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Development and *in situ* application of stir bar sorptive extraction for the determination of agricultural pesticides in surface water

Summary

Passive sampling has recently been developed as an alternative to grab or average automated sampling, in order to obtain at lower cost, more realistic estimates of the average concentrations of organic contaminants in surface waters. The aim of this study was to develop and validate the *in situ* application of stir bar sorptive extraction (SBSE) as a passive sampling technique for the monitoring of 16 pesticides in a small river of an agricultural watershed located in the Beaujolais region. Stir bars (Twister[®]) were deployed for several periods of one or two weeks during two one-month campaigns in 2010 and in 2011. With prior in-lab calibration, the *in situ* application of SBSE allowed the integration of a quick concentration peak and the determination at lower cost of average concentrations of the target pesticides similar to those obtained from water samples collected by an automated sampler.

Keywords: Passive sampling, pesticides, SBSE, surface water

Développement et application *in situ* de l'extraction sur barreau pour la quantification de pesticides agricoles dans les eaux de surface

Résumé

L'échantillonnage passif est une technique récemment développée qui représente d'ores et déjà une alternative simple et économique aux échantillonnages ponctuel et moyennés automatisés pour la détermination d'estimations réalistes de la contamination des eaux de surface par des micropolluants organiques. L'objectif de cette étude est de développer et de valider l'application *in situ* de la stir bar sorptive extraction (SBSE) en tant que technique d'échantillonnage passif pour le suivi de 16

pesticides dans une rivière d'un bassin versant agricole, situé dans le Beaujolais. Des barreaux SBSE (Twister®) ont été déployés pendant plusieurs périodes d'une ou deux semaines, lors de deux campagnes d'étude d'un mois réalisées en 2010 et en 2011. Après une phase d'étalonnage en laboratoire, l'application *in situ* de la SBSE a permis de capter un pic de pollution très court et de déterminer à moindre coût des concentrations moyennes des pesticides ciblés semblables à celles obtenues d'échantillons collectés à l'aide d'un préleveur automatique.

Mots-clés : Echantillonnage passif, pesticides, SBSE, eau de surface

I. Introduction

Monitoring of aquatic environment pollution by organic micropollutants such as pesticides is a major challenge for water protection policies designed to preserve the good chemical and ecological status of water bodies. Passive sampling is a recently-developed method that has emerged as a cheap and simple alternative to grab and automatic composite samplings for determining realistic estimates of surface water pollution by organic micropollutants (1). The technique produces time-weighted average (TWA) concentrations relative to sampler exposure period, but requires a prior calibration step that has to be performed under controlled lab conditions. This means the accumulation kinetics of pollutants of interest have to be studied in order to determine the corresponding sampling rates needed to calculate TWA concentrations. The past twenty years have seen the development of several passive samplers focused on different organic micropollutant targets presenting a range of physical-chemical properties (2). Hydrophobic compounds such as polycyclic aromatic hydrocarbons and polychlorinated biphenyls are generally sampled using the semipermeable membrane device (SPMD) (1), whereas the polar organic compound integrative sampler (POCIS) has demonstrated good results on polar organic micropollutants including pharmaceuticals and hydrophilic pesticides (2, 3). However, few studies have tackled passive sampling of hydrophobic pesticides.

Stir bar sorptive extraction (SBSE) is a solventless extraction technique used for moderately hydrophobic-to-hydrophobic organic compounds (i.e. with a log K_{ow} ranging from 2 to 5) in aqueous

matrices and air (5). The stir bar used for sample extraction is a polydimethylsiloxane (PDMS)-coated glass rod housing a magnet (named Twister[®]). The solutes extracted are then removed by chemical or thermal desorption prior to liquid or gas chromatography analysis. This technique was recently applied on site for the analysis of polycyclic aromatic hydrocarbons in seawater (6). The aim of this study was to develop and validate passive SBSE as a passive sampling approach for monitoring 16 pesticides in a river located in a catchment area of the Beaujolais wine-farming region.

II. Material & Methods

1. Selected pesticides

Sixteen pesticides and pesticide metabolites were selected for this study: acetochlor, atrazine, azoxystrobin, chlorfenvinphos, chlorpyrifos-ethyl, 3,4-dichloroaniline, diflufenican, dimethomorph, fenitrothion, flufenoxuron, isoproturon, metolachlor, norflurazon, procymidone, simazine, and tebuconazole. These analytes, from different families and presenting a broad range of physical-chemical properties ($2.3 < \log K_{ow} < 5.0$), are frequently found in rivers located in catchment areas of wine-farming regions (7). Standard calibration solutions were prepared from stock solutions of pesticides (VWR, Strasbourg, France).

2. Passive sampling theory and in-lab calibration

For the determination of TWA concentrations, the calibration of the passive sampler has to be carried out. In other words, the accumulation kinetics of the target analytes in the receiving phase of the passive sampler have to be studied in controlled conditions (water temperature, flow rate, and analyte concentration). Assuming isotropic exchange, the accumulation of an analyte in the sampler -initially empty- over time with constant ambient concentration can be described as follows (Eq. 1):

$$N(t) = C_w K_{sw} V_s (1 - \exp(-k_e \cdot t)) \quad (1)$$

where N (μg) is the mass of analyte accumulated in the receiving phase; V_s (mL) is the volume of the receiving phase; K_{sw} (adimensional), described by the ratio of the concentration of analyte in the

sampler C_s ($\mu\text{g mL}^{-1}$) and the concentration of analyte in the water phase C_w ($\mu\text{g mL}^{-1}$), is the receiving phase/water partitioning coefficient; t (d) equals time; and k_e (d^{-1}) is the elimination constant (8).

The graphical representation of Eq. 1 is curvilinear with a plateau corresponding to an equilibrium phase (described by K_{sw}). In the initial accumulation phase, when the exponential term is small ($\ll 1$), chemical accumulation is linear and integrative. Thus, in the initial accumulation phase, Eq. 1 is reduced to (Eq. 2):

$$N(t) = C_w R_s t \quad (2)$$

where R_s is the sampling rate of the analyte (mL d^{-1}).

The calibration of the passive sampler allows the determination of the sampling rates R_s of the target analytes, thereafter used for the calculation of TWA concentrations over the course of field application campaigns.

The Twisters (20 mm bars with a 1 mm-thick film coat and a volume of 126 μL) used for the calibration step were supplied by Gerstel (Mülheim an der Ruhr, Germany). They were placed in meshed plastic deployment bags to keep the PDMS film under a protective seal while allowing direct exposure. In order to mimic the conditions of surface water hydrodynamics, the Twisters were calibrated in pump-driven flow channels delivering tap water spiked with the 16 target pesticides. We opted to use continuous-flow spiked tap water in order to correct for pesticide sorption on the calibration system and thereby keep constant pesticide concentrations throughout the calibration phase. The accumulation kinetics of pesticides in the Twisters were monitored for 7 days at 20°C and 2.5 cm s^{-1} . Each Twister sampled was washed in ultrapure water, dried using lab-grade lint-free wipes, and then left at -18°C at least overnight before desorption and analysis of the accumulated pesticides.

3. Passive SBSE and chemical analysis

The *in situ* extraction of target pesticides was carried out with the same Twisters as those used for the calibration step. The Twisters were again placed in meshed plastic deployment bags. The deployment bags were then installed in small cages ready for in-river exposure. On completion of the *in situ*

exposure period, the Twisters were washed in ultrapure water, dried using lab-grade lint-free wipes, then left at -18°C at least overnight. The Twisters used for *in situ* extraction and those used for the calibration phase were chemically desorbed (LD) by sonication for 15 minutes in 200 μL of a methanol/acetonitrile (50/50, v/v) mixture and analyzed by liquid chromatography coupled with tandem mass spectrometry (Agilent 1100 system LC and API4000 system triple quadrupole MS; AB Sciex) according to a lab-validated SBSE-LD-LC-MSMS method (9). Quantification was performed by internal calibration with diuron-d6 as analytical standard.

4. Application site

The field study was conducted in a river (the Morcille river) located in a Haut-Beaujolais-region vineyard catchment area at 70 km north of Lyon that has already been the site of proven surface water contamination by pesticides (7). The river was sampled at two selected sites: one intermediate site (named Les Versauds) and one downstream site (named St Ennemond). Triplicate Twister experiments were set up for one or two-week periods at each of the two sites. Two 4-week deployment campaigns were carried out, one in June 2010 and one in June 2011.

In order to compare the performances of the passive SBSE technique, we also ran grab sampling and time-weighted automatic composite sampling at the intermediate site on the Morcille river, and grab sampling at the downstream site.

III. Results and Discussion

1. Validation of the SBSE-LD-LC-MSMS method

A validation procedure was performed regarding linearity, limit of quantification (LOQ), and trueness and precision, based on the reference standards AFNOR NF T90-210:2009 and ISO/IEC 17025:2005 (10, 11). Additionally, measurement uncertainty (U) of the analytical method was assessed according to reference standards AFNOR XP T 90-220:2003 and ISO 11352:2012 (12, 13). The results of the validation of the analytical method are reported in Table I. Excellent linearity was obtained ($r^2 > 0.996$) for all pesticides. The validated LOQ in water ranged from 0.02 to $1 \mu\text{g L}^{-1}$ depending on the

compound. Trueness and precision were evaluated at 3 concentration levels of the pesticide calibration curves (LOQ level, medium level and high level). Trueness ranged from 89 to 103% whereas precision ranged from 6.6 to 25%. Finally, method uncertainties were determined experimentally and ranged from 13.3 to 51% for all studied pesticides and at the same 3 concentration levels as for the determination of trueness and precision (9).

2. Passive SBSE in-lab calibration

Passive SBSE calibration was performed in-lab in order to determine pesticide sampling rates and subsequently calculate mean pesticide concentrations after in-field sampler exposure campaigns.

The target pesticides showed accumulation kinetics that are similar to the theory (8), reproducing the initial linear phase of accumulation that then drops off until hitting a plateau marking the equilibrium phase (Figure 1 for fenitrothion). The linear accumulation period corresponds to the period during which the passive sampler can be exposed in-habitat and allow the calculation of TWA concentrations. Beyond this segment of the linear accumulation curve, the computed mean concentration is considered non-integrative. It thus follows that a passive sampler that demonstrates linear micropollutant accumulation over a long exposure period can therefore give a mean concentration that spans a relatively long exposure window. The linear accumulation periods were thus determined for each of the pesticides studied, and varied from 32 h to 96 h. Logistics imperatives meant that the Twisters were ultimately exposed in the river water for one to two weeks. Consequently, the mean concentrations determined here cannot be considered integrative and may be slightly skewed compared to the actual values.

Nevertheless, this quick-burst kinetics curve, which consequently leads to short periods of linear accumulation, lends passive SBSE rapid responsiveness along with the possibility of integrating transient pollution peaks lasting just a few hours.

3. Comparison between passive SBSE and grab sampling

Grab sampling is still the most popular strategy employed by water quality monitoring and surveillance networks. However, in hydrosystems with high flow rate variability, grab sampling cannot track transient pollution peaks unless the grab campaign is designed to collect a huge number of samples. For the purpose of comparing passive SBSE against grab sampling in terms of representativity over time, triplicate Twister experiments were set up downstream of the Morcille river (at the St Ennemond site) for two weeks, and one grab sample was taken at the same site first when the Twisters were deployed (d0) and then again when they were retrieved (d14).

Figure 2 illustrates the cumulative concentrations of the target pesticides per use class, as determined by passive SBSE and by grab samples taken at the start and end of the Twister exposure period during the June 2010 monitoring campaign. The grab samples were extracted by SBSE and pesticide concentrations were then determined by LD-LC-MS/MS. The results show that passive SBSE captured high concentrations of insecticides (predominantly chlorpyrifos-ethyl). The Twisters visibly integrated a concentration peak triggered by a flood that had occurred two days before the end of the exposure window, whereas the grab sample taken at the end of this same exposure window failed to detect this pollution peak.

4. Comparison between active sampling and passive sampling

In order to determine mean pesticide concentrations, triplicate Twister experiments were deployed over 4 one-week periods at an intermediate point (Les Versauds) of the Morcille river, during two separate exposure campaigns.

A parallel set of water samples collected from these same sites (grab samples and time-averaged) were extracted by SBSE at the lab and then analyzed by LD-LC-MS/MS. Figures 3a and 3b chart the pesticide concentrations obtained in-stream at the Les Versauds site by two active sampling techniques compared to the mean concentrations obtained by the passive SBSE technique. Figure 3a reports the results for the June 2010 exposure campaign. Time-averaged sampling and passive SBSE produced similar concentration values for several target pesticides such as tebuconazole, azoxystrobin and

dimethomorph. Figure 3b reports the results for the June 2011 exposure campaign. Time-averaged sampling and passive SBSE gave comparatively the same scale of dimethomorph and tebuconazole concentrations. Passive SBSE sampling therefore appears to yield the same information as active sampling but at significantly lower cost and with significantly less need for infrastructure logistics.

IV. Conclusion

This study assessed the performances of SBSE Twister used as a passive sampling tool for moderately hydrophobic-to-hydrophobic organic compounds (i.e. with a log K_{ow} ranging from 2 to 5). The results showed that in a hydrosystem with high flow rate variability, the passive SBSE technique was able to integrate the pollution peaks and offered better time-course representativity of target pesticide concentrations than grab sampling. It was also shown that passive SBSE gave similar concentrations of several target pesticides to automatic composite sampling, but at significantly lower cost and with significantly less need for infrastructure logistics. With prior lab-calibration, passive SBSE emerges as perfectly applicable for sampling and screening pesticides at trace level in surface waters.

Lab experiments are currently carried out to assess the impact of the exposure conditions of the passive SBSE (flow rate and water temperature) on the accumulation kinetics of the target pesticides. We also plan to run a fine-grained analysis of the passive SBSE response times when exposed to pollution peaks, in order to better interpret the TWA concentration values obtained using this passive sampling technique.

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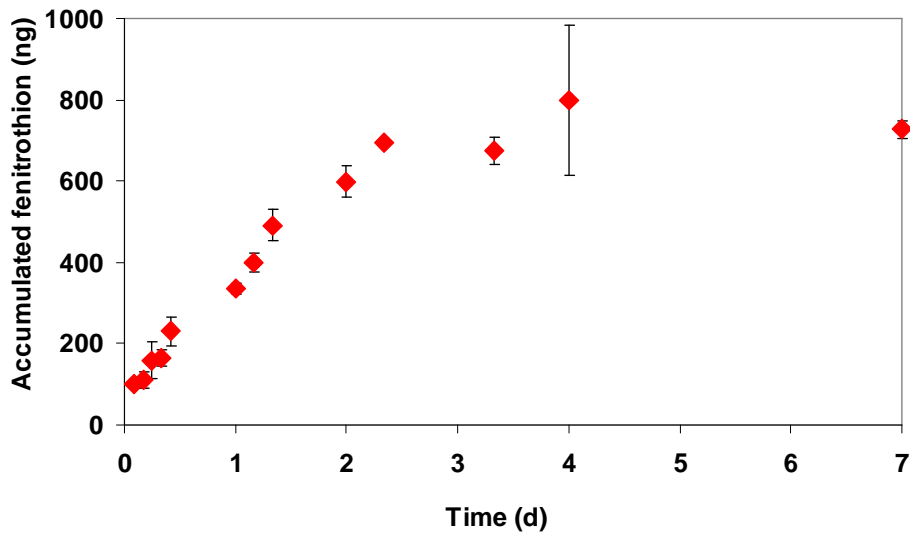


Figure 1. Accumulation kinetics of fenitrothion in Twisters during flow-through calibration for 7 days at 20°C and 2.5 cm s⁻¹. Errors bars represent standard deviation (n = 3)

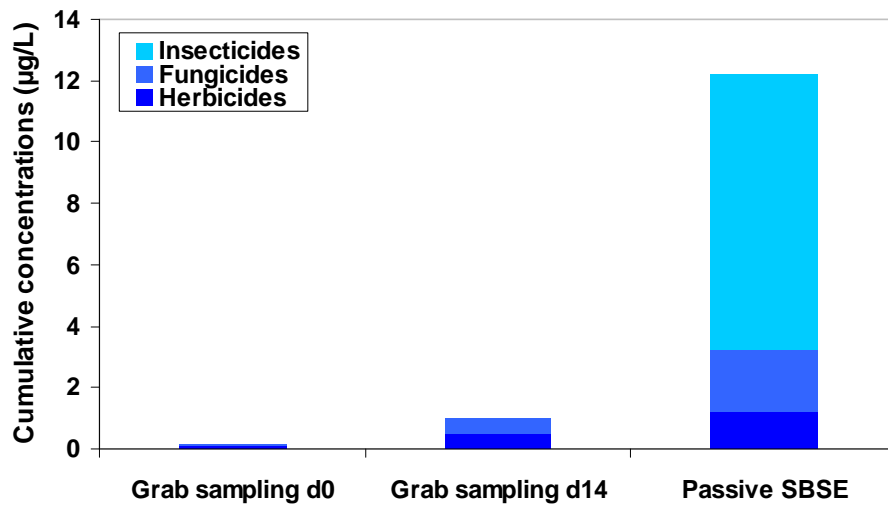


Figure 2. Cumulative concentrations of pesticides per use class measured at the downstream Morcille site (St Ennemond) according to sampling technique (June 2010 monitoring campaign)

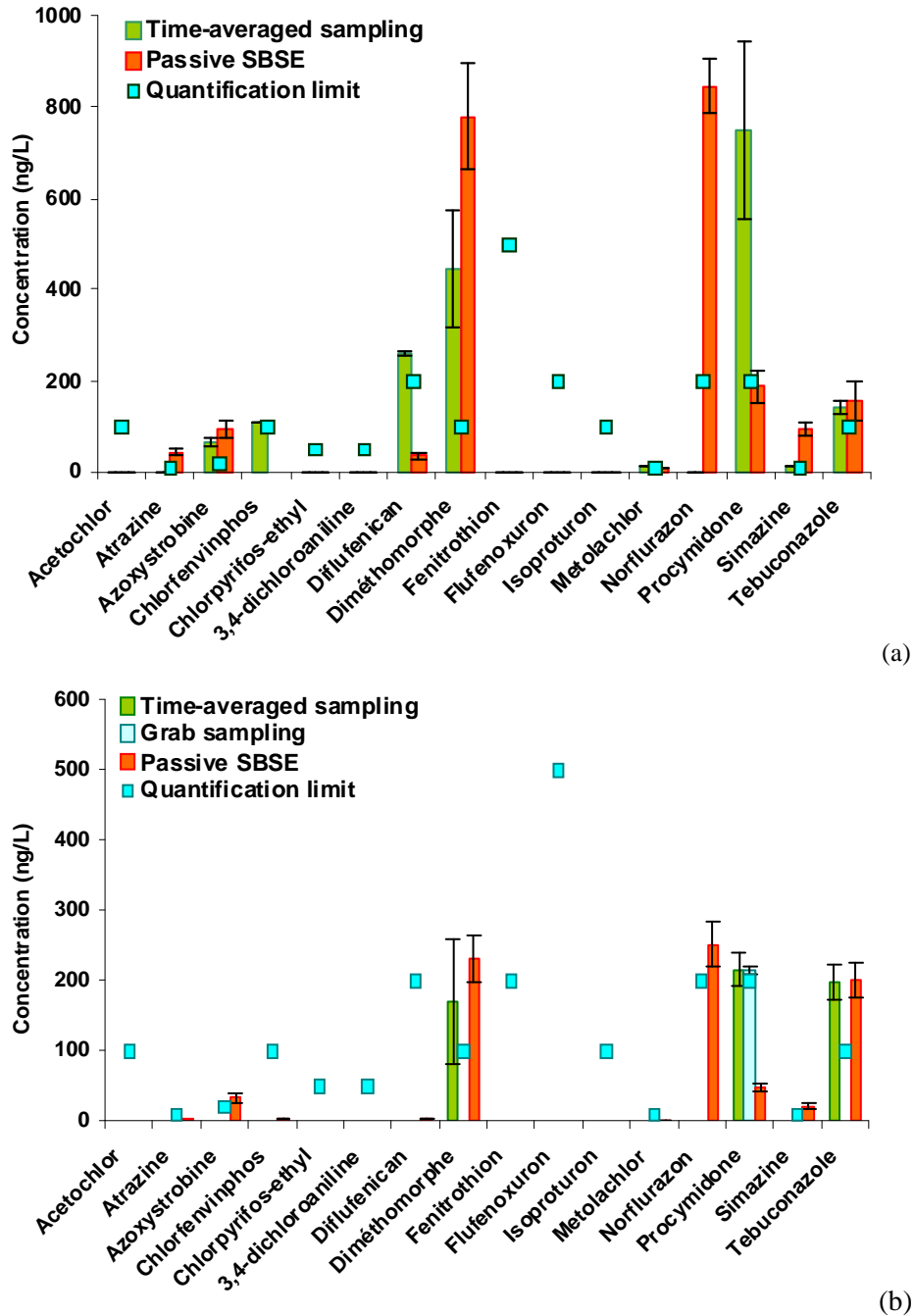


Figure 3. Pesticide concentrations as obtained by different sampling techniques at the intermediate point (Les Versauds) of the Morcille river over the course of (a) the June 2010 exposure campaign and (b) the June 2011 exposure campaign. Errors bars represent standard deviation (n = 3)

Table I. Linear dynamic range, mean recoveries (n=10) and measurement uncertainties (U, n=30) for the selected pesticides for the 3 concentration levels (from Margoum et al. (9))

Compound	Concentration range ($\mu\text{g L}^{-1}$)	Regression coefficient (r^2)	LOQ level			Medium level			High level		
			Conc. $\mu\text{g L}^{-1}$	Recovery (RSD) (%)	U (%)	Conc. $\mu\text{g L}^{-1}$	Recovery (RSD) (%)	U (%)	Conc. $\mu\text{g L}^{-1}$	Recovery (RSD) (%)	U (%)
Azoxystrobine	0.02 – 1.0	0.9980	0.02	98.7 (8.1)	16.0	0.20	94.3 (21)	42.2	0.80	93.7 (9.4)	19.2
Chlorfenvinphos	0.10 – 5.0	0.9990	0.10	96.1 (12)	23.5	1.0	98.4 (22)	44.1	4.0	92.6 (7.4)	14.8
Chlorpyrifos-ethyl	0.05 - 2.5	0.9980	0.05	99.6 (9.2)	18.7	0.50	93.0 (20)	40.3	2.0	101 (6.6)	13.3
Diuron	1.0 - 50	0.9990	1.0	97.3 (9.8)	19.7	10	89.3 (23)	45.5	40	99.8 (9.9)	19.7
3,4-dichloroaniline	0.05 - 2.5	0.9987	0.05	95.7 (10)	20.5	0.50	96.2 (8.0)	46.2	2.0	91.6 (7.4)	14.8
3-(3,4-dichlorophenyl)-1-methylurea	1.0 - 50	0.9972	1.0	98.4 (7.1)	14.3	10	94.2 (21)	41.5	40	95.4 (9.0)	18.2
Diflufenican	0.20 - 10	0.9997	0.20	98.7 (11)	21.8	2.0	92.2 (22)	44.6	8.0	90.8 (6.9)	13.9
Dimethomorph	0.10 – 5.0	0.9988	0.10	101 (10)	20.8	1.0	97.3 (24)	47.4	4.0	103 (8.9)	17.8
Fenitrothion	0.50 - 25	0.9958	0.50	96.0 (8.7)	17.5	5.0	92.9 (22)	42.8	20	93.6 (10)	20.0
Isoproturon	0.10 – 5.0	0.9982	0.10	95.5 (11)	21.9	1.0	96.9 (25)	51.0	4.0	88.7 (9.4)	19.0
Linuron	0.10 – 5.0	0.9989	0.10	97.9 (8.9)	17.9	1.0	95.1 (22)	44.8	4.0	95.0 (11)	21.6
Norflurazon	0.20 - 10	0.9985	0.20	95.4 (8.5)	16.9	2.0	100 (21)	42.5	8.0	95.8 (7.4)	15.1
Procymidon	0.20 - 10	0.9995	0.20	105 (6.7)	13.4	2.0	95.9 (20)	40.5	8.0	102 (7.3)	14.6
Spiroxamine	0.02 – 1.0	0.9990	0.02	96.0 (8.0)	16.2	0.2	92.2 (22)	44.8	0.80	91.1 (11)	21.5
Tebuconazole	0.10 – 5.0	0.9989	0.10	100 (11)	21.3	1.0	96.1 (23)	45.7	4.0	96.7 (12)	23.5