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Glyphosate and AMPA passive sampling in freshwater using a microporous polyethylene diffusion sampler

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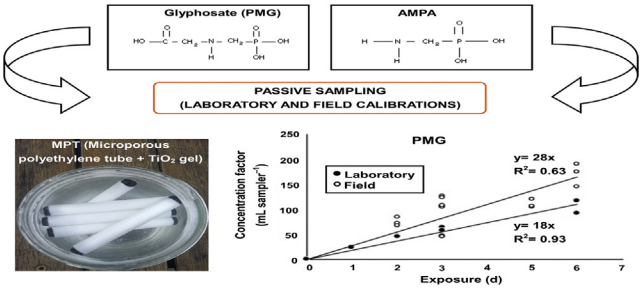
HIGHLIGHTS

- A novel passive sampler based on diffusion through microporous polyethylene was developed.
- A novel passive sampler was adapted for glyphosate and its transformation product AMPA.
- The first in situ application of passive sampler for glyphosate is described.
- The cylindrical geometry of the sampler allows adapting sampling rates.

GRAPHICAL ABSTRACT



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ABSTRACT

Glyphosate (PMG) is one of the most widely used herbicides with a reported 8.6 million tons applied globally in 2016. Due to widespread use and limited understanding of long-term environmental impacts, it is expected that future monitoring requirements for PMG and its primary metabolite aminomethyl phosphonic acid (AMPA) in aquatic environments will increase, along with the need for low cost monitoring and risk assessment strategies. The aim of this study was to investigate a microporous polyethylene tube (MPT; 2-mm thickness, 17.6 cm^2 surface area, 35% porosity, 2.5 μm pore size) as a diffusive layer for the passive sampling of PMG and AMPA. Levels of PMG and AMPA sorbed to MPT were low (K_{mw} close to 1 mL g^{-1}), validating MPT as a diffusive layer. Uptake experiments were conducted first under controlled laboratory conditions (pH = 6.8, 6 days), followed by an in situ freshwater lake system deployment (pH = 7.3, 11 days). PMG and AMPA accumulated linearly (slope relative standard deviation < 6%) under laboratory conditions with sampling rates (R_s) of 18 and 25 mL d^{-1}, respectively. PMG in situ R_s was 28 mL d^{-1}, and was not different from the one found in the laboratory. AMPA was below the limit of quantification (LOQ, 1 ng mL^{-1}) in grab water samples, but was detected (>LOQ) in all passive samplers. Results illustrate the gain in sensitivity provided by the passive sampling technique, and the applicability of the device developed for the passive sampling of PMG and AMPA.

1. Introduction

Glyphosate (*N*-phosphonomethyl glycine, i.e. PMG) is the active

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substance of more than 750 commercial formulations (i.e., glyphosate-based herbicides, GBHs) and the most widely used herbicide for agricultural and non-crop uses, both in Australia (15,000 tons y^{-1}) and worldwide (826,000 tons y^{-1}) (Benbrook, 2016). The primary breakdown pathway of this polar (log K_{ow} = −4.59 to −1.70) and ionic (zwitterion at all pH) organic compound is through microbial degradation, resulting in the production of aminomethyl phosphonic acid, i.e. AMPA (Annett et al., 2014). After spraying onto land of GBHs, the leaching of PMG and AMPA and consequent transport into waterways will depend on application rates, soil properties and rainfall (Borggaard and Gimsing, 2008). Another crucial parameter affecting PMG transport, degradation and availability is the formation of complexes with natural occurring metal cations (Magbanua et al., 2013; Shushkova et al., 2010; Zhou et al., 2013). However, due to the high solubility of PMG (10.1–15.7 g L^{-1} at 25 °C) and AMPA (5.8 g L^{-1} at 25 °C) in water, they are typically mobile and are usually found together in most water bodies (Annett et al., 2014; Aparicio et al., 2013; Battaglin et al., 2014; Comoretto et al., 2007; Coupe et al., 2012; Mercurio et al., 2014; Stewart et al., 2014).

PMG and AMPA present complex chemical properties (i.e., high water solubility, poor solubility in organic solvents, high complexation capacity) which complicate their extraction and analysis in water at environmental trace levels. Accordingly, a derivatization step is needed to increase the selectivity and sensitivity of the analysis (Arkan and Molnár-Perl, 2015; Dong et al., 2015). Thus, PMG and AMPA are often not included in routine monitoring programs, as they require specialized analysis which increases the costs of monitoring programs, although PMG and AMPA are prioritized by the European network Norman (www.normandata.eu). Otherwise, these substances were recently the subject of a considerable debate concerning their carcinogenic effect on human health (Portier et al., 2016). Due to limited knowledge of the effects of chronic exposure to low levels of PMG and AMPA (i.e., low ng L^{-1} range in aquatic systems), it is expected that future monitoring requirements for these compounds in aquatic environments will increase, along with the need for reliable, highly-sensitive and low-cost monitoring techniques. Passive sampling may address these three fundamental requirements.

Since their development in the early 2000's (Alvarez et al., 2004; Kingston et al., 2000), passive sampling techniques of polar compounds (i.e., the Polar Organic Chemical Integrative Sampler (POCIS) and Chemcatchers) have been successfully used for the measurement of a wide range of organic compounds in aquatic systems. Subsequently, passive sampling methods were adapted for the monitoring of ionizable organic compounds in water systems (Fauvelle et al., 2014, 2012, Kaserzon et al., 2014, 2012; Li et al., 2011). Aiming to target PMG and AMPA, a previous study adapted the Diffusive Gradient in Thin-film (DGT) passive sampling technique with a TiO_2 receiving phase (Fauvelle et al., 2015), while another adapted the POCIS design using molecularly imprinted polymer (MIP) as a receiving phase (Berho et al., 2017). Both TiO_2 and MIP sorption phases successfully accumulated these analytes. However, limitations of the developed sampling tools include:

i) the low sampling rates (R_s) achieved for PMG and AMPA with the DGT based sampler, i.e. around 10 mL day^{-1} (Fauvelle et al., 2015), which affects the sensitivity and applicability of the sampler under environmental conditions
ii) the dependency of the analytes flux and sampling rates on the external water velocity (i.e., water boundary layer thickness; WBL) with the POCIS based sampler, which can increase the uncertainty of water concentration estimates (Berho et al., 2017; Fauvelle et al., 2017)
iii) the absence of in situ testing of the devices developed

A higher R_s (Eq. (1)) can be obtained by increasing the product of the exposure surface area of the sampler (A) and the overall mass transfer coefficient (k_o):

$$R_s = A \times k_o \quad (1)$$

k_o (Eq. (2)) is dependent on the MTCs (mass transfer coefficients) of each successive compartment of the sampler (Booij et al., 2017), as evidenced by the expression of the resistance to mass transfer ($1/k_o$):

$$\frac{1}{k_o} = \frac{1}{k_w} + \frac{1}{K_{mw}k_m} + \frac{1}{K_{sw}k_s} \quad (2)$$

where k_w, k_m, k_s are the MTC for the WBL, the membrane (microporous polyethylene tube in our case, MPT), and the sorbent respectively, and K_{mw}, K_{sw} are the sorption coefficients of the membrane and the sorbent. When $K_{mw} = 1$, and transport through the membrane (MPT) is only via the pore space (i.e., filled with water), Eq. (2) becomes (Fauvelle et al., 2017):

$$\frac{1}{k_o} = \frac{\delta}{D_w} + \frac{d\theta^2}{\phi D_w} + \frac{1}{K_{sw}k_s} \quad (3)$$

where δ and d are WBL and membrane thicknesses, D_w is the contaminant diffusion coefficient in water, θ is the tortuosity, and ϕ is the membrane porosity.

Otherwise, a promising way to limit the influence of WBL thickness can be found in increasing the second term of Eq. (3), e.g. increasing d (Belles et al., 2017; Chen et al., 2013; Fauvelle et al., 2017).

In the present study, we propose to assess MPT (d = 2 mm thick, A = 17.6 cm^2, ϕ = 35% porosity, 2.5 μm pore size) as a diffusion barrier filled with a receiving phase consisting of TiO_2 particles embedded in an agarose gel. Compared to the conventional DGT, A is increased from 3.14 to 17.6 cm^2 (factor of 5.6), d is increased from 0.8 to 2 mm (factor of 2.5), ϕ is decreased from almost 100% to 35% (factor of 3), and θ^2 could also be decreased from 3 to 1. Indeed, θ^2 is supposed to be much higher in a gel than in MPT, as Belles et al. observed lower (factor of 3 to factor of 9) diffusion coefficients for polar organic substances in hydrogels than in water (Belles et al., 2017). Therefore, in light of Eq. (3), MPT could increase R_s by a factor of 2, and as R_s is proportional to A, increasing MPT length will increase R_s accordingly, when required. Otherwise, resistance to mass transfer induced by MPT should be 4 times higher than the one induced by the WBL, considering a worst case δ value of 1.50 ± 0.013 mm in an unstirred medium (Warnken et al., 2006; with d = 2 mm, θ^2 = 1, ϕ = 35%), suggesting a full MPT control (i.e., low dependency on flowing conditions) of the diffusion of PMG and AMPA across the sampler.

The objectives of this study were i) to determine K_{mw} for PMG and AMPA to ensure their transport is occurring only via the pore space and to avoid any interferences during the sampling, ii) to verify that MPT is the compartment of the sampler providing the higher resistance to mass transfer, and iii) to evaluate the performances of the sampler in situ.

2. Experimental section

2.1. Chemicals and reagents

Acetonitrile (ACN), methanol (MeOH) and dichloromethane (DCM) were purchased from Merck (Darmstadt, Germany) and their purity were higher than 99.8%. Trimethylamine (TEA) was obtained from Atifina Chemicals Inc. (USA) and its purity was 99.5%.