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Time-integrated sampling of glyphosate in natural waters

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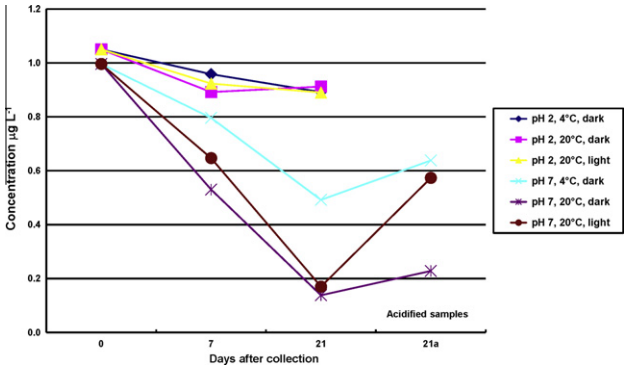
HIGHLIGHTS

- Glyphosate losses are likely in monitoring programs using time-integrated sampling.
- Losses are partly due to degradation, partly to binding to metals or humus.
- Refrigerated time-integrating samplers reduces degradation and increases recovery.
- Acidification during sampling increases recovery by reversing metal and humus binding.
- Labelled surrogate standards are imperative to identify false negatives.

GRAPHICAL ABSTRACT

Glyphosate loss from natural waters.



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ABSTRACT

Environmental monitoring of pesticide residues in surface water is often done with time-integrated sampling where a specified volume is sampled each hour during, e.g., a week, thus avoiding at momentary high or low extreme concentrations. However, sampling over an extended period of time can result in losses of easily degradable analytes, why the stability of the target analytes over the timespan of the sampling must be checked. Glyphosate is one of the most widely used herbicides. Because of its chemical complexity, glyphosate binds differently to metals and colloids at different pH, and the degradation may also be affected. Recovery of glyphosate from spiked natural waters after 1 and 3 weeks of storage was higher when the samples were acidified to approximately pH 2 rather than at their natural pH. Keeping the samples refrigerated to 4 °C in darkness also enhanced recovery, while glyphosate losses were substantial from samples kept at their natural pH at 20 °C. Total loss of glyphosate was observed in some samples kept at natural pH, 20 °C, and daylight; a loss partly due to binding to metals or colloids that could only partially be reversed by acidification. For 1-week time-integrated sampling a small amount of hydrochloric acid in a piece of heat-sealed hydrophobic micro-porous tubing is added to the sampling bottles before deployment, a procedure that acidifies the samples during collection keeping them below pH 2 until analysis, thus minimising losses of glyphosate. The method also allows determination of the primary degradation product aminomethylphosphonic acid (AMPA).

1. Introduction

The Swedish national environmental monitoring programme for pesticides in agricultural areas currently includes some 126 different compounds (Graaf et al., 2010; SLU, 2012a). In addition, various regional or local monitoring programmes essentially include

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the same analytes, but sometimes with less elaborate sampling regimes (SEPA, 2004; Törnquist et al., 2005a,b). Sampling within these monitoring programmes is usually based on 1-week time-integrated sampling, where a specified volume is sampled each hour (SEPA, 2004). Although problems with momentary high or low concentrations at the time of sampling is avoided by time-integrated sampling, it introduces another problem; pesticides may degrade during sampling and transport as more than 1 week will pass between the start of the sampling and the arrival of the sample at the laboratory. Within the national environmental monitoring programme, the samplers are refrigerated so that the samples are kept below +4 °C during the sampling period to minimise analyte degradation, but regional or local monitoring programmes at times use samplers that are not refrigerated (Törnquist et al., 2005a). Irrespective if the individual monitoring programme uses refrigerated samplers or not, transport from the sampling site to the laboratory will take at least 1 d, during which time the sample temperature, in the worst case, may rise to ambient.

Glyphosate [*N*-(phosphonomethyl)glycine] is one of the most widely used herbicides in Sweden, and constitutes 40–45% of the total amount of herbicides sold nationally (KemI, 2010). It is, therefore, an important compound to include in environmental monitoring. However, glyphosate chemistry is complex. The molecule has four ionizable functional groups (Smith et al., 1989), is a zwitterion at the pH of most natural waters (Sheals et al., 2001), and has different propensity for binding to metal ions or colloids at different pH (Subramanian and Hoggard, 1988; Piccolo et al., 1996; Daniele et al., 1997; Sheals, 2002; Barja and dos Santos Afonso, 2005). The whole series of acid dissociation constants includes pK_{a1} 0.8 (1st phosphonic), pK_{a2} 2.3 (carboxylate), pK_{a3} 6.0 (2nd phosphonic), and pK_{a4} 11.0 (amine) (Virtual Museum, 2012). However, the zwitterionic character of glyphosate, where one proton leaves the phosphonic moiety and binds to the amine, makes pK_{a1} difficult to measure (Smith et al., 1989), and most sources (e.g., Bleeke, 1998; Mackay et al., 2006) only give the three acid dissociation constants corresponding to pK_{a2} to pK_{a4} here. Because of complications such as these, predicting how glyphosate will behave in a specific environment is difficult.

The complex chemistry makes glyphosate difficult to include in multi-residue methods, why glyphosate and its primary degradation product aminomethylphosphonic acid (AMPA) are usually determined with a separate method. But AMPA also has other sources than glyphosate degradation (Jaworska et al., 2002; Nowack, 2003). The presence of AMPA without the simultaneous detection of glyphosate, therefore, is an ambiguous indicator of the release of glyphosate into the environment. Hence, the stability of the mother compound during sampling and storage is imperative to draw firm conclusions about residues of glyphosate in the environment. Stability is particularly important in monitoring programmes that use time-integrated sampling; glyphosate should not degrade during the time-span of the sampling or the concentrations will be underestimated.

This paper describes a study of the stability of glyphosate in natural waters during time-integrated sampling based on the sampling and analytical protocol developed for the Swedish national environmental monitoring programme. Based on the stability test, during which light regime, temperature, and pH varied, a method to acidify the samples during time-integrated sampling was developed.

2. Materials and methods

2.1. Chemicals

2.1.1. Standards

Native glyphosate and AMPA, both >99%, and their isotope-labelled analogues (glyphosate-1,2-$^{13}C_2{}^{15}N$, AMPA-$^{13}C^{15}N$) used as surrogate standards were from Dr. Ehrendorfer (Augsburg, Germany).

2.1.2. Other chemicals

Pesticide grade methanol and pesticide grade ethyl acetate were from Labscan (Stillorgan, County Dublin, Eire). Analytical grade hydrochloric acid (HCl), analytical grade sodium hydroxide (NaOH), analytical grade potassium hydroxide (KOH), HPLC-grade water, and analytical grade cotton wool were all from VWR-International (Spånga, Sweden). Trifluoroacetic anhydride (TFAA) and trifluoroethanol (TFE) were from Sigma–Aldrich (Haninge, Sweden). Ethanol (96%) was from Solveco (Rosersberg, Sweden). Ion exchange resin (AG 1-X8 formate form, 100–200 mesh, 1.2 meq mL^{-1}) Bio-Rad Laboratories, Hercules, CA, USA). Isolute C18 solid-phase extraction (SPE) cartridges (3-mL polypropylene reservoir) were from Biotage (Uppsala, Sweden).

2.2. Water samples

2.2.1. Stability test

The design of the stability test was based on a previous exploratory study with water from River Vendelån (60°2.4′N, 17°40.0′E) that runs through an agricultural area north of Uppsala, Sweden (Kreuger, 2003). The larger stability test described here was performed using water from River Stångån (at Vimmerby, 57°37.7′N, 15°51.2′E), River Helge å (at Yngsjö, 55°52.5′N, 14°13.2′E), Lake Havagyl (in Blistorp, at 56°12.5′N, 14°26.7′E), and a groundwater well close to Lake Havagyl. The locations of the different test sites are shown in Fig. 1. The three surface water locations were chosen to be representative of different types of surface water in Sweden. River Stångån is a medium-size river typical for southern Sweden with both forested and agricultural areas in the catchment. River Helge å is a larger river with forest in the upper reaches of the catchment, but the intense agriculture in the lower reaches (where the sample was taken) makes this part of the river rich in nutrients and microbes. Lake Havagyl is a small lake with a little low-intensive pastureland (<5% of the area), but mainly forest and bog in the catchment. The catchment also holds a small disused iron mine and the bedrock is rich in various metals. Due to the low intensity of agriculture with almost no fertilizer use within the catchment, Lake Havagyl has lower levels of nutrients than the two rivers. On the other hand, the metal rich bedrock and high percentage of forest and bog in the catchment leads to higher concentrations

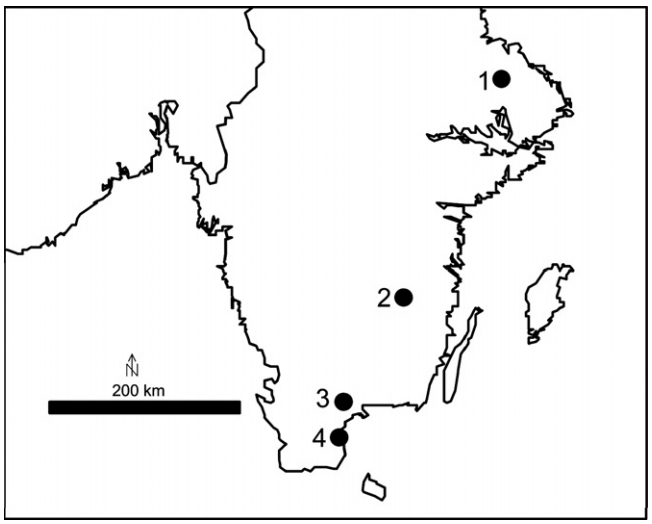

Fig. 1. Sites from which water samples were taken for stability tests. (1) River Vendelån, (2) River Stångån, (3) Lake Havagyl and groundwater Well, (4) River Helge å.