

<Original article>

## Analysis of Polycyclic Aromatic Hydrocarbons in Agricultural Waterways in Chungbuk and Gyeongbuk Provinces in Korea

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**Abstract** - An efficient, quick and low-cost extraction and clean up method for the determination of 14 polycyclic aromatic hydrocarbons (PAHs) in the agricultural water samples was optimized using gas chromatography-tandem mass spectrometry (GC-MS/MS). The extraction of the target compounds in water sample was carried out with acetonitrile, followed by partitioning promoted by the addition of salt. As a clean-up procedure, dispersive solid phase extraction was employed to purify the analytes of interest for GC-MS/MS analysis. This method was successfully applied for the quantification of PAHs in real water samples collected for the purpose of monitoring from the waterways located in Chungbuk (15 sites) and Gyeongbuk (6 sites), S. Korea. Phenanthrene (0.54 to 2.53  $\mu\text{g L}^{-1}$ ) was detected in all the water samples collected from both the sites. Fluoranthene was detected in the water samples collected from the two sites in Gyeongbuk province, but other PAHs were not determined in these water sampling sites. Based on these results, the determined PAHs were conducted using an environmental risk assessment. The risk characterization ratios (RCRs) for phenanthrene ranged from 0.37 to 3.21. These RCR values referred to as risk was not controlled because RCR values of some sites were greater than 1. In conclusion, it is proposed that the optimized method in combination with GC-MS/MS could be successfully employed for the determination of PAHs in any environmental samples including water samples.

**Keywords** : gas chromatography tandem mass spectrometry, monitoring, phenantherene, Environmental risk assessment

### INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) are organic compounds with multiple fused aromatic rings (two to seven rings) generally released by various human activities including the burning of fossil fuels, the incomplete burning of carbon-containing materials (*e.g.* gasoline and coal), tire particles, motor oil spills, vehicle exhaust, and crumbling asphalt (WHO 2000). Therefore, the contamination of PAHs in the agricultural waterways in Korea can be predictable

since many of them are located between car roads and agricultural lands. PAHs do not biologically break down due to their aromatic ring structures and some PAHs (*e.g.* benzo(a) pyrene) are known to be carcinogenic and mutagenic (IARC 2010). In addition, noncarcinogenic PAHs including phenanthrene, fluoranthene and pyrene in water can react with nitrite ( $\text{NO}_2^-$ ) in the air and form nitrated PAHs (nitro-PAHs) known to be more toxic than the parent PAHs (Shailaja *et al.* 2006). It should be noted that the water from the waterways is mainly used by Korean farmers to supply their crop and increasing vehicular traffic or air pollution may also cause increase in levels in PAHs around the waterway environment (Lin *et al.* 2015).

To prevent the serious contamination, it is important to

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continuously monitor the levels of PAHs in the water environment using a more simplified and advanced analytical method. In many studies on monitoring and assessment of PAHs, conventional extraction methods combined with gas chromatography mass spectrometry (GC-MS) have been adopted to determine the concentration of PAHs in various environmental samples (Maliszewska-Kordybach *et al.* 2008; Huang *et al.* 2014). In this study, QuEChERS (quick, easy, cheap, effective, rugged and safe) extraction method combined with GC tandem mass spectrometry (GC-MS/MS) was modified for PAHs analysis. The QuEChERS method is effective but greatly reduces analysis time and costs much less than the traditional extraction method involved with the large amount of organic solvent, tedious concentration procedures or cross contamination. This method was originally introduced for the determination of pesticide residues in agricultural produce (Anastassiades *et al.* 2003). It has been gradually extended to the analysis of organic contaminants such as mycotoxins (Jettanajit *et al.* 2016), veterinary drugs (Guo *et al.* 2015) and PAHs. Pesticide residues and PAHs in fresh herbs were determined using a modified QuEChERS method and GC-MS (Sadowska-Rociek *et al.* 2014).

GC-MS/MS were mainly used for multiresidue pesticide analysis (Zou *et al.* 2016) but it became the analytical tool of choice when target compounds are analyzed in a very complicated matrix (*e.g.* environmental samples and drug residues or metabolites in biological samples). The target analytes can be detected regardless of the sample matrix or other coeluted compounds of interest (or interferences) since the selected precursor or parent ions from the first stage of MS/MS are induced to further dissociate by collision energy. In this manner, MS/MS can confirm the compounds at trace levels (ppb level) lower than single MS can detect (Hayward *et al.* 2015). Multiclass pesticides and PAHs in fatty fish were analyzed using GC-MS/MS at trace level and recoveries at 10, 25 and 50  $\mu\text{g kg}^{-1}$  ranged from 60 to 120% with RSD < 11% (Chatterjee *et al.* 2016).

This study was aimed to optimize modified QuEChERS extraction and dispersive solid phase extraction (d-SPE) clean-up methods to extract and purify PAHs in water samples for the GC-MS/MS analysis. The optimized analytical method was applied to evaluate the level of PAHs in the waterways in Chungbuk (15 sites) and Gyeongbuk (6 sites). These results were also assessed associated with possible

PAHs sources. The determined PAHs were also assessed their environmental risks using ECOSAR. With these results, safety in agricultural ecosystems will be kept from persistent organic pollutants including PAHs.

## MATERIALS AND METHODS

### 1. Chemicals

Certified reference standards of each PAH had >98% purity and were purchased from Sigma Aldrich (US). Acetonitrile (ACN) was purchased from Merck (Darmstadt, Germany). QuEChERS salt packets (4 g anhydrous  $\text{MgSO}_4$ , 1g NaCl, 1g trisodium citrate dehydrate and 0.5 g disodium hydrogen citrate sesquihydrate) were purchased from Ultra Scientific (Seoul, Korea) and d-SPE tubes containing primary secondary amine (PSA, 25 mg) and anhydrous magnesium sulphate ( $\text{MgSO}_4$ , 150 mg) were purchased from Restek<sup>®</sup> (US).

### 2. Sample Preparations

ACN (10 mL) was added to water sample (10 mL) in 50 mL of poly propylene plastic tube and vigorously shaken for 1 min. While contacting crushed ice with an extraction tube in order to cool down the extract, the salt was added to the tube for the partitioning and vigorously shaken for 1 min and centrifuged for 5 min (3,500 rpm). For clean-up, 1 mL of each extract was added to 2 mL of d-SPE tube containing PSA and  $\text{MgSO}_4$  and vigorously shaken for 1 min. After being centrifuged (15,000 rpm), 0.5 mL of extracts were taken into a GC vial and evaporated under the gentle stream of nitrogen gas. ACN (0.1 mL) was added to the vial for the GC-MS/MS analysis.

### 3. Instrumental Analysis

The sample analysis was carried out with Bruker SCION TQ (Triple Quadrupole mass spectrometry) in SRM (selected reaction monitoring) with CP-8400 autosampler. For separation of the analytes, ZB-SemiVolatiles (30 m  $\times$  0.25 mm  $\times$  0.25  $\mu\text{m}$  film thickness, Phenomenex) was used. The injection volume was 2  $\mu\text{L}$  with splitless pulsed pressure mode at 250 kPa. The carrier gas was helium with constant flow (1.0 mL  $\text{min}^{-1}$ ) and inlet temperature was set at 300°C.

The initial oven temperature with 90°C was held for 3 min, ramped into 170°C at 25°C min<sup>-1</sup> and ramped into 300°C at 5°C min<sup>-1</sup> (held for 4 min). Mass spectrometer was run with EI (electron-impact ionization) mode with 70 eV and transfer line and ion-source temperatures were set at 300 and 280°C, respectively.

#### 4. Method Validation and Fortification Studies

Linearity, limits of quantification (LOQs), method detection limit (MDL), limits of detection (LODs), accuracy and precision were determined during validation of the analytical method. External standard method was employed for quantitative analysis. For accuracy and precision, the recovery and reproducibility experiments were performed by fortifying blank agricultural water sample (10 mL) in three replicates at two spiking levels: 10 and 50 µg L<sup>-1</sup>. Using matrix matched standards, the quantification of each compound was carried out by plotting a calibration curve (1, 5, 10, 25, 50, 100, 250, and 500 µg L<sup>-1</sup>) for linearity ( $R^2 > 0.99$ ). LOQs of the optimized method were calculated as the lowest concentration giving signal-to noise ratios of 10 (S/N = 10) by injecting matrix matched calibration standard into GC-MS/MS. MDL was calculated by multiply LOQs by five, the concentration factor obtained in sample preparation.

#### 5. Agricultural Water Sample Analysis

Water samples were obtained from Chungbuk (15 sites) (site 1: 37°02'25.9"N 127°55'31.5"E, 2: 37°02'27"N

127°55'1"E, 3: 37°02'29"N 127°54'45.0"E, 4: 37°02'32.2"N 127°54'34.9"E, 5: 37°02'38.5"N 127°54'20.0"E, 6: 37°02'52.5"N 127°53'29.9"E, 7: 37°02'22.5"N 127°55'46.8"E, 8: 37°02'14.6"N 127°56'12.2"E, 9: 37°02'13.3"N 127°56'46.0"E, 10: 37°02'20.4"N 127°57'03.2"E, 11: 37°02'45.4"N 127°57'27.1"E, 12: 37°05'03.3"N 127°57'22.5"E, 13: 37°05'21.1"N 127°57'35.0"E, 14: 37°04'28.6"N 127°55'50.3"E, 15: 37°02'25.9"N 127°55'31.5"E) and Gyeongbuk (6 sites) (1: 35°37'44.9"N 128°26'06.1"E, 2: 35°57'19.6"N 128°20'05.6"E, 3: 35°57'00.7"N 128°19'37.7"E, 4: 35°55'57.1"N 128°34'02.3"E, 5: 35°35'58.4"N 128°28'28.4"E, 6: 35°53'07.3"N 128°36'04.9"E). Replicate samples from Gyeongbuk were collected. All the samples were prepared using the analytical methods proposed in this study. For the quantitative analysis of water samples, matrix matched standards were prepared with blank agricultural water sample, pre-checked by the preliminary analysis.

Measured PAHs were evaluated for their environmental risks using risk characterization ratios (RCRs) in relation to predicted no-effect concentrations (PNEC) calculated by ECOSAR (version 2.0). If RCR value is greater than 1, risk is not controlled. Otherwise, risk is adequately controlled if the RCR value is less than 1.

## RESULTS AND DISCUSSION

### 1. GC-MS/MS Analysis and Sample Preparation

For the optimization of the MS parameters, all the ana-

**Table 1.** Quantifier and qualifier with collision energy optimized for the GC-MS/MS analysis

PAHs	RT <sup>#</sup> (min)	Quantifier (CE <sup>**</sup> )	Qualifier (CE <sup>**</sup> )	MDL <sup>***</sup>
1-Acenaphthenone	10.9	140 > 139 (25)	140 > 89 (30)	0.2
Phenanthrene	12.6	178 > 152 (30)	178 > 177 (25)	0.2
Anthracene	12.8	178 > 152 (30)	178 > 176 (25)	0.2
Fluoranthene	16.9	202 > 200 (30)	202 > 152 (10)	0.2
Pyrene	17.8	202 > 201 (25)	202 > 176 (30)	0.2
Benz(a)anthracene	23.0	228 > 226 (25)	226 > 202 (25)	0.2
Chrysene	23.2	228 > 226 (30)	226 > 202 (30)	0.2
Benzo(b)fluoranthene	27.6	252 > 252 (15)	252 > 226 (10)	0.2
Benzo(k)fluoranthene	27.75	252 > 250 (25)	252 > 226 (25)	0.2
Benzo(e)pyrene	28.7	252 > 252 (15)	226 > 226 (30)	0.2
Benzo(a)pyrene	28.9	252 > 252 (10)	252 > 226 (25)	0.2
Indeno(123cd)pyrene	32.9	276 > 274 (30)	276 > 275 (30)	0.2
Dibenz(ah)anthracene	33.1	278 > 276 (30)	278 > 277 (30)	0.2
Benzo(ghi)perylene	33.7	276 > 276 (10)	276 > 274 (30)	0.2

<sup>#</sup>RT: retention time; <sup>\*</sup>MW: molecular weight; <sup>\*\*</sup>CE: collision energy; <sup>\*\*\*</sup>MDL: method development limit

**Table 2.** Recoveries with the relative standard deviation (RSD) at two spiking levels: 10 and 50  $\mu\text{g kg}^{-1}$ 

PAHs	Spiking level 10 $\mu\text{g kg}^{-1}$		Spiking level 50 $\mu\text{g kg}^{-1}$	
	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)
1-Acenaphthenone	71.4	19.1	78.5	7.5
Phenanthrene	71.8	12.2	71.0	0.9
Anthracene	62.2	12.6	69.9	0.3
Fluoranthene	81.9	5.3	85.2	3.7
Pyrene	72.3	4.9	88.9	1.5
Benzo(a)anthracene	90.5	5.3	102.7	0.7
Chrysene	98.0	3.6	106.6	2.5
Benzo(b)fluoranthene	90.0	3.7	99.2	2.2
Benzo(k)fluoranthene	97.6	2.2	106.2	2.2
Benzo(e)pyrene	100.1	2.3	106.4	2.2
Benzo(a)pyrene	99.2	3.0	103.6	0.8
Indeno(123cd)pyrene	100.6	5.0	108.2	1.5
Dibenz(ah)anthracene	105.1	5.4	111.3	3.3
Benzo(ghi)perylene	103.6	4.8	109.2	1.7

**Table 3.** Ecological risk assessment of measured phenanthrene in the waterways of two provinces in Korea. PNEC values were calculated from ECOSAR v2.0 and the RCR values denote that risk is properly controlled if RCR value is less than 1

Sites	Measured concentration ( $\mu\text{g L}^{-1}$ )	PNEC <sup>1</sup> values ( $\mu\text{g L}^{-1}$ )			RCR <sup>2</sup> values		
		Green algae	Daphnid	Fish	Green algae	Daphnid	Fish
Chungbuk 1	1.1				0.75	1.36	0.96
Chungbuk 2	0.9				0.61	1.11	0.78
Chungbuk 3	1.0				0.68	1.23	0.87
Chungbuk 4	1.5				1.02	1.85	1.30
Chungbuk 5	0.6				0.41	0.74	0.52
Chungbuk 6	0.9				0.61	1.11	0.78
Chungbuk 7	1.2				0.82	1.48	1.04
Chungbuk 8	1.7				1.16	2.10	1.48
Chungbuk 9	1.25				0.85	1.54	1.09
Chungbuk 10	1.1				0.75	1.36	0.96
Chungbuk 11	0.85	1.47	0.81	1.15	0.58	1.05	0.74
Chungbuk 12	0.9				0.61	1.11	0.78
Chungbuk 13	0.6				0.41	0.74	0.52
Chungbuk 14	0.7				0.48	0.86	0.61
Chungbuk 15	1.3				0.88	1.60	1.13
Gyeongbuk 1	0.6				0.41	0.74	0.52
Gyeongbuk 2	0.55				0.37	0.68	0.48
Gyeongbuk 3	0.68				0.46	0.84	0.59
Gyeongbuk 4	2.6				1.77	3.21	2.26
Gyeongbuk 5	0.7				0.48	0.86	0.61
Gyeongbuk 6	0.15				0.10	0.19	0.13

<sup>1</sup>PNEC: Predicted no-effect concentration; <sup>2</sup>RCR: Risk characterization ratio

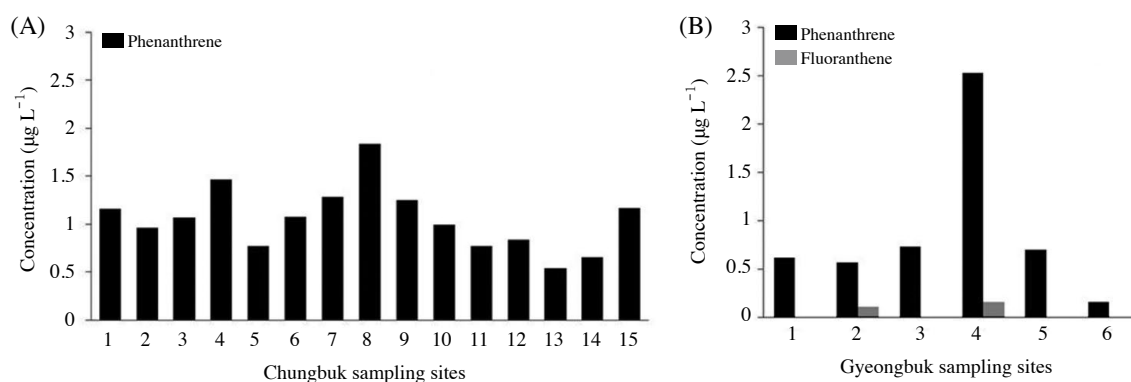
lytes were initially monitored in full scan mode in the 50–550 m/z ranges and then, one or two precursor ions (or parent ions) for each analyte were selected (by considering selectivity (specificity) and sensitivity. When the precursors (or parent ions) were dissociated once more by the collision energy, the best product ions were selected for each transition in a multiple reaction monitoring (MRM) experiment. The most intense transition of each analyte was selected

for the quantifier analysis and the second most intense for the qualifier analysis. Due to structural stability of aromatic rings (two to seven rings) in PAHs, high collision energies were required to produce product ions. The quantification and identification ions and collision energy for each PAH selected in MRM experiment are shown in Table 1. The consequential specific product ion spectrum confirmed the target compound identified by retention time of each

**Table 4.** Ecological risk assessment of measured fluoranthene in the waterways of two provinces in Korea. PNEC values were calculated from ECOSAR (version 2.0) and the RCR values denote that risk is properly controlled if RCR value is less than 1

Sites	Measured concentration ( $\mu\text{g L}^{-1}$ )	PNEC <sup>1</sup> values ( $\mu\text{g L}^{-1}$ )			RCR <sup>2</sup> values		
		Green algae	Daphnid	Fish	Green algae	Daphnid	Fish
Gyeongbuk 1	0.13				0.19	0.44	0.33
Gyeongbuk 4	0.21	0.66	0.29	0.39	0.32	0.72	0.54

<sup>1</sup>PNEC: Predicted no-effect concentration; <sup>2</sup>RCR: Risk characterization ratio

**Fig. 1.** Levels of polycyclic aromatic hydrocarbons in the agricultural water samples obtained from Chungbuk and Gyeongbuk provinces in Korea.

compound. In this way, selectivity of MS/MS enhanced the signal to noise so low limit of detections (LODs) for the PAHs (e.g. LOD of phenanthrene is  $1 \mu\text{g L}^{-1}$ ) were achieved in this experiment. MDLs were  $0.2 \mu\text{g L}^{-1}$  for all the target compounds. Some studies showed that LOD of phenanthrene ranged from  $2.5$  to  $3.5 \mu\text{g L}^{-1}$  using GC-MS (Zhao *et al.* 2015; Zou *et al.* 2016). It was demonstrated that signal-to-noise ratios of PAHs determined using GC-MS/MS was much superior to those of them using GC-MS (Zou *et al.* 2016).

The QuEChERS extraction method is a streamlined approach recently developed to separate organic compounds (pesticide residues or PAHs) in a complex matrix (Anastassiades *et al.* 2003). This technique provides an environmentally friendly alternative to conventional liquid-liquid and solid phase extractions, requiring the large amount of organic solvent. The procedure involves two simplified steps; sample extraction and d-SPE clean-up. In this study, the sample (10 mL) extraction and partitioning were carried out using a minimal amount of organic solvent (10 mL) and salt. Then, the target analytes in extract were purified using a 2 mL d-SPE tube containing PSA alone. The RSD data

validated that the proposed method was reproducible. Fourteen PAHs provided recoveries in the range of 60–110% at the two fortified levels of 10 and  $50 \mu\text{g L}^{-1}$  associated with RSDs ( $<20\%$ ) (Table 2). Good linearity ( $R^2 > 0.99$ ) for all the target analytes was achieved for both solvent and matrix matched standards for quantification. Phenanthrene, anthracene and 1-acenaphthenone gave lower recoveries (approx. 70%) rates than other compounds (85–110%). These compounds must be lost during the evaporating procedure since they have lower molecular weight and more volatile than other PAHs (Vane *et al.* 2014).

## 2. Levels of PAHs in Water Samples

To determine the concentration of 14 PAHs in real water samples, water was sampled in the waterways located in Chungbuk (15 sites) and Gyeongbuk (6 sites), Korea. Except phenanthrene and fluoranthene, all the PAHs analyzed in the water samples were not detected. Phenanthrene was detected in all the water samples from both Chungbuk and Gyeongbuk areas. The concentration of phenanthrene ranged from  $0.54$  to  $2.53 \mu\text{g L}^{-1}$  and the distribution of phenanthrene and fluoranthene in both places is shown in

Fig. 1A and B. One of the sampling sites in Gyeongbuk gave the highest concentration ( $2.53 \mu\text{g L}^{-1}$ ) of phenanthrene out of other sites (Table 3). Considering that the sampling area is located near a tire factory, the compound was possibly derived from runoff of oil spills or tire particles. It may be one of petrogenic PAHs, exclusively dominated by the C1 to C4 alkylated homologues of certain parent PAHs, in particular, naphthalene, phenanthrene, dibenzothiophene, fluorene, and chrysene (Wang *et al.* 2007).

On the other hand, fluoranthene was detected in water samples from only two sites ( $0.11$  and  $0.16 \mu\text{g L}^{-1}$ , respectively) in Gyeongbuk (Fig. 1B). Considering that the presence of fluoranthene indicates less efficient or lower-temperature combustion, this compound may be possibly due to combustion of the vehicles passing by the waterways.

Considering both compounds in waterways are less toxic than other PAHs and “not classifiable as to its carcinogenicity to humans” (IARC 2010), water from waterways from two areas may be safe for crop irrigation. However, it should be noted that these compounds can react with  $\text{NO}_2^-$  in the atmosphere, producing nitro PAHs such as nitro-phenanthrene or nitro-fluoranthene. Lin *et al.* demonstrated that the presence of  $\text{NO}_2^-$  would cause the PAHs-nitro-PAHs transformation. Considering that nitro-PAHs tended to be more toxic, the combined pollution of PAHs and  $\text{NO}_2^-$  may threaten the ecosystem. Even though PAHs are not detected in the most water samples, this monitoring should be expanded to analyze other toxic compounds (*e.g.* POPs) or levels of PAHs in sediment should be determined. Zhang *et al.* (2004) demonstrated that the concentration of total PAHs in sediment was higher than those in surface water. According to the study, the PAHs were dominated by 2-3-ring compounds in water samples and by 3-4-ring compounds in sediment.

With Tables 3 and 4, risks by phenanthrene in the two provinces in Korea well controlled because RCR values is less than 1 or close to the 1. The site Gyeongbuk 4 is the site, which we should monitor annually because RCR values for the three aquatic organisms is ranged from 1.77 to 3.21. Similarly, two sites of Gyeongbuk provinces (sites 2 and 4) contained fluoranthene in the waterways, however, their RCR values were below 1. It means that all sites were controlled properly for the fluoranthene.

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