume that since the occurrence of diatom species is bound to specific habitat and wetness conditions, such knowledge can be a biorecorder for the

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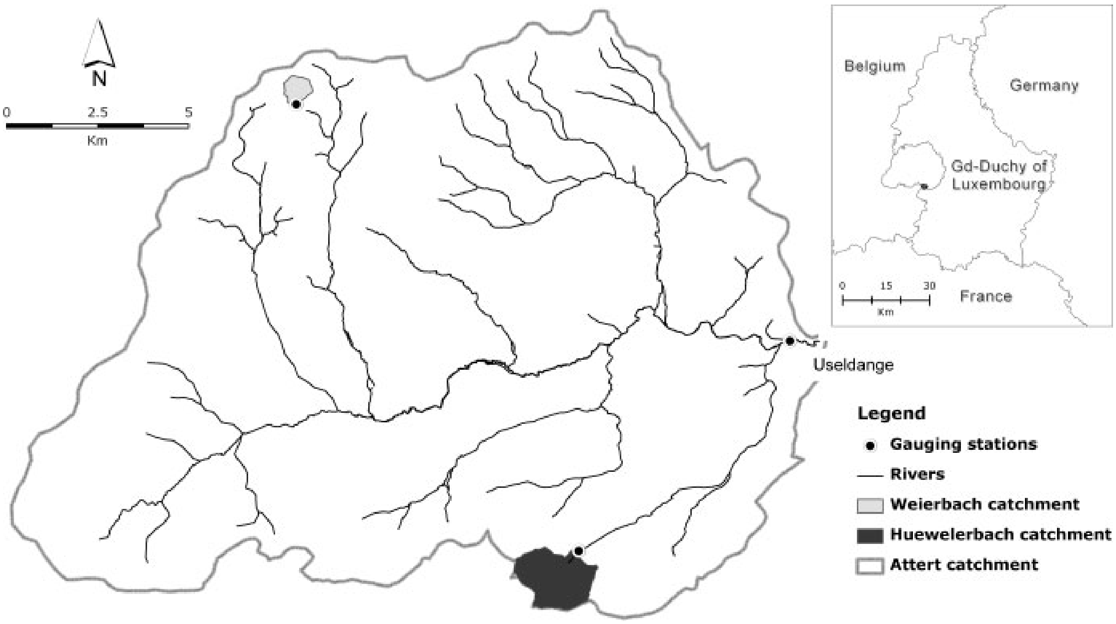

Figure 1. Localization map of the Weierbach, Huewelerbach and Attert catchments

Table I. Classification of the occurrence of diatoms in relation to moisture (Van Dam *et al*., 1994), diatom habitats and hypothesised-related hydrological functional units

Category	Diatom occurrence	Diatom dominant habitat	Hydrological functional unit
1	Never, or only very rarely, occurring outside water bodies	Aquatic	A—Aquatic zone (stream channel)
2	Mainly occurring in water bodies, sometimes on wet places	Aquatic	AR—Aquatic/Riparian transition zone
3	Mainly occurring in water bodies, also rather regularly on wet and moist places	Aquatic	R—Riparian zone
4	Mainly occurring on wet and moist or temporarily dry places	Terrestrial	RU—Riparian/Upland transition zone
5	Nearly exclusively occurring outside water bodies	Terrestrial	U—Upland zone

storm-flow source. The classification system shown in Table I is based on five classes of occurrence, forced by wetness. The classification is reorganized into two habitat categories, namely aquatic and terrestrial, and we attribute the five diatom occurrence classes to five hydrological functional units: A—Aquatic zone, A/R—Aquatic/Riparian transition zone, R—Riparian zone, R/U—Riparian/Upland transition zone, U—Upland zone.

The total drift corresponds to the complete diatom species assemblage determined for each individual streamwater sample. Certain recorded diatom species are not present in the list of Van Dam *et al*. (1994) (designed for fresh and weakly brackish water). Consequently, the sum of the individual percentages of the various categories that we present below (calculated on the basis of the total number of counted valves) is often less than 100%. In all three watersheds, diatom identification and counts revealed enough valves for a representative species classification based on habitats and prevailing wetness conditions (Table II).

Detecting the onset/cessation and geographic origin of surface runoff with diatoms

The onset/cessation of surface runoff with diatoms can be quantified through binary classification of terrestrial and aquatic diatom species. While aquatic species prevail at base flow, the percentage of terrestrial species will gradually increase with the onset of surface runoff connected to the stream. Moreover, the species classification based on their preferred wetness conditions has the potential to identify the geographical sources of surface runoff (i.e. hydrological functional units) that are connected to the stream. The changing percentages of aquatic and terrestrial species in our collected water samples are shown in Table II. The various identified species appear to indicate the geographic origin of runoff, expressed as hydrological functional units of surface runoff connected to the stream.

Base flow velocities in the Weierbach were too low to cause any mobilization of diatoms. Consequently, no drift diatoms were found in the water

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Table II. Relative proportion of diatom taxa (in %) determined for five moisture classes (Van Dam *et al.*, 1994), presumed hydrological functional units (HFUs) (A: Aquatic zone; A/R: Aquatic/Riparian transition zone; R: Riparian zone; RU: Riparian/Upland transition zone; U: Upland zone) and species habitats (Aquatic and Terrestrial) during baseflow and flood peak conditions (Weierbach, Huewelerbach and Attert catchments) in early 2009. Total number of counted valves indicates the number of diatom units identified in the microscopic slides for the calculation of the relative abundance of species

Date	Catchment	Regime	Moisture class - HFU						Habitat		Total N° of counted valves
			1-A %	2-A/R %	3-R %	4-R/U %	5-U %	Not classified %	Aquatic %	Terre-strial %	
23/01/2009		base flow	0	0	0	0	0	0	0	0	2
23/01/2009	Weierbach	rising limb	1	10·1	61·4	12·1	0	15·5	72·5	12·1	207
24/01/2009		flood peak	1·7	1·4	89·5	1·4	0·2	5·7	92·6	1·6	420
23/01/2009	Huewelerbach	base flow	4·7	13	57·3	7·3	0	17·7	75	7·3	192
23/01/2009		flood peak	4	11·9	29·8	23·2	0	31·1	45·7	23·2	151
10/02/2009	Attert	base flow	8	10·4	77·3	1·3	0·3	2·7	95·7	1·6	299
11/02/2009		flood peak	6·1	16·6	56·8	11·8	0	8·8	79·5	11·8	297

samples taken prior to the rainfall event in the Weierbach watershed. In the water sample taken during the rising limb of the flood hydrograph, the total number of counted valves (207) was split into 73% aquatic species and 12% terrestrial species (15% could not be classified). With the onset of rainfall, increasing flow velocities and water levels in the Weierbach progressively mobilized aquatic species (e.g. *Eunotia implicata, E. muscicola* var. *tridentula, E. tenella, Fragilariforma virescens, Karayevia oblongella*). Moreover, the presence of terrestrial species in the Weierbach during the rising limb of the flood hydrograph is a clear indicator of the onset of surface runoff connected to the stream. While the terrestrial species presumably originate from the riparian/upland transition zone, the drift was, not surprisingly, also largely composed of aquatic species (Table II).

In the schistous Weierbach watershed, flood peaks are often delayed by 2 to 3 days due to considerable throughflow via the weathered and fractured bedrock (Krein *et al.*, 2007). At flood peak, the total number of counted valves was 420, of which 93% were aquatic species, mobilized by the higher water levels and flow velocities. Terrestrial species accounted for only 2% of the total number of counted valves at the flood peak, which suggests that surface runoff had either ceased or was no longer connected to the stream at this stage of the flood event. Approximately 5% of the identified species could not be classified.

In the Huewelerbach watershed, the total number of counted valves in the base flow sample was 192, split into 75% aquatic species and 7% terrestrial species (18% could not be classified; Table II). Fed by numerous springs in the sandstone area, the base flow of the Huewelerbach remains remarkably stable throughout the seasons (Krein *et al.*, 2007). Water levels and velocities are sufficiently high to mobilize benthic diatoms even under base flow conditions. The terrestrial species found in the base flow sample presumably originate from a previous rainfall event. At peak flow, the total number of counted valves was 151, split into 46% aquatic species and 23% terrestrial species (31% could not be classified). The strong increase in abundance of terrestrial species indicates the onset of surface runoff connected to the stream during the rainfall event. When used in conjunction with a conventional geochemical hydrograph separation technique, this finding suggests the use of drift diatoms as an independent information source for confirming or rejecting the assumption of the occurrence of surface runoff during a rainfall–runoff event.

The drift detected during low flow in the Huewelerbach watershed was dominated by aquatic diatom species commonly occurring in the phytobenthos of European rivers (e.g. *Achnanthidium minutissimum, Cocconeis euglypta, Navicula tripunctata Planothidium lanceolatum*). During peak flow the drift community changed completely, mobilizing diatoms living on wet and moist or temporarily dry places (e.g. *Hantzschia abundans, Stauroneis thermicola*). These diatoms usually do not inhabit substrates in running waters and their appearance in the drift during the flood peak strongly suggests a connection between the riparian/upland transition zone and the stream during the rainfall event (Table II).

The base flow sample taken in the Attert river revealed 299 counted valves, split into 96% aquatic species and 2% terrestrial species (3% could not be classified; Table II). The dominant drift algae were typical benthic, eutraphentic species commonly occurring in European rivers (*Navicula lanceolata, N. gregaria*). At peak flow, the total number of counted valves was 297, split into 80% aquatic species and 12% terrestrial species (9% could not be classified; Table II). Terrestrial diatom species (*Hantzschia amphyoxis, Luticola mutica, Pinnularia obscura*) were observed in the flood peak drift. The increase in relative abundance of terrestrial species from 2 to 12% between base flow and peak flow indicates the occurrence of surface runoff originating from the riparian/upland transition zone temporarily connected to the stream during rainfall.

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Conclusions

Diatoms are ubiquitous in most aquatic ecosystems and are frequently applied to geological, archaeological and water quality research (Van Dam *et al*., 1994; Stoermer and Smol, 1999). Here, we have explored how drift diatoms have the potential to link the terrestrial and aquatic worlds. Our preliminary results show that diatoms can help detect the onset/cessation of surface runoff connected to the river and are a new way to quantify the geographical sources of surface runoff. This is a new type of information that can be used by hydrologists to confirm or reject the existence of a surface runoff component in total runoff and to constrain assumptions made on a potential surface runoff component in conventional tracer based hydrograph separations. While additional investigations over a longer period and range of events are clearly needed, diatoms appear to be well suited for documenting both the intermittent character of hydrological connectivity between upland, riparian and aquatic zones and the spatio-temporal variability of storm flow generation at the catchment scale.

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