## Understanding the pathways and dynamics of agricultural diffuse pollution from intensively farmed grassland: the application of natural and artificial tracing techniques

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### Introduction

The impacts of diffuse agricultural pollution on river systems arising from the application of slurry and inorganic fertilisers are widely acknowledged. Particulate, colloidal and dissolved phases of slurry may be important sources of organic material and vectors of phosphorus. However, the mobilisation, transport and dynamics of each of these phases have not been quantified. Knowledge of these processes is essential to assess the effectiveness of catchment sensitive farming procedures for slurry application and to support their future refinement (Water Code, 1998). The objectives of this study are to: apply tracers to elucidate the transport of particulate, dissolved and colloidal slurry phases through experimental grassland plots and to consider their significance for phosphorus transport.

### **Experimental design**

Slurry (grass- and maize-derived with artificial fluorescent tracer) was applied, at a rate of 21 m<sup>3</sup> ha<sup>-1</sup>, to four of the 1-ha Rowden experimental platforms (Devon, SW England) in April 2006. Surface and subsurface drainage waters from both drained and undrained grassland plots were sampled prior to slurry application and during subsequent rainfall events. Three novel applications of tracing techniques were used to explore the movement of the various phases of slurry: 1) natural fluorescence (dissolved phase), 2) fluorescent-labelled particles (matched to slurry particulates), and 3) carbon isotopes (dissolved and particulate). The carbon isotopes thus provide an independent assessment of both the natural and artificial fluorescence methods.

**Natural fluorescence** may be used to detect the presence of animal waste in water (Baker, 2002). Technological advances enable fluorescence to be analysed rapidly on small water samples with extreme sensitivity. During analysis fluorescent organic

molecules are excited with UV light (wavelengths 200-400nm). Fluorescent centres in optical space are produced by the molecules emitting energy as they return to their ground state. Distinct fluorophores are produced by aromatic proteins (tryptophan and tyrosine) and high molecular weight organic molecules (humic-like and fulvic-like substances). The relative intensities of these fluorophores will reflect the source of organic matter whereas their absolute intensities will reflect their concentrations (Baker, 2002). Emission-excitation matrices of farm wastes have strong tryptophan-like and tyrosine-like fluorophores indicating the usefulness of the technique for detecting farm waste in water (Baker, 2002). Fluorescence intensity is also influenced by the absorbance of the water samples produced by dissolved organic matter. Absorbance was measured and used to correct the fluorescence data.

Artificial fluorescent particles were used to trace the movement of particulate slurry. The particle size distribution of the slurry was determined and a commonly occurring size thought to be important for phosphorus transport was identified. Fluorescent particles of this size (with a density equivalent to organic matter) were produced. Electrical and chemical properties of the slurry are more difficult to mimichence the importance of any corroborative evidence from the carbon isotope method.

**Naturally occurring carbon isotope (**<sup>13</sup>**C)** tracer may be used to trace organic matter in the fluvial environment. As organic forms of phosphorus are linked to carbon (Bol *et al.*, 2006) slurry derived organic phosphorus may be traced by tracing slurry derived carbon. By applying C<sub>4</sub> plant (maize) derived slurry (enriched in <sup>13</sup>C) to the grassland plots enrichment of <sup>13</sup>C in drainage waters should indicate the presence of the applied slurry (see Granger *et al.*, 2006 for details).

### **Preliminary results**

Results are shown which illustrate the breakthrough of the different phases of slurry over selected hydrological events. A signal consistent with a contribution of the dissolved component of slurry to the drainage waters is illustrated for a small hydrological event in Figure 1. This event was monitored in the subsurface drainage waters of Plot 4 in May 2006. During the first 12 hours of this event both tryptophan-like and tyrosine-like fluorescence increase in intensity over the rising limb of the hydrograph and then flatten off. An important observation is that total dissolved phosphorus (TDP) also increases in concentration for the first 3 hours of this period. This is consistent with the natural fluorescence signal detecting the contribution of the phosphorus rich dissolved phase of slurry. Total phosphorus (TP) tends to increase at a faster rate over the first 12 hours of the event. As suspended sediment concentration (SSC) peaks early in the event the increasing TP may reflect high concentrations of TDP.

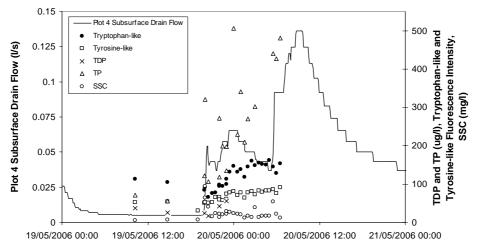


Figure 1. Natural fluorescence, TDP, TP and SSC in subsurface drainage water of Plot 4 during a small flow event, May 2006 (illustrating dissolved phase slurry tracing).

Results from an event simultaneously monitored in subsurface drainage waters of Plot 9 (slurry applied) and Plot 12 (no slurry applied) also illustrates the natural fluorescence signal of a contribution of dissolved phase slurry. Tryptophan-like and Tyrosine-like fluorescence intensities and TDP remain relatively constant preceding and during the event on Plot 12. However, on Plot 9 there is a strong increase in fluorescence and TDP during the event, confirming the results from Plot 4.

The movement of the particulate phase of the slurry was successfully traced using fluorescent-labelled particles. Data collected from the subsurface drainage waters of Plot 9 during a large event in May 2006 are presented in Figure 2. During this flow peak clear responses were observed in fluorescent particle counts and the concentrations of total and volatile suspended solids. It is also significant that TP also shows a similar pattern. Preliminary carbon isotope data also show an enrichment of <sup>13</sup>C during this event which is consistent with a contribution of slurry particles. Furthermore, the corresponding peak in TP during the event suggests that phosphorus-rich slurry particles are being traced. Interpreting data from tracing slurry in surface/interflow drainage waters (0-30 cm) has been more difficult owing to fewer samples of this more episodic and, at low flows, less spatially connected hydrological pathway.

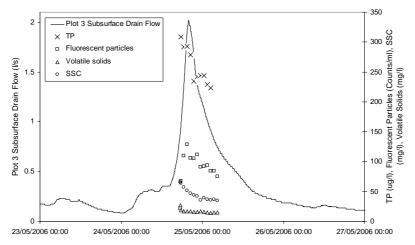


Figure 2. Artificial fluorescent particles, TP, Volatile solids and SSC in subsurface drainage waters of Plot 9 during a large event, May 2006 (illustrating particulate slurry phase tracing).

### Conclusions

The novel tracing applications presented in this paper suggest that dissolved phases of slurry may be successfully traced using natural fluorescence while particulate phases may be traced using artificially labelled fluorescent particles and naturally occurring carbon isotopes. Preliminary carbon isotope data corroborate the results from the artificial fluorescent particle tracing. Isotopic analysis of the dissolved carbon is currently being carried out and will be used to corroborate the signals from natural fluorescence. The close correspondence between TDP and natural fluorescence and TP and the artificial fluorescent particles is consistent with the tracing of phosphorus-rich dissolved and particulate slurry phases. Extension of the tracing methods to provide a quantitative assessment of the contribution of slurry to the quality of drainage waters is currently being investigated.

#### References

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