Analysis of AMPA, Glyphosate and Glufosinate in environmental water using direct injection

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INTRODUCTION

Routine analysis of anionic polar pesticides has become a requirement for many environmental laboratories. Monitoring these highly polar, small molecules such as glyphosate, AMPA and glufosinate in environmental water from diverse sources presents a significant challenge. Accurate and reliable methods are required to monitor water samples for compliance with regulatory limits and to gain a more complete understanding of the presence of these compounds in the environment and in drinking water. Over the years, this would often be analysed by the time consuming FMOC derivatization method with high or mid Tier quadrupole MS systems. With current EU regulatory limits (ng/l) in mind, with the introduction of a high sensitivity mass spectrometry system and dedicated Waters Anionic Polar Pesticides Column (APP) (p/n: 186009287), the development of a direct injection method was introduced for the analysis of several anionic polar pesticides. Waters has published several application notes in the area of anionic polar pesticides analysis and focusing on resolution, retention and quantification with the APP column, solving several of the most critical challenges associated with this application.

SAMPLE PREPARATION AND SAMPLE ORIGIN

No sample preparation was needed for tap water, however centrifugation and sample filtration (through 0.2 µm PVDF filters) was performed on environmental water samples. Labeled internal standards for AMPA, Glufosinate and Glyphosate were used at a concentration of 100 ng/L .

To evaluate the performance of the method, tap water and surface water samples were taken throughout the UK. Groundwater and surface water samples from Germany were kindly provided by the Department of Analytical Chemistry of Helmholtz Centre for Environmental Research – UFZ.

Recommendations,

- Use of EDTA as an additive in samples and calibration standards (approx.: 0.25 mM)
- Use of Isotopically labelled standards

METHOD DETAILS

LC	ACQUITY™ UPLC™ I-Class FTN System
MS	Xevo™ TQ Absolute Mass spectrometry
Column	Anionic Polar Pesticides Column (2.1 x 100 mm, 5µm) p/n: 186009287
Mobile Phase	0.9% formic acid in water and 0.9% formic acid in Acetonitrile
Injection Volume	50 µL
Run Time	15 min

LINEARITY

The linearity of the three analytes was determined using bracketed calibration curves in tap water. Excellent performance was demonstrated over the range of 5 to 100 ng/L for all three analytes, where residuals were < ±15 % and correlation coefficient (R^2) higher than 0.995 (Figure 1).

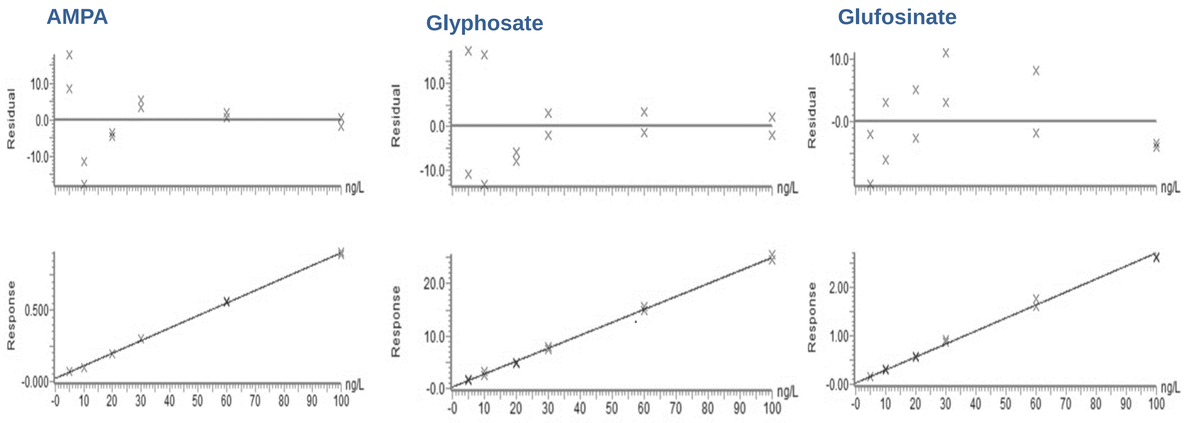

Figure 1: AMPA, Glyphosate, Glufosinate calibration curves in tap water

SENSITIVITY

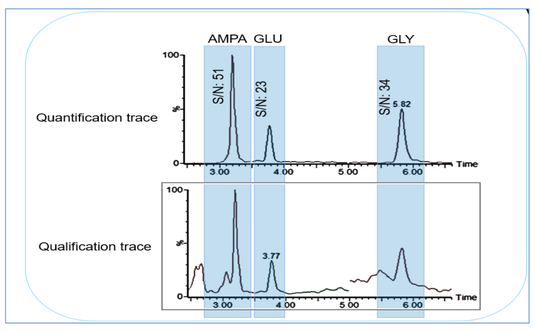

Figure 2: Quantification and qualification traces for AMPA, Glufosinate and Glyphosate in tap water

Sensitivity for AMPA, Glufosinate and Glyphosate was investigated by the calculation of the peak to peak (PtP) signal to noise (S/N) value for the lowest standard at **5 ng/L**. Figure 2 shows S/N values above 23 for all three analytes, thereby suggesting a limit of quantification (LOQ, S/N = 10) below 5ng/L and demonstrating the excelled sensitivity of the Xevo TQ Absolute MS for these polar pesticides.

INTERDAY & INTRADAY SAMPLE ANALYSIS

Two interday batches and one intraday batch were analyzed to evaluate the trueness and repeatability at various concentration levels for AMPA, Glyphosate and Glufosinate in tap water. In total, 110 injections were performed. The two interday batches were run on two consecutive days and consisted of replicate injections (n=11) of low (20 ng/L) and high (60 ng/L) level spiked tap water samples including bracketed calibration curves. For the intraday batch, repeated injections (n=30) of a 60 ng/L spiked tap water sample were performed in combination with bracketed calibration curves. Interday results are summarized in figure 3, where excellent repeatability was observed, demonstrated by trueness values between 93 and 105% and RSD values below 10% for all analytes. Figure 4 illustrates similar results for the intraday data, including trueness varying between 98 and 107% and RSD values below 11% for all three compounds.

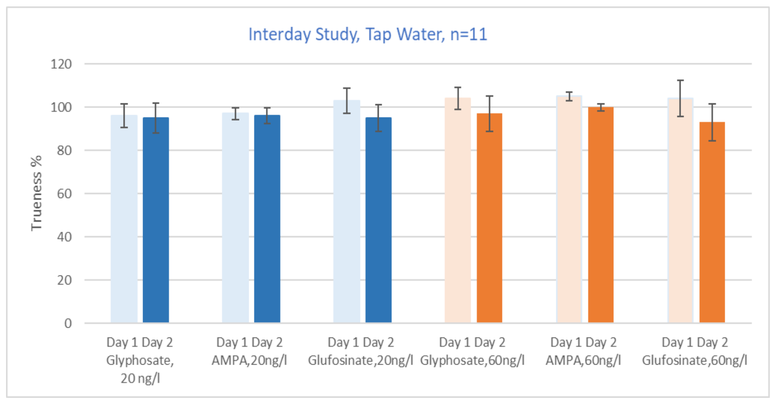

Figure 3: Interday study in tap water, Trueness (%) in Glyphosate, AMPA, Glufosinate spiked at 20 and 60 ng/l.

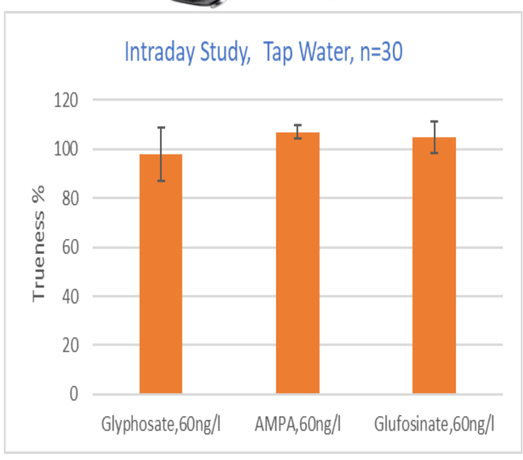

Figure 4: Intraday study in tap water, Trueness (%) in Glyphosate, AMPA, Glufosinate spiked at 60ng/l

ENVIRONMENTAL SAMPLES QUANTIFICATION

Various environmental water samples were collected from the UK and Germany including ground, surface and tap (soft/hard) water. Samples were spiked at 20 and 60 ng/L and quantified using a calibration curve in tap water in combination with the use of labeled internal standards. Figures 5,6,7, demonstrate accurate quantification of all analytes in all samples. The calculated trueness is summarized for the various environmental samples. For AMPA and Glyphosate trueness varied between 92 and 105%, whereas for Glufosinate slightly higher values were reported between 99 and 126%.

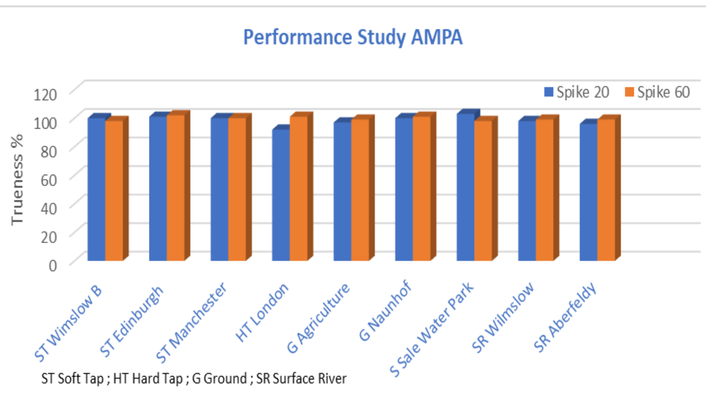

Figure 5 : Performance study AMPA, Trueness (%) in various water samples

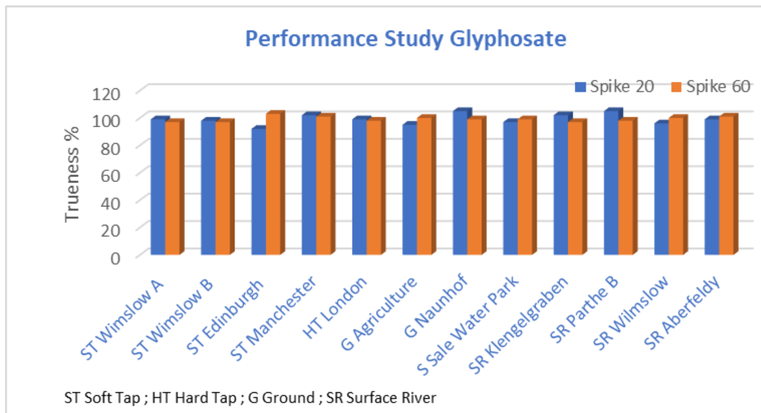

Figure 6 : Performance study Glyphosate, Trueness (%) in various water samples

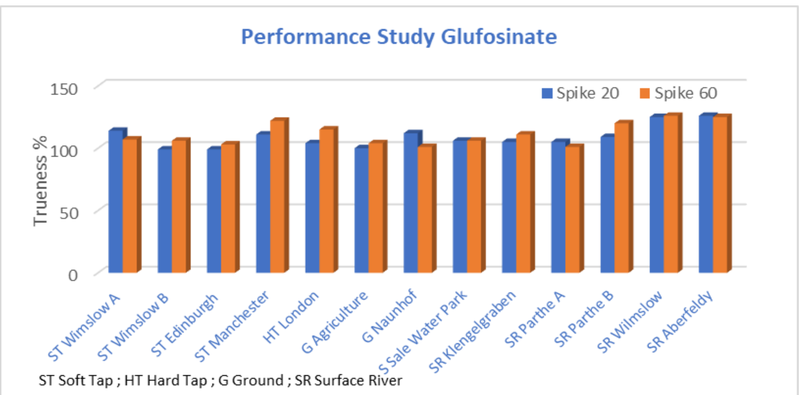

Figure 7 : Performance study Glufosinate, Trueness (%) in various water samples

QUANTIFICATION OF SURFACES WATER SAMPLES WITH INCURRED RESIDUES

For AMPA and Glyphosate, some water samples had high levels of incurred residues, therefore those samples were excluded from the bar chart and quantified using external calibration (Figure 8) and standard addition (Figure 9) functionality in TargetLynx™ application manager.

Matrix: River water | Type: Surface water | Concentration: 20 ng/L

Glyphosate results - Standard addition

Sample Type	Conc (ng/L)
Surface River Parthe A	4.02

AMPA results – external calibration

Sample Type	Conc (ng/L)
Surface River Klengelgraben	62.1
Surface River Parthe A	12.9
Surface River Parthe B	70.2

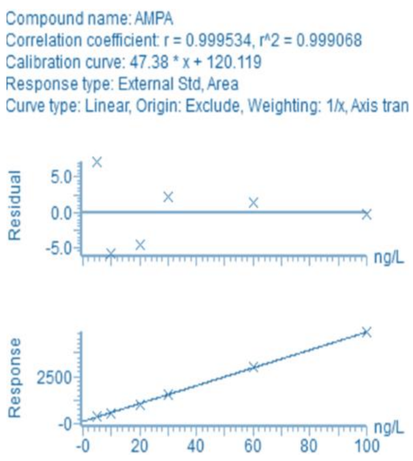

Figure 8 : AMPA external calibration curve

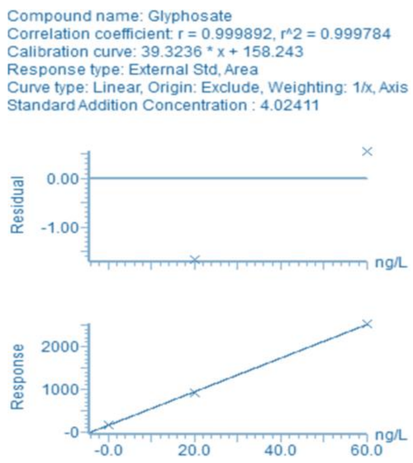

Figure 9 : Glyphosate standard addition curve

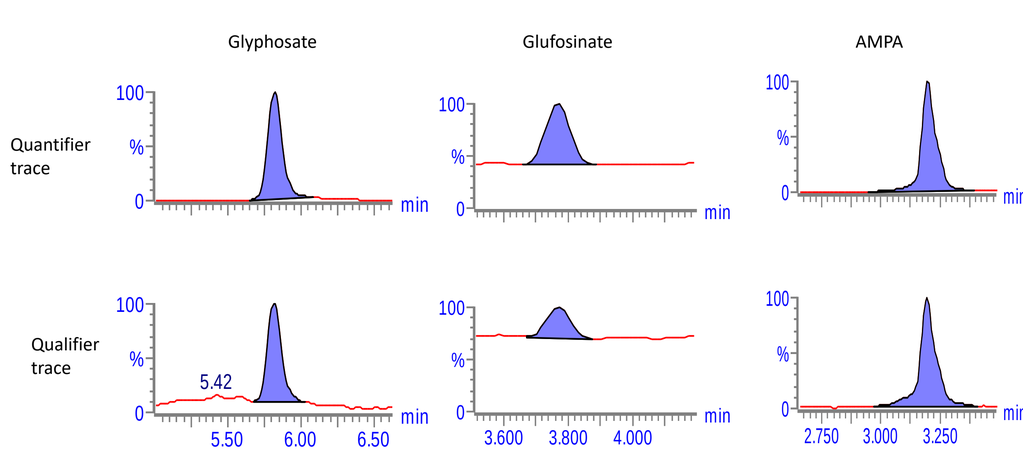

Figure 10 : Example chromatography of river water at 20 ng/L

CONCLUSION

Expanding on the established LC-MS/MS method for polar pesticides analysis in food, the APP column has demonstrated excellent performance for the routine analysis of polar pesticides in drinking and environmental waters.

Key benefits include:

- Improved chromatographic performance for AMPA, Glyphosate and Glufosinate using a direct injection method without the need for derivatization.
- Excelled sensitivity using our newest high end tandem quadrupole mass spectrometry, the Xevo TQ Absolute MS with LOQs below 5 ng/L for all analytes in tap water.
- Linear calibration curves achieved within the range of 5 to 100 ng/L (R^2 > 0.995, residuals < 15%)
- Repeatable quantitative analysis, with trueness between 93 and 107% and RSDs below 11% for interday (n=11) and intraday (n=30) studies achieved at 20 and 60 ng/L in tap water.
- Analytes accurately quantified in various tap, ground and surface water samples, demonstrated by trueness between 92 and 126% for 20 and 60 ng/L spiking levels.