New dispersive solid phase extraction sorbent of graphitic carbon nitride for field evaluation and dissipation kinetics of pesticides in wheat ecosystem by liquid chromatography tandem mass spectrometry

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ABSTRACT
Nanosheets of graphitic carbon nitride (GCN) were used as the dispersive solid-phase extraction (d-SPE) sorbent for the first time. GCN successfully purified complex matrices of soil, wheat, and wheat straw utilising a simple QuEChERS (quick, easy, cheap, effective, rugged, and safe) method with liquid chromatography tandem mass spectrometry. Pesticides recoveries in the range of 80–110%, small matrix effect, and decreased amounts guaranteed and distinguished this new sorbent. The application of a real formulation of pesticides under field conditions during 2015 in the wheat ecosystem illustrated the clean-up effect and application potential of GCN. It is a valuable and potential substitute for C18 according to the results comparison between two sorbents, including recoveries, matrix-matched calibration, and dissipation kinetics of pesticides. The new use of GCN also enriched the knowledge of d-SPE and sample preparation furthermore.

1. Introduction
Nanosheets obtained by the delamination of layered compounds have been recognised as a novel class of nanostructured materials due to their unique structural feature of ultimate two-dimensional anisotropy with extremely small thickness in nanometer and even subnanometer scale [1–4]. Due to the quantum confinement effects, new physicochemical properties of nanosheets have emerged, leading the application into optoelectronics, spintronics, catalysts, chemical and biological sensors, supercapacitors, solar cells, and lithium ion batteries [5]. As for photocatalysts, for example, nanosheets promote photocatalysis efficiency dramatically due to larger bandgap produced by shifting conduction and valence bands in opposite directions [6,7]. Besides, its large specific surface area can provide abundant reaction sites as well as small bulk diffusion, contributing to a stronger redox ability [5].
Graphitic carbon nitride (GCN) with a layered structure has the potential of forming graphene-like nanosheets with unusual physicochemical properties due to weak Van der Waals force between layers. There are strong covalent C–N bonds instead of C–C bonds in each layer. Its planar, two-dimensional structure is desirable compared with both a three-dimensional and liner and one-dimensional backbone considering for example the quantum confinement effect and optoelectric properties. The tri-s-triazine ring structures (Figure S1) give it practical chemical inertness, extraordinary electronic structure, and surface basicity [8]. Thus, it has been used in the energy, catalysis, and environmental fields, such as water splitting [9,10], oxygen-reduction reactions [11,12], selective hydro-carbon oxidation [13], carbon dioxide activation [14], and pollutant control [15].

Solid-phase extraction (SPE) has been widely applied as sample preparation technology nowadays. New methods, sorbents, miniaturisation, and automation based on SPE have been developing to achieve higher efficiency and higher selectivity [16]. GCN has been used in SPE to determine benzoylurea pesticides [17]. However, the immobilisation of the sorbent with a cartridge needs relatively large sorbent amounts and sample volumes and thus increases its cost and limits its application. Thus, dispersive-SPE (d-SPE) has emerged as a valuable alternative SPE technology because the sorbent is dispersed in a sample solution and separated from the latter after extraction [18]. Due to the increased active contact area between the analytes and the dispersed sorbents, efficiency of d-SPE is high and thus the extraction time is dramatically reduced compared with the conventional catridge-based SPE [19]. Meantime, the relatively small sorbent amount also reduces the cost. Besides, the circumvented immobilisation of sorbents distinguished d-SPE most for the possibility to use in-house prepared sorbents to expand the d-SPE application.

As an independent sample preparation, d-SPE has been used in analysis of a wide range of analytes, such as UV filters [19], pharmaceuticals [20], food additives [21], and so on, in various aqueous samples including water [22,23], urine [21], and blood [20]. On the other hand, d-SPE is also a part of QuEChERS (quick, easy, cheap, effective, rugged, and safe) method which involves the salting-out extraction and d-SPE clean-up [18]. For the advantages of safety, simplicity, affordability, effectiveness, efficiency, and dependability of results, QuEChERS which was introduced in 2003 has been widely used as pesticide multi-residue method by many governments, organisations, and laboratories, especially in vegetables, fruits, and many other matrices [24–27], including milk [28], water [29], and so on. Due to perfect amenability to liquid chromatography–mass spectrometry (LC–MS), it has also been used for the determination of mycotoxins [30], polycyclic aromatic hydrocarbons [31], and pharmaceuticals and personal care products [32] in different matrices.

In d-SPE, primary secondary amine (PSA) is the frequently used d-SPE sorbent, which can remove various polar organic acids, polar pigments, some sugars, and fatty acids. C18 or graphitised carbon black (GCB) has also been used in modified QuEChERS to remove lipids, pigments, and so on. New d-SPE sorbents, such as chitin [33], graphene [34], amine-modified graphene [35], magnetic GCB [36], multiwalled carbon nanotubes [37,38], supel QuE Z-Sep (+) [39], and chitosan [40], have been used to improve recoveries for specific types of analytes or matrices.

Pesticides, more specifically herbicides, are widely used to increase cropping intensity and yield by controlling weeds. Due to their inherent toxicity and the
potential misuse against good agriculture practice, herbicides are likely to jeopardise not only environment but also human health [41]. Thus, the dissipation information is essential for calculating both the residue concentration and the half-life which represents environmental persistence, food safety, and potential health risk of herbicides on target plants, especially those widely consumed and cultivated, such as wheat [41].

In this study, nanosheets of GCN were synthesised and utilised as a new d-SPE sorbent. Its clean-up effect was verified by analysing pesticides, more specifically, herbicides, in soil, wheat grain, and wheat straw by a simple LC–MS method with modified QuEChERS sample preparation. Field experiments with the application of a real formulation of a water dispersible granule (WDG) at Beijing, China, in the year of 2015 were carried out to simulate dissipation kinetics in the real world. Herbicides including their metabolites such as florasulam (PubChem CID: 11700495), carfentrazone-ethyl (PubChem CID: 86222), fluroxypyr (PubChem CID: 50465), and fluroxypyr-meptyl (PubChem CID: 54745) were selected as targets. Particular attention was devoted to the recoveries to demonstrate GCN’s robustness as sorbents. The results using the new sorbent were compared with those with the C18 sorbent.

2. Experimental

2.1. Chemicals

Four standards from commercial sources were used: florasulam (98.5%) from Jiangsu Agrochem Laboratory (Jiangsu, China), carfentrazone-ethyl (92.0%) from Beijing KeFaWeiYe Co. Ltd. (Beijing, China), fluroxypyr-meptyl (99.7%) from National Institute of Metrology China (Beijing, China), and fluroxypyr (97.0%) from Agro-Environmental Protection Institute Ministry of Agriculture (Tianjing, China). Dicyandiamide (99%) was purchased from Aldrich (St. Louis, MO). Acetonitrile and formic acid from Fisher Scientific (Far Lawn, New Jersey) were of LC grade. Anhydrous magnesium sulphate (MgSO₄), sodium chloride (NaCl), and acetic acid of analytical grade were purchased from Beijing Chemical Reagents Company (Beijing, China). C18 (50 μm, 60 Å) and GCB (120–400 mesh) were purchased from Agela Technologies (Tianjing, China). The WDG of 26% florasulam-carfentrazone-ethyl-fluroxypyr-meptyl (Shandong Dehao Chemical Science Co. Ltd) was tested to investigate their dissipation and terminal residues. The recommended dosage was 58.5–97.5 g active ingredient per hectare.

2.2. Synthesis and characterisation of GCN

GCN was synthesised according to a procedure described by Niu et al. [42]. Bulk GCN has been synthesised by heating dicyandiamide at 550°C for 4 h in static air with a ramp rate of 2.3°C/min. The cooling rate was kept at around 1°C/min. The resultant yellow agglomerates were milled into powder in a motor. The nanosheets were prepared by thermal oxidation etching of the bulk GCN by heating at 500°C for 2 h with a ramp rate of 5°C/min. A light yellow powder of GCN nanosheets was finally
obtained. The surface morphology by scanning electron spectroscopy was shown in Figure 1.

2.3. Solution preparation
The stock solutions were prepared separately by dissolving 10 mg standards in acetonitrile into a 10-mL volumetric flask. The stock solutions were mixed and diluted with acetonitrile to obtain tested standard solutions for spiking and calibration. All standard solutions were freshly prepared, filtered through 0.22-μm membrane filters, and kept in the dark at 4°C.

2.4. Field trials
The field trials including the dissipation and residue experiments were carried out in Beijing, China (116.46°E, 39.92°N), in 2015 according to NY/T 788-2004 (Guideline on pesticide residue trials issued by Ministry of Agriculture PR China). The application time of the WDG was one. The characteristic properties of the sandy brown soil used in the field were as follows: organic matter of 2.7%, pH 6.73 and cation exchange capacity of 29.7 cmol/kg. During the experimental period, the average temperature was 21°C and there were four rainfall events. The untreated plots were sprayed with water as control. Each experiment plot was 30 m². A buffer zone was adopted between the plots of different treatments.

The dissipation experiments of soil and straw were carried out on different plots with 1.5 times of the recommended dosage, by spraying on bare soil and the surface of plants, separately. The terminal residue experiments in different matrices including soil, wheat

Figure 1. Characterisation of synthesised graphitic carbon nitride by scanning electron spectroscopy.
grain, and wheat straw were conducted at the recommended dosage and the one of 1.5 times, separately. Each treatment was carried out in triplicate. Representative samples (2 kg straw, 2 kg grain, and 1 kg soil) were randomly collected on the day of application and then at day 1, 3, 5, 7, 10, 14, 21, and 30 as well as at harvest time (53 days after application). Soil was randomly sampled from 0 to 10 cm in each plot using a soil sample drill (30 cm height x 40 mm id). All samples were stored in dark at −20°C for further analysis.

2.5. Sample preparation by modified QuEChERS

Homogenised soil (5 g), wheat (5 g), and wheat straw (2 g) were weighed into a 50-mL Teflon centrifuge tube, separately. For soil samples as an example, they were ultrasonically extracted for 15 min with a mixture of 10 mL acetonitrile, 100 μL acetic acid, and 2 mL water. Anhydrous NaCl (1 g) and anhydrous MgSO₄ (2 g) were added and vortexed vigorously for 1 min. Following centrifugation at 1600 relative centrifugal force (rcf) for 3 min, 1 mL of the supernatant was transferred into a 2.0-mL centrifuge tube containing 200 mg MgSO₄ and 10 mg GCN. The mixture was then shaken vigorously for 1 min and centrifuged for 3 min at 1400 rcf. Finally, the acetonitrile layer was filtered through a 0.22-μm membrane filter for injection.

Straw samples were amended with 1 mL of water. Moreover, different contents of GCB were tested for different matrices to obtain satisfactory clean-up as follows: 0 mg for soil, 5 mg for wheat, and 10 mg for wheat straw.

2.6. Apparatus and conditions

All experiments were performed with Agilent 1260 infinity LC system (Agilent Technologies, CA, USA) with a Zorbax SB-C18 column (Agilent Technologies) (50 mm x 2.1 mm id, 1.8 μm). Compounds were separated with a mobile phase consisting of 0.1% aqueous formic acid (v:v) and acetonitrile. The gradient run consisted of 10% acetonitrile (v:v) applied at a flow rate of 0.4 mL/min, which was then increased to 80% after 1 min, and 100% after 2 min, and decreased to 10% after 6 min. The injection volume for all samples was 5 μL and the column temperature was 30°C.

The LC system was coupled on-line to Agilent 6420 Triple Quadrupole mass spectrometer (Agilent Technologies) equipped with an electrospray ionisation source. The MS operating conditions were optimised as follows: positive electrospray voltage, 4000 V; nebuliser pressure, 55 psi; drying gas (N₂) flow rate, 10.0 L/min; and dry gas temperature, 325°C. MS experiments were performed in selected reaction monitoring mode using optimised Q1/Q3 (m/z) values for the particular compound, for example 360.1/129.1 for florasulam; 412.1/346.1 for carfentrazone-ethyl; 367.0/254.9 for fluoroxypr-mepyl; 255.1/209.0 for fluoroxypr.

2.7. Calculations

Masshunter software version B.06.00 (Agilent Technologies) was used. Excel (Microsoft Corporation) was used for detailed calculation.
3. Results and discussion

3.1. Optimisation of QuEChERS sample preparation with GCN

In our previous work [43], a QuEChERS LC–MS method with C18 as the d-SPE sorbent has been established for these four herbicides in soil, wheat grain, and wheat straw. Based on this, the experimental conditions with GCN as the d-SPE sorbent were further optimised by investigating the effects of main parameters.

The first extraction step also adopted acetonitrile which guaranteed satisfactory recoveries. The modified acetic acid over the range of 0–2% (v:v) was optimised. For soil samples as an example, the influence of the amount of acetic acid was demonstrated by the change of the peak areas of four herbicides (Figure 2). The amount of acetic acid didn’t have a significant effect on the extraction of four herbicides, for there was no significant change of peak areas. Thus, considering the method sensitivity and the practical comparison with our previous method, 1.0% acetic acid was selected. Besides, 2 g MgSO$_4$ and 1 g NaCl were used in the extraction to induce the phase separation. Additional water was added to dewatered samples to obtain necessary moisture. For soil and wheat, 2 mL of water was added, while 1 mL of water was added to straw samples because of the relatively higher water content.

d-SPE sorbent types and amount significantly affect the clean-up effect by retaining matrix components and allowing the analytes of interest into the acetonitrile phase. As nanosheets, large specific surface areas of GCN will facilitate the clean-up effect of d-SPE. The effect of amount of GCN was investigated from 5 to 50 mg as shown in Figure 2. For

![Figure 2](image-url)

**Figure 2.** Effects of different conditions on sample preparation: (a) effect of amount of acetic acid on soil extraction with graphitic carbon nitride (GCN); (b) effect of amount of GCN on soil clean-up; (c) effect of amount of GCN on plant clean-up; and (d) clean-up effects comparison of C18 and GCN. See Section 2 for conditions.
all pesticides in soil, 10 mg GCN led to relatively higher peak area when the amount of GCN increased from 5 to 50 mg. For all pesticides in straw, the increase of GCN from 5 to 50 mg didn’t lead to significant change of the peak area. Besides, GCB was also added assistantly (e.g., 0, 5, and 10 mg for soil, wheat grain, and wheat straw samples, respectively). Peak areas of four herbicides in both soil and plant matrix were all relatively higher with 10 mg sorbent.

Particular attention was paid to recoveries considering the newly adopted d-SPE sorbent. It was defined as the ratio between the determined concentration and the added one. The detailed recovery data for all four herbicides in three matrices are summarised in Figure S2. Considering the importance of wheat grain, four levels of 0.005, 0.01, 0.1, and 0.2 mg/kg were tested. For the non-edible matrices, including soil and straw, the levels were 0.01, 0.1, and 0.2 mg/kg. The repeatability and trueness of the method were studied by carrying out five consecutive extractions of spiked matrices. The recoveries of four herbicides in all test levels (n = 5) ranged from 80% to 110% (80.1–98.5% for soil, 86.5–110% for wheat, and 85.5–110% for wheat straw). Relative standard deviations (RSDs) were below 14% for all cases (1.2–14% for soil, 2.0–13% for wheat, and 1.4–14% for wheat straw).

Overall, a simple LC–MS/MS with modified QuEChERS pretreatment with GCN as the d-SPE sorbent for the determination of florasulam, carfentrazone-ethyl, fluroxypyr-mephtyl, and fluroxypyr was developed (Figure S3). The most suitable modified QuEChERS method included the extraction by 10 mL acetonitrile, 1–2 mL water, and 1.0% acetic acid followed with the partitioning of the analyte molecules in organic solvent in the presence of 2 g MgSO₄ and 1 g NaCl. The acetonitrile phase was further cleaned up and dried by mixing with 10 mg GCN, variable amounts of GCB, and 200 mg anhydrous MgSO₄.

3.2. Quantitation and matrix effects

Change of ionisation efficiency in the presence of other compounds is called matrix effect [44,45]. The main consequence of matrix effect is an increasing or decreasing analyte signal in the presence of the matrix relative to the same analyte in solvent. Such effects are influenced by the specific analyte as well as the sample preparation and can be corrected by either isotopically labelled standards or matrix-matched calibration. Because of the high cost and low availability of standards, matrix-matched calibration was chosen in this study.

To evaluate the matrix effect, the slopes of regression equations in different matrices were compared with that of acetonitrile (Table 1). A matrix effect is calculated as follows: (the slope of standards in matrix–the slope in solvent)/the slope in solvent. A negative ratio indicates suppression and a positive result shows enhancement. And ±20% is acceptable. For example, carfentrazone-ethyl, fluroxypyr-mephtyl, and fluroxypyr presented both enhancement and suppression effect in three matrices according to the variable ratios (Figure 3). The negative slope ratios of florasulam indicated the matrix suppression effect in three matrices (Figure 3). For example, the matrix effect of four herbicides with GCN as the d-SPE sorbent in the straw was in the range of −12.9–5.01%. Thus, matrix effect of four herbicides with GCN as the d-SPE sorbent varied and differed
| Compound       | Matrix      | Linear range (μg/mL) | Linear regression | \( R^2 \) | RSD (%) (n = 6) | Instrumental quantification limit (μg/L) | Method quantification limit (mg/kg) |
|----------------|-------------|----------------------|-------------------|-----------|----------------|--------------------------------------|----------------------------------|
| Florasulam     | Solvent     | 1.2 × 10^{-3} − 0.50 | \( y = 2.30x + 5.73 \) | 0.9999    | 0.68           | 1.2                                  | 2.4 × 10^{-3}                    |
|                | Soil        |                      | \( y = 2.20x + 118 \) | 0.9989    | 1.0            | 2.4 × 10^{-3}                          |                                  |
|                | Wheat       |                      | \( y = 1.65x + 9.81 \) | 0.9999    | 2.4            | 2.4 × 10^{-3}                          |                                  |
|                | Wheat straw |                      | \( y = 2.00x − 1.62 \times 10^2 \) | 0.9925    | 4.9            | 6 × 10^{-3}                           |                                  |
| Carfentrazone-ethyl | Solvent     | 1.2 × 10^{-3} − 0.50 | \( y = 0.523x + 22.2 \) | 0.9996    | 3.2            | 1.2                                  | 5 × 10^{-3}                       |
|                | Soil        | 2.5 × 10^{-3} − 0.50 | \( y = 0.374x + 213 \) | 0.9842    | 3.6            | 2.4 × 10^{-3}                          |                                  |
|                | Wheat       | 1.2 × 10^{-3} − 0.50 | \( y = 0.468x + 24.2 \) | 0.9999    | 1.7            | 2.4 × 10^{-3}                          |                                  |
|                | Wheat straw | 1.2 × 10^{-3} − 0.50 | \( y = 0.549x + 2.02 \times 10^2 \) | 0.9859    | 2.2            | 2.4 × 10^{-3}                          |                                  |
| Fluroxypyr-mep-tyl | Solvent     | 1.2 × 10^{-3} − 0.50 | \( y = 0.879x + 74.4 \) | 0.9984    | 3.5            | 1.2                                  |                                  |
|                | Soil        |                      | \( y = 1.08x + 89.7 \) | 0.9982    | 1.8            | 2.4 × 10^{-3}                          |                                  |
|                | Wheat       | 2.5 × 10^{-3} − 0.50 | \( y = 0.757x + 37.0 \) | 0.9996    | 2.3            | 2.4 × 10^{-3}                          |                                  |
|                | Wheat straw | 1.2 × 10^{-3} − 0.50 | \( y = 0.925x + 57.4 \) | 0.9995    | 1.9            | 6 × 10^{-3}                           |                                  |
|                | Wheat straw | 1.2 × 10^{-3} − 0.50 | \( y = 0.813x + 68.6 \) | 0.9981    | 2.4            | 2.4 × 10^{-3}                          |                                  |
| Fluroxypyr     | Solvent     | 1.2 × 10^{-3} − 0.50 | \( y = 0.796x + 56.3 \) | 0.9988    | 2.4            | 1.2                                  |                                  |
|                | Soil        |                      | \( y = 0.674x + 32.0 \) | 0.9994    | 0.98           | 2.4 × 10^{-3}                          |                                  |
|                | Wheat       | 2.5 × 10^{-3} − 0.50 | \( y = 0.833x + 42.2 \) | 0.9995    | 1.4            | 6 × 10^{-3}                           |                                  |

\( y = \text{Area.} \)

\( ^a x = \text{Concentration (μg/mL)} \times 10^4; ^b \text{determination coefficient; } ^c \text{relative standard deviation.} \)
from pure solvent for each matrix. Therefore, it was necessary to use matrix calibration to enable accurate quantitation.

Table 1 shows the regression equations describing the relationship of the concentration to the peak area of the four herbicides obtained by the versatile QuEChERS LC–MS method, together with their determination coefficients which were higher than 0.99. The instrumental repeatability was confirmed by analysing a mixed solution of 0.05 μg/mL for four herbicides in different matrices. As shown in Table 1, RSD values (n = 6) of peak areas were lower than 4.9%, demonstrating that reproducibility was acceptable. The limits of quantitation (LOQ) of each analyte are also listed in Table 1.

Overall, GCN was successfully used as the d-SPE sorbent for the clean-up of three matrices, including soil, wheat grain, and wheat straw. In addition, the recovery test and the matrix matched-calibration illustrated this method’s robustness and accuracy.

3.3. Dissipation in the wheat ecosystem under open field

Herbicides dissipate through volatilisation, washing off, leaching, hydrolysis, chemical and biological degradation, and other processes reducing their amounts in plants after application. However, their dissipation is substance and possibly plant species-specific. To protect not only human health but also environment, it is essential to obtain herbicides’ dissipation information in the open field. In addition, pesticides degradation in soil has frequently been reported, but there is a lack of half-life information in plants.
under field conditions [46], which is particularly important, when pesticides follow different degradation pathways in soil and in plants [47]. Thus, it is necessary to obtain such information for soil and plants simultaneously. In order to verify this new d-SPE sorbent’s potential, four herbicides in soil and wheat straw samples were analysed by this QuEChERS LC–MS method. Samples were collected at different intervals after application of a real formulation of 26% florasulam-carfentrazone-ethyl-fluroxypyr-meptyl WDG to the field. Residues of four herbicides in different matrices were tested and the kinetic equations as well as the half-lives are shown in Table 2 and Figure 4.

The dissipation kinetics of the four herbicides was determined by plotting the concentration (mg/kg) against time (days). The dissipation kinetics followed the first-order kinetic equation $C_t = C_0 \exp(-kt)$ where $C_t$ represents the concentration of the herbicide (mg/kg) at time (days), $C_0$ represents the initial concentration, and $k$ is the rate constant. The half-life is equal to the ratio of ln 2 and $k$.

For 26% WDG, the active analytes of florasulam, carfentrazone-ethyl, fluroxypyr-meptyl, and fluroxypyr were determined, considering the rapid degradation of fluroxypyr-meptyl to fluroxypyr. Generally, four herbicides degraded faster in wheat straw than those in soil with overall half-lives of between 2.0 and 4.6 days. Degradation in soil was relatively slower, namely, half-lives of between 12 and 23 days, possibly due to the relatively cold weather (average temperature of 21°C) and few rain events (four times) at Beijing in the year of 2015.

### 3.4. Residues in the wheat ecosystem

To ensure the safety of food for consumers, the lowest maximum residue limits (MRLs) in wheat among United States, European Union, and China are 0.01 mg/kg for florasulam in the United States, 0.05 mg/kg for carfentrazone-ethyl in the European Union, and 0.02 mg/kg for fluroxypyr in China.

In this study, 26% WDG of florasulam-carfentrazone-ethyl-fluroxypyr-meptyl were applied to bare soil and plants in Beijing at the recommended dosage and the 1.5 times of this level. Samples of soil, wheat grain, and wheat straw were at harvest time collected (53 days after application) and determined by our method. None of the herbicides could be detected under the proposed method’s sensitivity. Besides, residues in all matrices were below the MRLs.
3.5. New GCN vs. conventional C18

Considering our previous method using conventional C18 where PSA was not suitable [43], comparison has been made between GCN and C18. Those following four aspects distinguished the new sorbent and promised it a potential substitute for C18.

First, decreased 2.5-fold amount. From the comparison in Figure 2, similar peak areas of four herbicides with 10 mg GCN and 25 mg C18 indicated comparable clean-up effect. Meanwhile, results using 10 mg C18 were not satisfactory. Furthermore, Figure 2 barely showed large change in the peak area as a function of the parameters, which indicated the method's ruggedness. The clean-up ability of GCN may be rooted in its large specific area.

Second, satisfactory recoveries and RSDs. The recoveries of the four herbicides in soil, wheat, and wheat straw with GCN as sorbents were in the range of 80–110% with RSDs below 14% for all cases. Those results are comparable with our previous method with C18 as d-SPE sorbents (e.g., recoveries of 89.7–110% for soil, 83.9–111% for wheat, and 88.3–111% for wheat straw; RSDs below 12% for all cases (1.6–6.5% for soil, 2.4–12% for wheat, and 1.0–10% for wheat straw)). These satisfactory recoveries and RSDs demonstrated the potential of GCN as d-SPE sorbents for determination of pesticide residues. Although the selected pesticides were not exhaustive, they suggested a sufficient level of efficacy when using GCN.

Third, small matrix effect. Matrix-matched calibration with different d-SPE
sorbents were conducted parallelly (Table 1 and Figure 3). From the slope ratios in Figure 3, the matrix effect with GCN as the d-SPE sorbent was smaller, especially in the most complex matrix of wheat straw. For example, the matrix effect of four herbicides with GCN as the d-SPE sorbent in the straw was in the range of −12.9–5.01%, whereas the ratios with C18 were as high as −7.40–65.6%. Besides, the increase of amount of GCN from 5 to 50 mg apparently didn’t lead to large interferences for the determination of these pesticides (Figure 2). Such interferences could result in either low or high peak areas. Thus, GCN showed superiority for clean-up due to its small matrix effect and ruggedness. Fourth, application for real samples. The dissipation kinetics of four herbicides under field conditions was determined with C18 and GCN as d-SPE sorbents parallelly. Results were similar (Table 2 and Figure 4) not only in soil but also in straw. For example, under open field conditions, when using GCN as the d-SPE sorbent, half-lives of these herbicides were 12–23 and 2.0–4.6 days in soil and straw samples, respectively, whereas the respective results of C18 as the sorbent were 10–23 and 2.0–4.6 days. All these verify the accuracy of this QuEChERS LC–MS method as well as the potential of GCN as the new d-SPE sorbent.

4. Conclusion

In this study, due to large specific surface areas, nanosheets of GCN were first used as the d-SPE sorbent for determination of four herbicides in different matrices. The QuEChERS LC–MS method was established and compared with the one with C18 as the d-SPE sorbent. Real samples under open field conditions in Beijing, China, in the year of 2015 were determined by the established method with GCN as the d-SPE sorbent. The small matrix effect and the decreased 2.5-fold amount distinguished GCN most as the d-SPE sorbent. Detailed recovery data, matrix matched-calibration, and results comparison with conventional C18 sorbent guaranteed the clean-up effect of GCN as the d-SPE sorbent. More importantly, the use of GCN opens up a new area for application, introducing it into d-SPE. It promises the analysis of new targets in different matrices in the future. Furthermore, it enlarges the scope of d-SPE as well as sample preparation.

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Disclosure statement

The authors declare no competing financial interest.

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