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Developing new adsorbents for the passive sampling of organic pollutants in the atmosphere – comparison with existing systems

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「データは嘘をつかないよ」
– 乾 貞治

“Data do not lie.”
– Inui Sadaharu

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List of acronyms

AAS: Active air sampler
ASE: Accelerated solvent extraction
ASPA: Association pour la surveillance et l'étude de la pollution atmosphérique en Alsace (Association for the monitoring and study of atmospheric pollution in Alsace)
BTEX: benzene, toluene, ethylbenzene, xylenes
CAR: Carboxen®
CNT: Carbon nanotubes
DC: Depuration compound
DVB: Divinylbenzene
GC: Gas chromatograph or gas chromatography
GFF: Glass fibre filter
HLB: Hydrophilic-lipophilic-balanced
HVS: High volume sampler
LC: Liquid chromatograph or liquid chromatography
LOD: Limit of detection
LOQ: Limit of quantification
LVS: Low volume sampler
MS / MSMS: Mass spectrometry / Tandem mass spectrometry
N-C: Nitrgoen-doped carbon
N-CNT: Nitrogen-doped carbon nanotubes
OCP: Organochlorine pesticides
PA: Polyacrylate
PAH: Polycylic aromatic compounds
PAS: Passive air sampler
PBDE: Polybrominated diphenyl ethers
PCB: Polychlorinated biphenyls
PCDD: Polychlorinated dibenzodioxins
PDMS: Polydimethylsiloxane
PM: Particulate matter
PSA: Primary-secondary amines
PUF: Polyurethane foam
SiC: Silicium carbide
SPE: Solid phase extraction
SPMD: Semi-permeable membrane device
SPME: Solid phase micro extraction
SR: Sampling rate
(S)VOC: (Semi-)volatile organic compounds
TSP: Total suspended particles

Résumé de thèse en français

Introduction

Les composés organiques semi-volatiles (COSV) sont des composés qui peuvent se retrouver dans l'air à la fois dans les phases gazeuse et particulaire de l'atmosphère. Ces polluants incluent les hydrocarbures aromatiques polycycliques (HAP), les polychlorobiphényles (PCB), les polybromodiphényléthers (PBDE), les phtalates et les pesticides. Ceux suivis dans cette étude sont les HAP, les PCB et les pesticides, cette dernière famille étant divisée entre les pesticides organochlorés (OCP), les non chlorés volatiles analysés par chromatographie gazeuse (GC) et les non chlorés peu volatils analysés par chromatographie liquide (LC).

Les PCB sont interdits en France depuis 1987, mais il est possible d'en retrouver dans d'anciens appareils électriques. Les HAP proviennent de combustions incomplètes et sont donc régulièrement émis par les industries et les particuliers. Les pesticides sont majoritairement utilisés dans l'agriculture, bien que certains insecticides pussent être utilisés par les particuliers. Les OCP sont interdits à la production et la vente dans tous les pays signataires de la convention de Stockholm, mais il est encore possible d'en retrouver des traces à cause de leur persistance dans l'environnement.

Plusieurs techniques existent pour suivre ces polluants dans l'air. La plus commune est l'utilisation d'échantillonneurs dits "actifs" : munis d'une pompe, ils aspirent l'air à un débit régulier pendant une durée définie. Les polluants en phase gazeuse sont retenus sur un adsorbant et les particules sont piégées sur un filtre. Les adsorbants les plus communs sont la mousse de polyuréthane (PUF) et la résine XAD®-2, tandis que les filtres sont majoritairement en fibres de quartz (GFF) ou de verre.
Les échantillonneurs actifs peuvent pomper entre 0.5 et 30 $m^3.h^{-1}$ selon qu'ils sont "haut débit" ou "bas débit". Connaître la quantité d'air mesurée est un avantage qui permet de calculer précisément les concentrations en polluants dans l'air.

Cependant, ces systèmes posent plusieurs inconvénients : ils sont volumineux, lourds à transporter, bruyants, et nécessitent de l'électricité et un entretien régulier.
Une alternative est l'échantillonnage dit "passif" : un adsorbant (en tube ou galette) est placé à l'endroit où l'on souhaite faire la mesure, et l'air diffuse librement à travers le matériau. Actuellement, les adsorbants les plus utilisés sont la PUF et la résine XAD®-2. Cependant, bien que ces matériaux permettent d'adsorber les polluants atmosphériques en phase gazeuse, la phase particulaire ne peut être recueillie que superficiellement.

On recherche donc un matériau utilisable comme capteur passif qui puisse à la fois adsorber la phase gazeuse et collecter les particules. C'est pourquoi la mousse de carbure de silicium (SiC) a été sélectionnée : sa surface spécifique moyenne peut être agrandie par greffage de carbone ou nanotubes de carbone (CNT), ce qui la rend efficace pour capter les gaz, et elle possède une porosité ouverte à larges fenêtres très adaptée au piégeage des particules. Une méthode d'analyse a été développée pour quantifier les polluants présent sur la SiC, ce qui a permis de comparer la mousse à la résine dans de multiples campagnes de mesure. Pour la vaste majorité des composés recherchés, la mousse de SiC donnait de meilleurs résultats de que la résine. Une fois cette conclusion faite, deux méthodes différentes ont été utilisées pour calculer les débits d'échantillonnage de la mousse, donnée indispensable pour les capteurs passifs.

Adsorbants pré-sélectionnés pour servir de capteurs passifs

Trois matériaux carbonés ont été sélectionnés comme alternative à la PUF et la résine XAD®-2. Il s'agit de la mousse de CNT, du feutre de graphite et de la mousse de SiC.

La mousse de CNT a beaucoup été étudiée en tant que cartouche de SPE (solid phase extraction) pour purifier des échantillons d'eau, mais des tests plus récents ont été réalisés en utilisant la mousse comme adsorbants de polluants dans l'air. Elle possède une grande surface spécifique pouvant aller de 50 à 1315 m² g^{-1}, ce qui la rend très efficace pour adsorber des composés gazeux. En revanche, elle possède des pores allant de 50 à 100 nm de diamètre, ce qui ne permettrait de piéger que les particules les plus fines, car elles peuvent aller jusqu'à 10 µm de diamètre.

Le feutre de graphite est principalement utilisé comme support de catalyseurs nanoscopiques ou comme cathode dans des systèmes électrochimiques. Il a été utilisé dans des systèmes de purification d'eau, mais toujours greffé avec un matériau ayant une plus grande surface spécifique. Celle du feutre de graphite est de l'ordre de 1 m² g^{-1}, similaire à la PUF. Cependant, sa porosité ouverte en fait un bon candidat pour la collecte de particules.

La mousse de SiC est utilisée majoritairement comme support de catalyseur. Sa structure rigide et sa porosité ouverte en font un excellent support, et dont des qualités recherchées pour un capteur passif d'air. Les fenêtres a sa surface ont entre 510 et 4000 µm de diamètre et conduisent à un réseau de macro- et mésopores adapté au piégeage de particules. La SiC a une surface spécifique moyenne, entre 10 et 100 m² g-1, qui peut être agrandie en y greffant du carbone ou des CNT dopés à l'azote (N-C ou N-CNT).

Tests en laboratoire

Tout d'abord, des tests ont été réalisés en laboratoire pour déterminer la capacité de ces trois matériaux à retenir les polluants et trouver une méthode d'extraction adaptée.

Chaque matrice a été dopée avec 100 µL d'une solution de HAP, PCB et OCP à 10 mg L^{-1}. Cette quantité a été répartie de manière aussi homogène que possible sur la surface des adsorbants. Ils ont ensuite été extraits par extraction accélérée par solvant (ASE) avec la méthode suivante : 3 cycles de 15 mn, à 150 °C et 1500 psi, avec 100 % d'acétonitrile. Les extraits ont été évaporés jusqu'à la goutte par des évaporateurs rotatifs, puis resolubilisés dans 1 mL d'acétonitrile. De l'eau salée (1,5 % NaCl) a été ajoutée pour obtenir une solution de 20 mL dans laquelle 20 µL de naphtalène d8 à 10 mg L^{-1} ont été ajoutés. Cette solution a ensuite été extraite par micro-extraction en phase solide (SPME) manuelle. L'extraction a été faite avec une fibre en polydiméthylsiloxane (PDMS) de 100 µm de diamètre, pendant 40 mn à 80 °C avec agitation. La fibre a ensuite été manuellement insérée et désorbée dans l'injecteur du GC. Le chromatographe était couplé à un spectromètre de masse utilisé en tandem (MSMS) équipé d'une trappe ionique.

Les résultats sont exprimés en aires relatives, qui sont obtenues en divisant l'air du pic d'un produit par l'aire du pic de son étalon interne.

Que ce soit pour les HAP, PCB ou OCP, de bien meilleurs résultats ont été obtenus pour la mousse de SiC, qui semble mieux extraite que la mousse de CNT et le feutre de graphite. Les aires relatives des pics des produits étaient dix fois supérieures dans les extraits de mousse SiC que dans les autres extraits. Ci-dessous, l'exemple des HAP sur la Figure 1 :

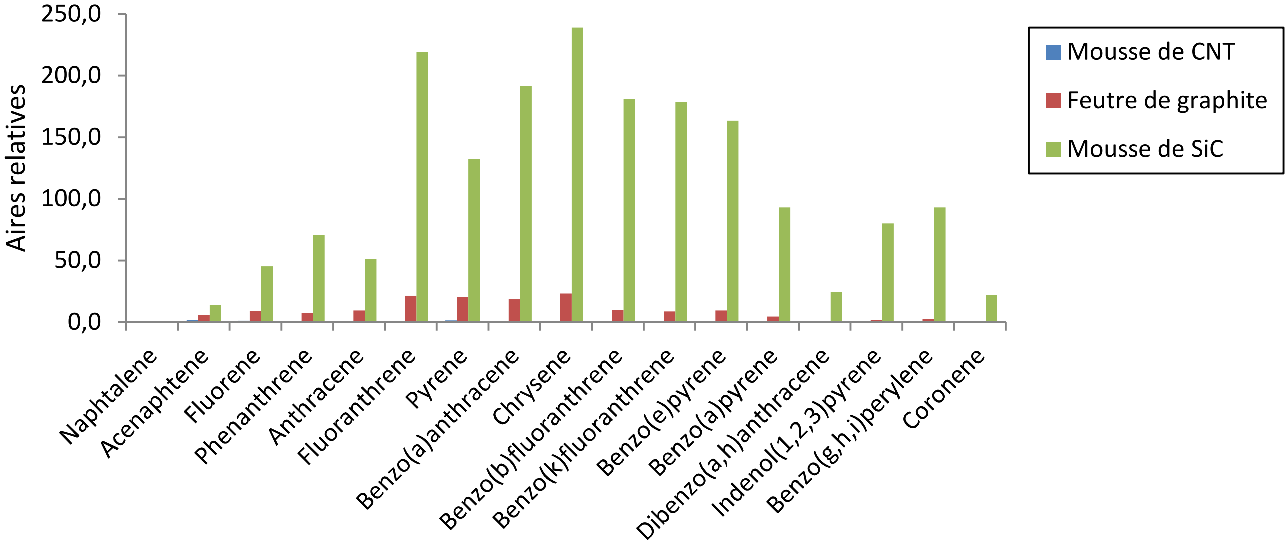


Figure 1 – Aires relatives des HAP extraits des trois adsorbants pré-sélectionnés

Peu de différences ont été constatées entre mousse de CNT et feutre de graphite pour les PCB et OCP, bien que les PCB les plus lourds aient été mieux extraits du feutre. Cependant, leurs résultats diffèrent grandement pour les HAP : seuls six HAP ont été extraits de la mousse de CNT, ceux ayant la plus légère masse moléculaire. Les dix-sept HAP ont tous pu être extraits du feutre de graphite, avec des aires relatives cinq fois supérieures à celles de la mousse de CNT. Les résultats sont présentés dans le graphe en Figure 2 :

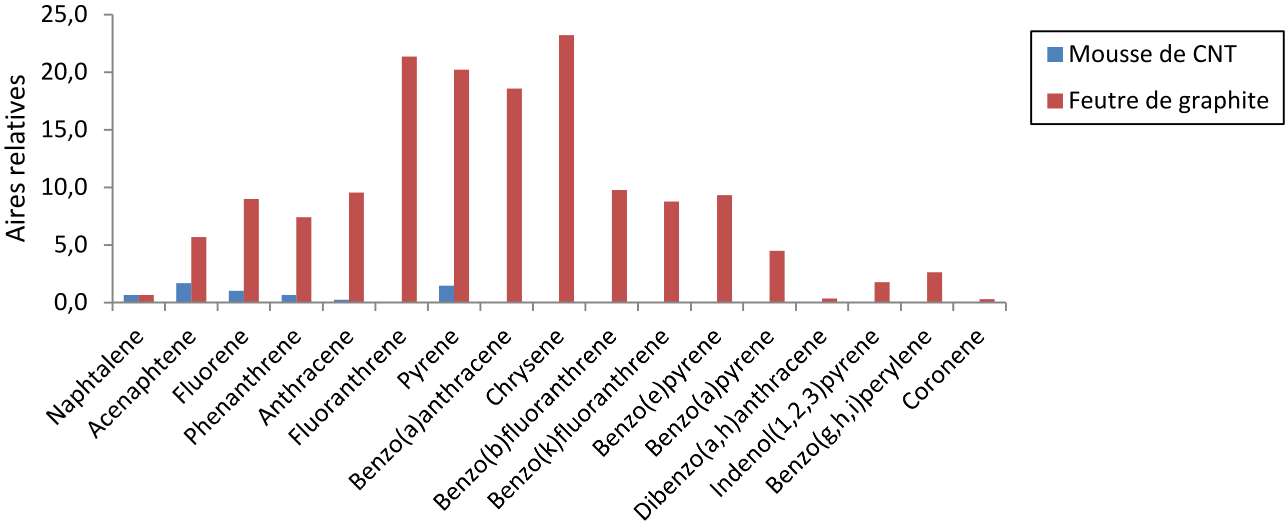


Figure 2 – Aires relatives des HAP extraits de la mousse de CNT et du feutre de graphite

Afin de confirmer les résultats importants de la mousse de SiC, d'autres mousses ont été dopées et extraites, mais les résultats obtenus étaient du même ordre de grandeur.
Pour vérifier que les HAP étaient en effet mal extraits de la mousse de CNT et que leurs faibles aires n'étaient pas dues à une interférence de la matrice, une nouvelle mousse propre a été extraite, et c'est l'extrait obtenu qui a été dopé. Les résultats ont confirmé que le problème était bien l'extraction des produits et non la matrice elle-même.

Ces résultats peuvent s'expliquer par l'hydrophobicité des produits et matériaux utilisés. La mousse de CNT est un matériau très hydrophobe, qui a donc une forte affinité pour les produits hydrophobes comme les HAP. Un solvant de moyenne polarité comme l'acétonitrile ne peut donc pas les extraire. La mousse de SiC est le matériau le moins hydrophobe des trois, il est donc plus facile d'en extraire les HAP, PCB et OCP.

Suite à ces observations, la mousse de CNT a été écartée. En plus de fortement retenir les HAP, ce matériau est difficile à synthétiser aux dimensions désirées : au-delà de 1,5 cm de hauteur, des fissures apparaissaient lors du traitement thermique en fin de synthèse. La mousse de CNT n'a donc pas été retenue comme capteur passif.

Campagne de mesure en extérieur

En complément des tests en laboratoire, une campagne de mesure à été réalisée au jardin botanique de Strasbourg afin de comparer le feutre de graphite et la mousse de SiC à la résine XAD®-2 actuellement utilisée.

En plus des HAP, PCB et OCP, les pesticides "GC" non chlorés ont été recherchés. La préparation des échantillons et l'analyse des pesticides se sont déroulées de la même façon que pour les autres composés.

La campagne a duré deux semaines ; chaque semaine, un feutre, une mousse et un tube de résine étaient placés côte à côte à l'extérieur, et récupérés à la fin de la semaine.

Les résultats des HAP et pesticides GC étaient contradictoires : la première semaine la résine XAD®-2 donnait les meilleurs résultats, tandis que la deuxième semaine la mousse de SiC était plus efficace. Pour les OCP, les trois adsorbants donnaient des résultats similaires.

Pour les PCB, en revanche, une même tendance a été observée les deux semaines, différenciant les capteurs. Les graphes de résultats sont présentés dans les Figures 3 et 4.

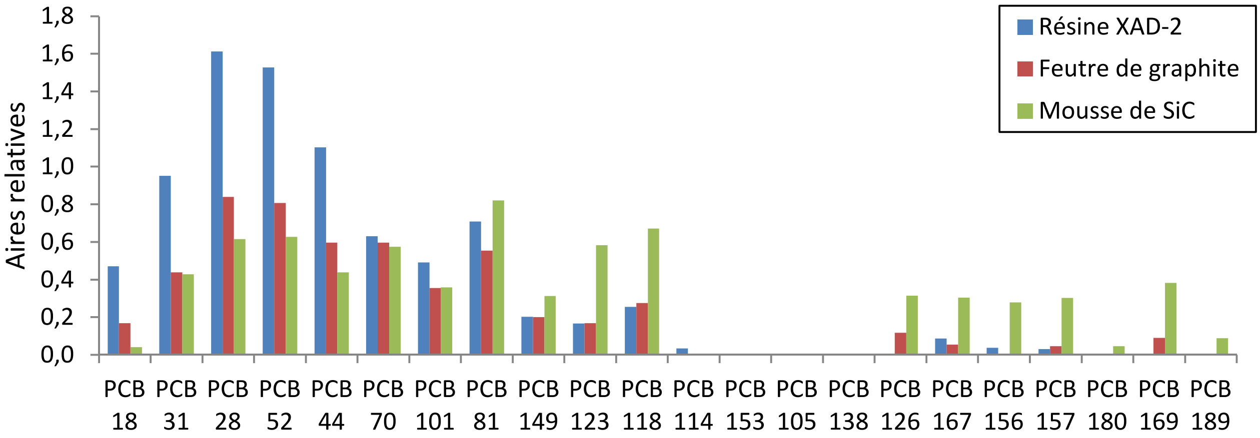


Figure 3 – Aires relatives des PCB détectés la première semaine de mesure

Les PCB les plus volatils ont été adsorbés en plus grandes quantités dans la résine XAD®-2, tandis que pour les PCB de plus haut poids moléculaire, la mousse de SiC était le meilleur capteur. Le feutre de graphite avait des résultats proches de la SiC, mais est comme la résine plus efficace pour les composés légers.

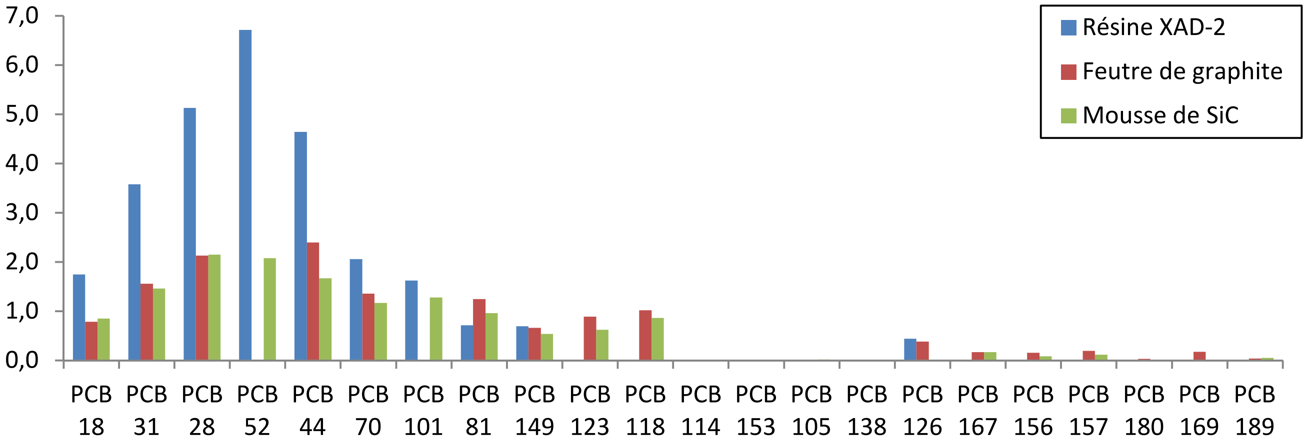


Figure 4 – Aires relatives des PCB détectés la deuxième semaine de mesure

Ces résultats étaient ceux attendus au vu des caractéristiques des matériaux : la résine a une grande surface spécifique de 300 m² g^{-1}, adaptée à l'adsorption de composés gazeux, mais elle possède des pores nanoscopiques dans lesquelles peu de composés particulaires peuvent être piégés. A l'inverse, la SiC a une surface spécifique dix fois inférieure mais possède des macropores, ce qui explique sa capacité à capter les polluants sur une large gamme de masses moléculaires. Le feutre de graphite possède la plus petite surface spécifique à 1 m² g^{-1}, ce qui en fait le moins bon candidat à la collecte de composés volatils malgré les bons résultats obtenus durant cette campagne de mesure. Sa porosité ouverte, bien qu'adaptée au captage de particules, n'est pas aussi efficace que celle de la mousse de SiC.

Conclusion

La mousse de CNT a été le premier matériau écarté de l'étude en raison de sa trop grande affinité avec les composés hydrophobes, particulièrement les HAP qui ne sont presque pas extraits de cette matrice.

Le feutre de graphite, bien que donnant des résultats similaires à la mousse de SiC, est également très hydrophobes et certains composés de haut poids moléculaire sont plus difficilement extraits. De plus, sa très faible surface spécifique pourrait être une limite à la quantité de polluant adsorbée sur de plus longues durées.

C'est pourquoi la mousse de SiC a été retenue. Sa structure rigide et son réseau de macro- et mésopores en font un excellent matériau pour la collecte de particules, et bien que sa surface spécifique moyenne de 30 m² g^{-1} ne soit pas aussi efficace que la résine XAD®-2 pour l'adsorption de composés gazeux, elle pourra être augmentée via greffage de N-C ou N-CNT. De plus, étant le moins hydrophobe des matériaux considérés, elle permettra de capter un plus grand nombre de composés, notamment des pesticides polaires.

Chapitre 2 : Développement d'une méthode d'analyse

La méthode proposée dans cette étude utilise la GC et la LC couplées à la spectrométrie de masse en tandem (MSMS) pour l'analyse des composés, techniques couramment utilisées. En revanche, la préparation des échantillons utilise successivement l'ASE, l'extraction en phase solide (SPE) et la SPME. Ces trois techniques n'ont encore jamais été couplées pour la préparation d'échantillons environnementaux.

Evaporer les extraits d'ASE dans un évaporateur rotatif conduit à des pertes des produits les plus volatils comme le naphtalène lorsqu'ils ne sont présents qu'à l'état de traces dans l'échantillon.

Utiliser la SPE permet de concentrer l'extrait sans risquer l'évaporation de ces produits. De plus, la SPE est également une technique de purification ; elle réunit donc deux étapes de préparation en une seule. Pour finir, la SPME est une deuxième concentration qui sert également d'étape d'injection. Coupler ces trois techniques permet de préparer rapidement des échantillons en utilisant un minimum de solvants et en se passant d'étapes d'évaporation agressives. Les concentrations et purifications successives permettent d'obtenir des limites de détection et de quantification plus basses qu'avec d'autres techniques de préparation.

Extraction accélérée par solvant (ASE)

Les extractions ont été faites sur un appareil DIONEX® ASE 300, qui accepte des cellules de 34, 66 et 100 mL. Les tubes de résine ont été faits aux dimensions des cellules de 100 mL (16.0 × 3.0 cm), tandis que les cylindres de mousse de SiC ont été découpés aux dimensions des cellules de 34 mL (5.1 × 3.0 cm). Cette plus petite taille avait été choisie durant la phase de tests pour réduire la consommation de solvants, mais la mousse s'est par la suite révélée efficace à ces dimensions et elles ont été conservées.

Une méthode de nettoyage par ASE existait déjà : un cycle de 10 mn à 80 °C et 1500 psi avec un mélange 50/50 (v/v) hexane/dichlorométhane. Cette méthode était utilisée pour la résine XAD®-2, mais est également efficace pour la mousse de SiC. Les capteurs sont nettoyés avec cette méthode avant et après utilisation.

Une méthode d'extraction validée était également en place : trois cycles de 10 mn à 150 °C et 1500 psi avec 100 % d'acétonitrile. Cette méthode a été testée sur de la résine XAD®-2 et de la mousse de SiC dopée avec 50 µL d'une solution de HAP, PCB et OCP à 10 ml L^{-1}. L'extraction était efficace, mais très longue et requérait une grande quantité de solvant. Plusieurs tests ont été réalisés afin d'optimiser l'extraction.

Tout d'abord, la durée des cycles a été réduite de 15 à 10 mn, n'entraînant aucune perte pour les trois familles de composés, même les HAP. Ensuite, le nombre de cycles a été réduit de trois à deux. Seuls certains HAP sont encore détectés après un troisième cycle d'extraction ; les PCB et OCP sont extraits en quasi-totalité dès le premier cycle. La Figure 5 montre l'exemple des PCB :

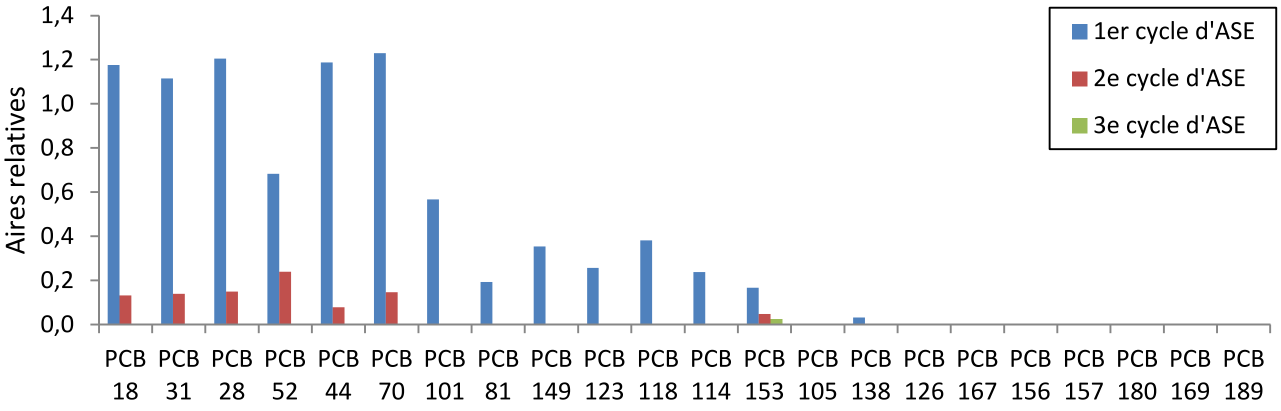


Figure 5 – Aires relatives des PCB extraits de la mousse de SiC après 1, 2 et 3 cycles d'ASE

La méthode retenue est donc la suivante : 2 cycles de 10 mn à 150 °C et 1500 psi. L'acétonitrile a été conservée comme solvant car les étapes suivantes, SPE et SPME, se font dans des solutions aqueuses. Un solvant miscible à l'eau était donc nécessaire.

Extraction en phase solide (SPE)

Les extraits obtenus en ASE ont un volume d'environ 100 mL d'acétonitrile. Afin d'augmenter l'affinité des polluants pour la phase apolaire des cartouches de SPE, un solvant plus polaire que l'acétonitrile était nécessaire ; de l'eau est donc ajoutée à l'extrait pour obtenir des échantillons d'un litre. La solution aqueuse est mise à pH 3 par ajout d'acide nitrique afin que les pesticides polaires du mélange soient protonés et puissent être retenus par les cartouches SPE.
Un volume d'un litre a été choisi afin que l'acétonitrile puisse jouer le rôle de "modificateur organique". Il s'agit d'un solvant organique communément ajouté aux solutions aqueuses lorsque des HAP sont extraits en SPE afin de favoriser leur extraction. La quantité de modificateur peut varier de 5 à 25 % du volume de la solution, mais il n'y a en général pas d'amélioration particulière au-delà de 10 %. C'est pourquoi les extraits de 100 mL d'acétonitrile sont mis en solutions aqueuses d'un litre.

Les HAP et PCB sont communément extraits avec des cartouches C_{18}, bien que les PCB puissent être extraits avec des cartouches plus polaires. Les pesticides, OCP ou non chlorés, sont plus couramment extraits avec des cartouches plus polaires comme les HLB (hydrophilic-lipophilic-balanced) ou PSA (primary-secondary amines), mais ils peuvent être extraits avec des C_{18}. Ce sont donc ces cartouches C_{18} qui ont été retenues pour cette étude, étant un bon compromis pour l'extraction de tous les composés d'intérêt.
Le choix de l'éluant a été plus difficile. Les HAP sont principalement élués avec des solvants tels que le méthanol, l'acétone ou l'acétonitrile, bien que des solvants apolaires comme l'hexane et le dichlorométhane puissent être utilisés. Hexane et dichlorométhane, ainsi que le pentane, sont les solvants utilisés en majorité pour éluer les PCB. Enfin, les pesticides nécessitent des solvants plus polaires comme le méthanol, l'acétonitrile ou l'acétone.
La plupart des SPE n'utilisent qu'un seul éluant, bien qu'il soit possible d'en utiliser deux de polarités différentes. Dans cette étude, afin d'extraire au moins le grand nombre d'analytes différents, trois éluants sont utilisés successivement : l'acétate d'éthyle pour les HAP et pesticides, le toluène pour les PCB puis l'acétonitrile car tous les composés sont solubles dans ce solvant.

Les rendements d'extraction ont été calculés pour la majorité des composés. Ces calculs ont été faits après la SPE de trois solutions aqueuses de 1 L dopées avec 100 µL d'une solution de polluants à 10 mg L^{-1}. De manière générale, les PCB donnaient les meilleurs rendements avec une moyenne de 91,4 %, tandis que les HAP avaient les plus bas avec une moyenne de 87,0 %. Les OCP avaient des rendements autour de 89,3 % tandis que les autres pesticides étaient à 90,4 %.
Cette étape de SPE donnait donc de bons rendements. Sur les 67 composés testés, 47 (70 %) avaient des rendements supérieurs à 80,0 %.

Micro-extraction en phase solide (SPME)

Après la SPE, les échantillons sont évaporés sous hotte. Il s'agit d'un procédé plus doux que l'évaporateur rotatif ou l'évaporation sous azote, ce qui limite les pertes de composés volatils. La goutte restante est resolubilisée dans 1 mL d'acétonitrile, et 100 µL de cette solution sont injectés en LC-MSMS. De l'eau salée (1,5 % NaCl) est ajoutée aux 900 µL restants pour obtenir une solution de 20 mL. Celle-ci est ensuite extraite par SPME puis injectée en GC-MSMS.

Une méthode SPME existait déjà pour les HAP et PCB, et elle convenait également aux OCP qui ont été ajoutés à la même méthode d'analyse. L'extraction durait 40 mn à 80 °C en utilisant une fibre en PDMS de 100 µm de diamètre. Pendant la phase de test, il a été constaté que des HAP restaient adsorbés sur la fibre et contaminaient les échantillons suivants. La durée de désorption de la fibre a donc été augmentée à 15 mn, et entre chaque échantillon de l'acétonitrile pure était extraite 40 mn à 80 °C. Cette étape servait à la fois de nettoyage et de blanc.

Pour les pesticides de GC, deux méthodes SPME existaient selon que les pesticides devaient être dérivés ou non. Le but était de n'avoir plus qu'une seule méthode pour tous ces pesticides.

Tout d'abord, une fibre a dû être choisie entre une polyacrylate (PA) de 85 µm, une PDMS de 100 µm et une polydiméthylsiloxane-divinylbenzène (PDMS-DVB) de 65 µm. Trois extractions ont donc été faites sur des solutions aqueuses à pH 3 (ajout d'acide nitrique) et 1,5 % de NaCl contenant 50 µg L^{-1} de pesticides. Les extractions ont duré 40 mn à 50 °C avec agitation. Juste avant l'insertion de la fibre SPME dans le GC, 2 µL de l'agent de dérivation M*t*BSTFA ont été injectés manuellement avec une seringue.

La fibre PDMS-DVB donnait des résultats deux à quatre fois inférieurs à ceux des fibres PA et PDMS ; elle a donc été immédiatement écartée. Les fibres PA et PDMS donnaient des résultats similaires pour plusieurs pesticides, mais c'est la PA qui a été sélectionnée pour sa capacité à extraire les pesticides polaires qui étaient peu ou pas détectés avec la PDMS. Ces composés sont donnés en exemple dans la Figure 6 :

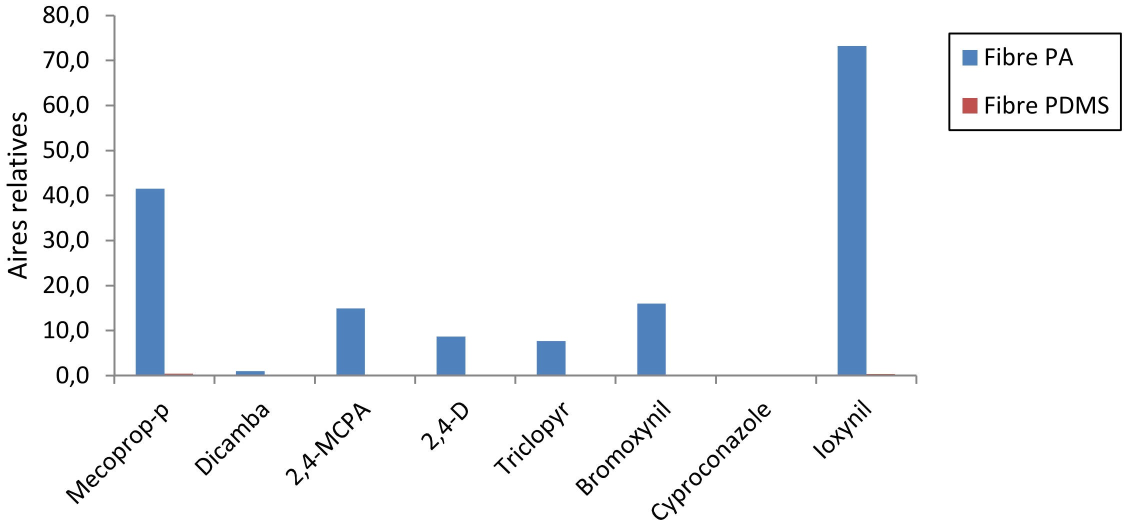


Figure 6 – Aires relatives des pesticides polaires extraits avec les fibres PA et PDMS

Le deuxième paramètre considéré a été le pH de la solution. Les pesticides ayant une fonction – OH doivent être dérivés pour être détectables, et utiliser une solution à pH 3 permet à ces pesticides d'être protonés et donc ciblés par l'agent de dérivation.

L'extraction a duré 40 mn à 50 °C avec agitation et a été réalisée avec une fibre PA de 85 µm. La solution extraite était de l'eau salée (1,5 % NaCl) contenant 50 µg L^{-1} de pesticides. La mise à pH 3 de l'une de ces solutions a été faite par ajout d'acide nitrique.

Les résultats montrent qu'une solution acide n'améliore pas l'extraction de la majorité des pesticides par rapport à une solution d'eau distillée, mais une nette amélioration est observée pour les composés polaires (Figure 7). Il a donc été décidé que les solutions pour SPME seraient toujours acidifiées avant extraction.

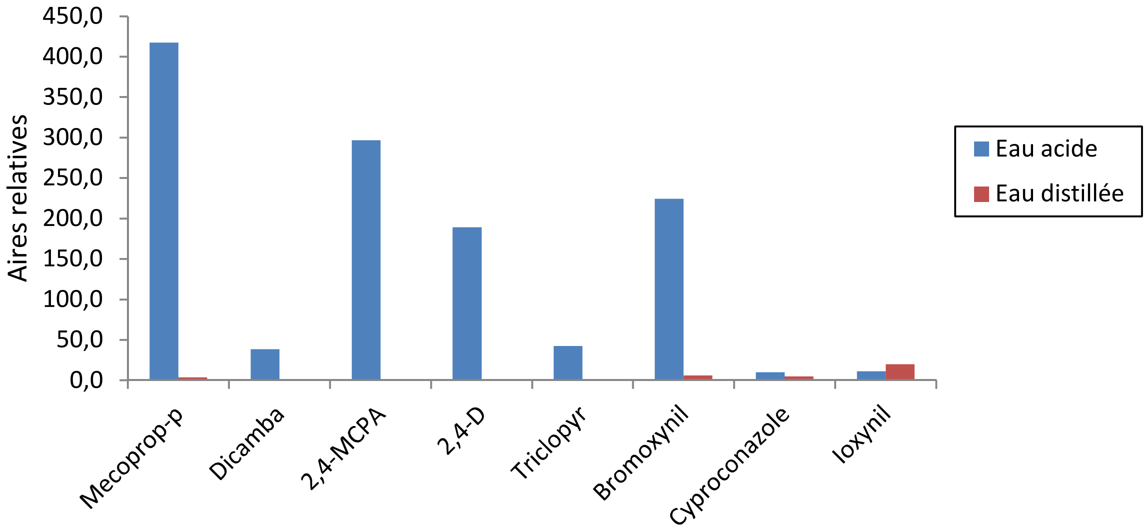


Figure 7 – Aires relatives des pesticides polaires extraits dans de l'eau acide ou distillée

Le troisième paramètre testé a été la durée de l'extraction, choisie par défaut à 40 mn. Une extraction plus longue permettrait d'améliorer l'adsorption sur la fibre des pesticides mettant du temps à atteindre l'équilibre, mais aurait l'effet inverse sur les composés atteignant rapidement l'équilibre. Une comparaison a donc été faite entre une extraction de 40 et 60 mn à 50 °C avec agitation, avec une fibre PA 85 µm. Les solutions extraites contenaient 50 µg L^{-1} de pesticides dans de l'eau salée (1,5 % NaCl) et acidifiée à pH 3 par ajout d'acide nitrique.

Les résultats de l'extraction de 60 mn sont deux à trois fois inférieurs à ceux de l'extraction de 40 mn pour tous les pesticides. De plus, certains pesticides n'ont pas été détectés alors qu'ils le sont tous après 40 mn d'extraction.

La durée d'extraction n'a donc pas été changée et reste 40 mn.

Enfin, le dernier paramètre considéré a été la température d'extraction. Par défaut, celle-ci était fixée à 50 °C. Une température plus élevée permettrait d'améliorer la mobilité des pesticides et donc leur adsorption sur la fibre SPME. En revanche, chauffer de manière trop importante fait diminuer le coefficient de distribution des produits, ce qui décroît la quantité adsorbée par la fibre.

Quatre extractions ont donc été faites à 30, 40, 50 et 60 °C, pendant 40 mn à 50 °C avec agitation, avec une fibre PA 85 µm. Les solutions extraites contenaient 50 µg L^{-1} de pesticides dans de l'eau salée (1,5 % NaCl) et acidifiée à pH 3 par ajout d'acide nitrique.

Pour la vaste majorité des pesticides, les résultats augmentaient avec la température. Cependant, la plupart de ces molécules atteignaient un palier entre 50 et 60 °C, raison pour laquelle des températures plus élevées n'ont pas été testées. Certains pesticides polaires étaient mieux extraits à 30 °C mais étaient toujours visibles à 60 °C. C'est donc l'extraction à 60 °C qui a été retenue.

Courbes d'étalonnage et limites de détection et quantification

En utilisant l'ASE, la SPE et la SPME, des courbes d'étalonnage ont été réalisées pour la résine XAD®-2 et la mousse de SiC. Chaque matrice a été dopée avec 15, 30, 50, 100, 500, 1500, 2000, 2500 et 3000 ng de polluants. Trois solutions à 10 mg L^{-1} ont été utilisées : une avec les HAP, PCB et OCP, une avec les pesticides analysés en GC, et une avec les pesticides analysés en LC.

L'analyse en GC utilisait les mêmes instruments que ceux notés au chapitre précédent. La LC était couplée à une MSMS utilisant un triple quadripôle.

Trois séries de résines et de mousses ont été dopée afin d'obtenir trois courbes par matrice par famille de produits. Chaque série de trois courbes a ensuite été moyennée pour obtenir une courbe d'étalonnage finale par matrice par famille de composés.

Les courbes d'étalonnage avaient la même allure pour la résine et la mousse. Celles des HAP, PCB, OCP et pesticides de GC étaient généralement quadratiques, tandis que celles des pesticides de LC étaient plus souvent linéaires. Cela pourrait être dû à l'étape de SPME, qui est absente dans la préparation des échantillons de LC.

Suite à cela, les limites de détection (LD) et de quantification (LQ) ont été calculées. La méthode de calcul se base sur les relations suivantes :

$$LD = 3 \times h \times R$$

$$LQ = 10 \times h \times R$$

h est la hauteur maximale du bruit de fond sur un chromatogramme blanc dans une fenêtre centrée sur le temps de rétention du produit, et R le facteur de réponse de la machine.

Dans les deux matrices, les HAP et PCB avaient en général les LD et LQ les plus stables et les plus basses, descendant jusqu'à 0,1 (LD) et 0,3 (LQ) ng capteur^{-1}.

Les pesticides de GC avaient en général les limites les plus élevées, principalement celles des pesticides polaires dérivés et des pesticides sortant tardivement de la colonne. En GC, 75 pesticides sont recherchés et l'élution dans la colonne dure plus d'une heure pour certains composés ; certains peuvent donc être dégradés en sortie de colonne et plus difficiles à détecter.

Les pesticides de LC, malgré certaines valeurs élevées dans les centaines de nanogrammes par capteur, avaient des LD et LQ basses similaires aux HAP et PCB.

Enfin, la répétabilité de la méthode a été testée. Un même jour, trois mousses de SiC ont été dopées avec 50 ng de polluants et trois avec 1500 ng. L'extraction, la préparation et l'injection ont été faites en même temps pour les six mousses. Ce test a ensuite été répété deux fois à une semaine d'intervalle. Les résultats étaient considérés répétables s'ils étaient dans une marge de 30 % du résultat médian.

De manière générale, comparer les échantillons préparés la même semaine donnait de meilleurs résultats (jusqu'à 93 % de résultats répétables) que comparer tous les échantillons préparés (jusqu'à 81,8 % de résultats répétables). La LC donnait les résultats les plus stables et les plus répétables par rapport aux pesticides de GC, HAP, PCB et OCP. Cela est probablement dû à l'utilisation de la SPME pour les composés injectés en GC : malgré l'automatisation de la SPME, cette étape reste une source d'incertitude. Elle est néanmoins une étape essentielle dans la préparation des échantillons, permettant d'atteindre des limites de détection plus basses qu'en injection liquide. La moins bonne répétabilité de cette méthode a donc été jugée acceptable, d'autant plus que les résultats obtenus tout au long de cette étude se sont révélés cohérents.

Conclusion

Cette méthode de préparation propose une nouvelle méthodologie pour les échantillons d'air, couplant ASE, SPE et SPME. L'ASE a été optimisée pour réduire le temps d'extraction et la quantité de solvant utilisée. La SPE permet de s'affranchir d'une étape d'évaporation agressive tout en purifiant l'échantillon, et la SPME offre une concentration supplémentaire de l'échantillon permettant d'atteindre de faibles limites de détection et quantification.

La SPE et la SPME ont dû être optimisées pour un grand nombre de composés et des compromis ont dû être faits. Cependant, ces deux étapes donnent de bons rendements et deux purifications successives permettent d'obtenir des chromatogrammes très propres et donc la capacité de pouvoir détecter des traces de polluants.

Chapitre 3 : Campagnes de mesure et comparaison de capteurs passifs

Une fois le nouvel adsorbant sélectionné et la méthode d'analyse développée, des campagnes de mesure de plus grande envergure ont pu être mises en place pour comparer les différents adsorbants.

Première campagne de suivi des pesticides – comparaison entre SiC et XAD®-2

Cette campagne a été réalisée conjointement avec l'Association pour la Surveillance et l'Etude de la Pollution Atmosphérique en Alsace (ASPA), chargée pour la 2^{e} année consécutive de suivre les quantités de pesticides dans l'air en Alsace.

Cette campagne a eu lieu entre avril et août 2014 sur cinq sites de topographies différentes : grandes cultures, viticulture, arboriculture, maraîchage et urbain. Chaque site a été instrumenté durant cinq semaines, par périodes d'une ou deux semaines. Pendant chaque période d'échantillonnage, un tube de résine XAD®-2 et un cylindre de mousse SiC étaient accrochés à proximité des appareils de l'ASPA. Ces appareils étaient des échantillonneurs actifs bas débit, pompant 1 m^{3} d'air par heure, et utilisant de la mousse PUF et un GFF pour collecter les pesticides. Dans le cadre de cette étude, le but était de comparer les deux capteurs passifs, et utiliser les résultats de l'ASPA pour déterminer leurs débits d'échantillonnage.

Les pesticides de GC ont été détectés en majorité dans la résine XAD®-2 : 37 détections et 22 quantifications, tandis que seuls 31 détections et 18 quantifications ont été faites pour la mousse de SiC. Quatorze pesticides différents ont été détectés dans la résine contre onze dans la mousse. Les quantités retrouvées dans la résine étaient également plus hautes avec une moyenne de 52,0 ng capteur^{-1} contre 21,5 dans la mousse. Cependant, différents pesticides ont été détectés : les produits piégés sur la mousse de SiC étaient en majorité des molécules moins volatiles que celles adsorbées par la résine, et tous les pesticides polaires détectés durant cette étude étaient sur la SiC.

On pouvait s'attendre à ce résultat car la résine XAD®-2 possède une plus grande surface spécifique plus adapté au captage de composés volatils, et est un matériau plus hydrophobe que la mousse de SiC.

Ces observations sont confirmées par les résultats des pesticides de LC, qui ont été détectés plus souvent et en plus grande quantité sur la mousse. Ces pesticides sont moins volatils que ceux analysés en GC, et sont donc plus sous forme particulaire. La mousse de SiC ayant une large porosité, elle est particulièrement adaptée au captage de particule. De plus, ces pesticides sont plus hydrophiles que ceux de GC et ont donc plus d'affinité avec la SiC que la résine XAD®-2. Au cours de l'étude, il y a eu 20 détections et 12 quantifications dans la résine contre 30 détections et 25 quantifications dans la mousse.

Les débits d'échantillonnage ont pu être calculés lorsque les capteurs actifs de l'ASPA et les capteurs passifs détectaient le même pesticide au même moment et au même endroit. Neuf débits ont pu être calculés pour la résine : ils étaient compris entre 0,78 et 4,91 m^{3} j^{-1}, en-dehors de deux valeurs aberrantes à plus de 60 m^{3} j^{-1}. Pour la mousse de SiC, huit débits ont été calculés entre 0,08 et 5,82 m^{3} j^{-1}, avec une valeur plus élevée que prévue à 16,28 m^{3} j^{-1}. Les hautes valeurs calculées ont été trouvées pour le même pesticide sur le même site à des dates très proches, il est donc possible que des conditions aient été réunies pour favoriser l'adsorption sur les capteurs passifs plutôt que sur l'actif. Il faut aussi faire remarquer que les échantillonneurs actifs utilisaient de la PUF comme adsorbant, qui a une plus faible capacité d'adsorption que la résine XAD®-2 et la mousse de SiC. La comparaison peut avoir artificiellement augmenté les résultats des capteurs passifs. Cependant, en-dehors de ces valeurs élevées, les débits d'échantillonnage calculés sont comparables aux valeurs données dans la littérature pour la résine XAD®-2.

Cette première campagne souligne donc les avantages de la mousse de SiC : le captage de particules et l'adsorption de composés polaires, que la résine XAD®-2 ne détecte pas. Cette différence se retrouve également dans les débits d'échantillonnage, où ceux de la résine sont plus élevés pour les pesticides de GC et ceux de la mousse pour les pesticides de LC.

Campagne de mesure au jardin botanique – utilisation de SiC greffée

Cette seconde campagne de mesure a été réalisée afin de comparer XAD®-2 et SiC pour le suivi de HAP, PCB et OCP en plus des pesticides non chlorés. De plus, cette campagne a été l'occasion de tester des mousses de SiC greffées avec du carbone et des CNT dopés à l'azote : SiC N-C et SiC N-CNT. La synthèse de ces mousses peut être suivie d'un traitement thermique à 900 °C, ou s'arrêter à la calcination à 450 °C. Une mousse de chaque type a été utilisée pour cette campagne.

La campagne a duré cinq semaines entre septembre et octobre 2014. Chaque semaine, deux tubes de résine et deux mousses SiC étaient accrochés à l'extérieur et récupérés après sept jours. La cinquième semaine, quatre SiC greffées ont été placées à côté : SiC N-C 450 °C, SiC N-C 900 °C, SiC N-CNT 450 °C et SiC N-CNT 900 °C.

Bien que les OCP aient été mesurés durant cette campagne, les résultats sont inutilisables : 19 sur 21 ont été détectés, à des quantités dépassant la centaine de millier de nanogrammes par capteur. Malgré la persistance de ces polluants, ils sont interdits depuis des dizaines d'années et ne peuvent pas avoir été détectés à ces quantités.

La différence entre la résine XAD®-2 et la mousse de SiC est parfaitement illustrée par les résultats des HAP, réunis dans la Figure 8 ci-dessous.

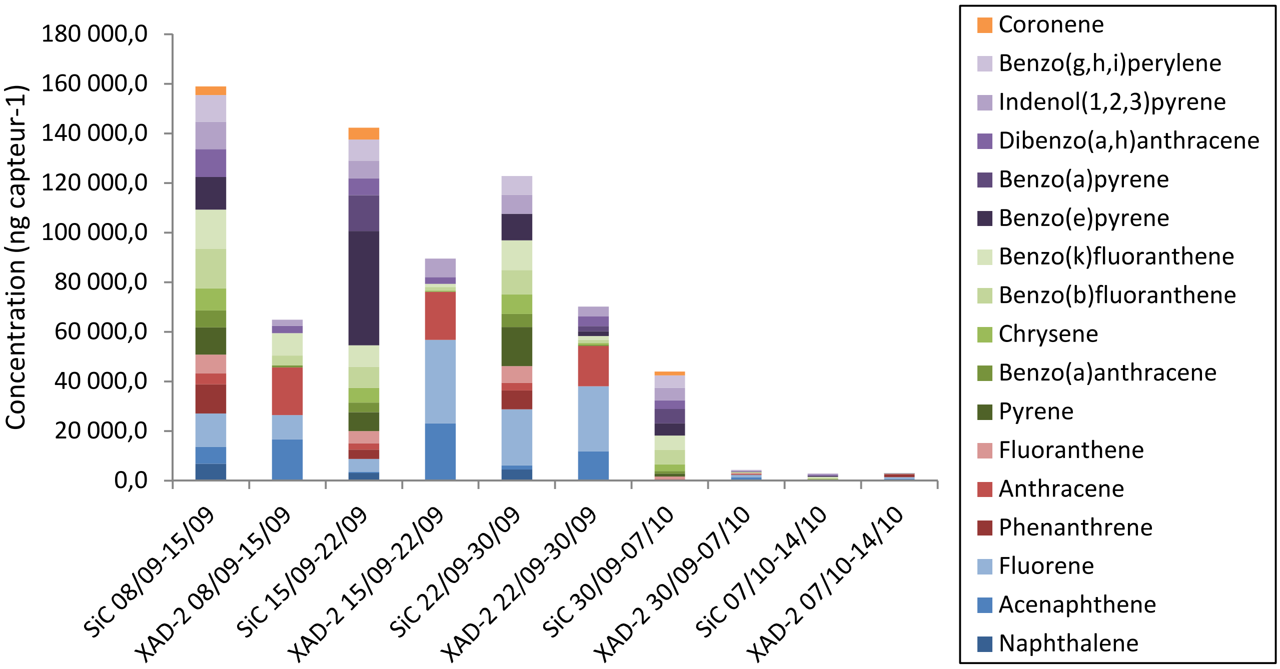


Figure 8 – Quantité de HAP détectés dans la mousse et la résine chaque semaine de mesure

Les couleurs utilisées représentent le nombre de cycles aromatiques allant de 2 (bleu) à 6 (orange), relatif à la masse moléculaire du produit. On constate que la résine XAD®-2 capte en général plus de produits légers (et donc volatils) que la mousse de SiC, qui elle capte la majorité des produits lourds (et donc particulaire). Cela se remarque également aux résultats chiffrés : pour les HAP à deux et trois cycles, la résine donne de meilleurs résultats 90 % du temps, tandis que pour les HAP de plus de trois cycles, la mousse a les plus hauts résultats 100 % du temps. En considérant tous les HAP, il y a eu 150 détections dans la SiC contre 96 dans la résine, avec des quantités moyennes respectives de 5864,4 et 3731,5 ng capteur^{-1}. La mousse de SiC apparaît donc comme le meilleur capteur pour ces composés.

Les PCB ont été plus souvent détectés dans la mousse que dans la résine avec 171 détections contre 130 sur toute la campagne, mais les quantités étaient également réparties avec une moyenne de 2026,0 ng capteur^{-1} dans la résine et 1818,8 ng capteur^{-1} dans la mousse.

La comparaison des résultats des pesticides non chlorés a donné des résultats similaires à la campagne de l'ASPA. Les pesticides de GC ont été détectés en pus grande quantité dans la résine XAD®-2 (291,4 ng campteur^{-1} en moyenne contre 178,6), mais un plus grand nombre a été retrouvé dans la mousse de SiC (9 pesticides contre 13). Un nombre similaire de pesticides de LC a été détectée dans les deux matrices, 8 dans la résine et 9 dans la mousse, mais les plus grandes quantités ont été retrouvées sur la mousse : la moyenne était de 15,2 ng capteur^{-1} dans la XAD®-2 et 66,8 ng capteur^{-1} dans la SiC.

La dernière semaine de mesure à été consacrée à la comparaison entre SiC, XAD®-2 et SiC greffées. Les résultats étaient similaires pour toutes les familles de composés, mais les HAP sont donnés en exemple sur la Figure 9.

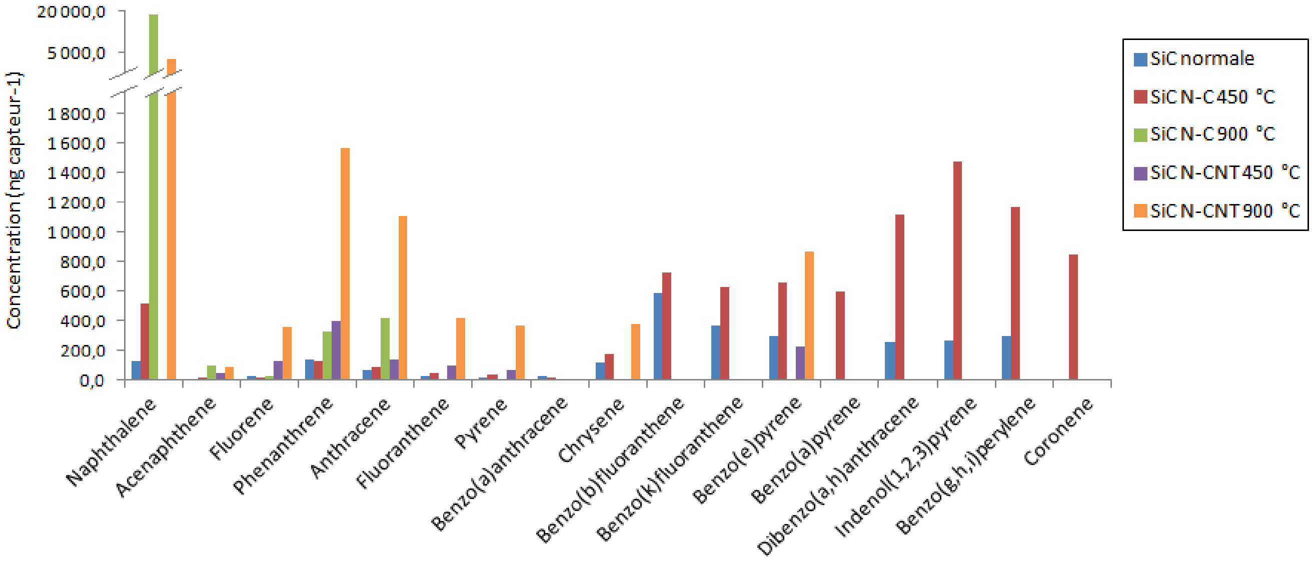


Figure 9 – Quantité de HAP détectés dans la SiC normale et les SiC greffées sur une semaine

La mousse SiC N-CNT traitée à 900 °C a un comportement similaire à la résine XAD®-2 et la mousse de CNT testée au début de cette étude : très efficace pour les HAP volatils de 2 à 3 cycles aromatiques, mais plus du tout pour les plus lourds. La SiC N-CNT ayant la même structure 3D que la SiC normale, il est probable que les HAP particulaires aient été piégés dans la mousse, mais que leur forte affinité avec les CNT hydrophobes n'ait pas permis de les extraire.

En revanche, la SiC N-C traitée à 450 °C est de loin le meilleur adsorbant pour les composés particulaires tout en étant capable de détecter les plus volatils.

Le même schéma a été observé pour les PCB. Trop peu de pesticides de GC ont été détectés pour conclure, mais pour les pesticides de LC la SiC N-C 450 °C était généralement plus efficace que la SiC N-CNT 900 °C. Cela est probablement dû à la grande hydrophobicité des CNT, qui sont donc moins aptes à adsorber ces pesticides.

Comparer les SiC greffées avec la résine XAD®-2 a clairement montré la supériorité des SiC greffées. La SiC N-CNT 900 °C est de loin le meilleur matériau pour les HAP et PCB volatils, tandis que la SiC N-C 450 °C est le plus adapté pour les particules. De plus, la SiC N-C 450 °C donne des résultats comparables à la résine pour les volatils. Elle semble donc être l'adsorbant le plus adapté pour détecter une large gamme de HAP (Figure 10) et PCB.

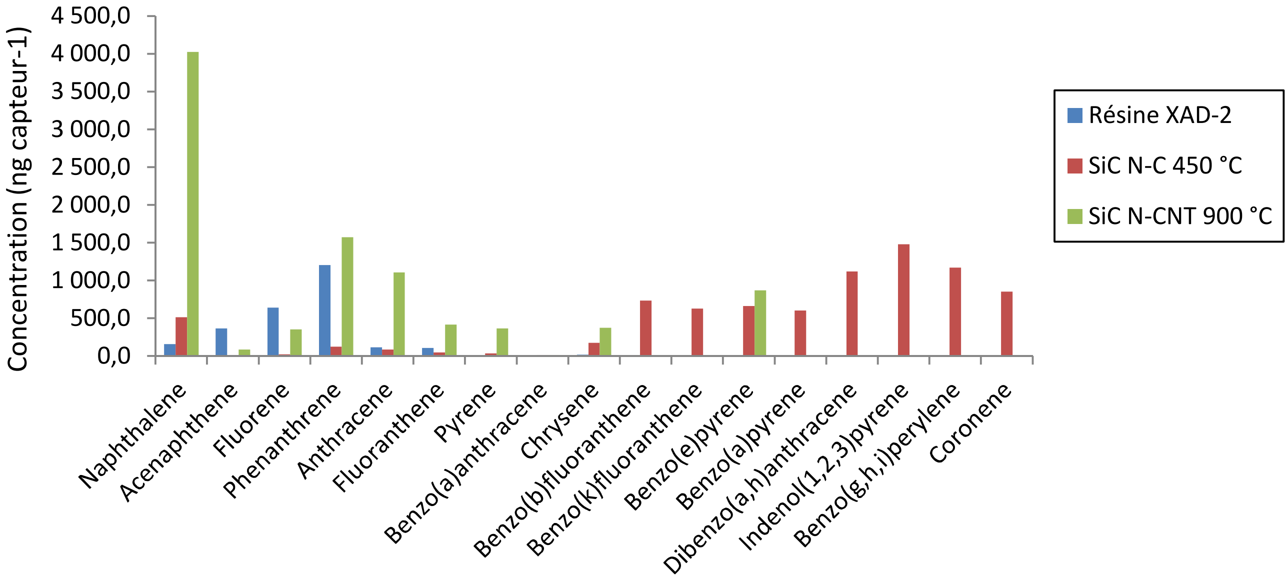


Figure 10 – Quantité de HAP détectés dans la résine XAD®-2 par rapport aux SiC greffées

Le peu de pesticides de GC détectés ne permet pas de conclure bien que la résine XAD®-2 donne toujours de bons résultats. A l'inverse, presque aucun pesticide de LC n'est détecté sur la résine tandis que N-C et SiC N-CNT donnent des résultats élevés.

Au vu de ces résultats, il a été décidé de continuer l'étude des mousses de SiC greffées, plus efficaces que la mousse de SiC normale et la résine XAD®-2 à laquelle elle était comparée jusqu'à présent.

Deuxième campagne de suivi des pesticides – comparaison entre SiC et XAD®-2

Cette campagne a été réalisée conjointement avec l'ASPA entre avril et août 2015. Elle a eu lieu sur cinq sites de topographies différentes : grandes cultures (deux sites), viticulture, arboriculture et urbain. Chaque site a été instrumenté durant cinq semaines, par périodes d'une semaine. Pendant chaque période d'échantillonnage, une mousse SiC N-C 450 °C et une SiC N-CNT 900 °C étaient accrochées à proximité des appareils de l'ASPA. Pendant cette campagne, deux types de préleveurs actifs ont été utilisés, deux "bas débits" utilisant de la PUF et un GFF. Les Partisol Plus avait un débit de 1 m^3 h^{-1} tandis que les Leckel pompaient à 2,3 m^3 h^{-1}.
Dans le cadre de cette étude, le but était de comparer les deux capteurs passifs, et utiliser les résultats de l'ASPA pour déterminer leurs débits d'échantillonnage.

Les pesticides de GC ont été détectés en plus grand nombre dans la SiC N-C, avec 90 détections et 65 quantifications contre 54 détections et 44 quantifications dans la SiC N-CNT. Cependant, les plus hautes concentrations ont été retrouvées dans la SiC N-CNT : lorsqu'un même pesticide était détecté dans les deux mousses, la N-CNT avait le meilleur résultat 77 % du temps. Cette observation est cohérente avec celles de la campagne précédente, où il a été établi que la grande surface spécifique de la SiC N-CNT était très adaptée à l'adsorption de produits volatils gazeux, mais que sa forte hydrophobicité l'empêchait de piéger des molécules plus polaires.

Les résultats sont plus équilibrés pour les pesticides de LC, avec 49 détections et 48 quantifications dans la SiC N-C et 50 détections et 47 quantifications dans la SiC N-CNT. Ces pesticides sont plus lourds et donc plus sous forme de particules que ceux de GC, ce qui peut expliquer ce résultat. SiC N-C et SiC N-CNT ont la même structure poreuse apte à piéger des particules, la seule différence est la surface spécifique plus élevée obtenue par greffage de CNT. Cependant, la plus grande hydrophobicité des CNT fait de cette mousse la moins adaptée pour les pesticides de LC, plus hydrophiles et plus facilement adsorbés sur la SiC N-C. Lorsqu'un même pesticide était détecté sur les deux mousses, la SiC N-C avait la plus haute quantité 65 % du temps.

Les débits d'échantillonnage ont pu être calculés lorsque les capteurs actifs de l'ASPA et les capteurs passifs détectaient le même pesticide au même moment et au même endroit. Sept débits ont pu être calculés pour la SiC N-C : ils étaient compris entre 0,28 et 9,97 $m^3 j^{-1}$, avec une valeur élevée de 81,80 $m^3 j^{-1}$. Onze débits ont été calculés pour la SiC N-CNT, compris entre 0,99 et 7,11 $m^3 j^{-1}$, mais quatre valeurs élevées ont été trouvées : 30,04 et 31,02 $m^3 j^{-1}$ pour les plus basses, et 196,76 et 331,73 $m^3 j^{-1}$ pour les plus hautes.

La plupart des débits élevés calculés étaient pour un même pesticide, la pendiméthaline. Il est donc possible que cela proviennent de la méthode d'analyse, qui pourrait conduire à une surestimation de notre part ou à une sous-estimation de l'autre laboratoire.

Les débits d'échantillonnage étaient, cependant, cohérents avec ceux calculés l'année précédente et avec les valeurs de la littérature pour résine XAD®-2. Pour les SiC greffées, les débits sont généralement plus élevés que ceux calculés pour la résine ou la mousse non greffée, mais c'était un résultat attendu dans la mesure où de plus grandes quantités sont détectées sur SiC N-C et N-CNT.

Conclusion

La première campagne de l'ASPA a montré les avantages de la mousse de SiC par rapport à la résine XAD®-2. Bien que la grande surface spécifique de la résine soit mieux adaptée à l'adsorption de composés gazeux, la SiC peut les adsorber aussi et offre d'excellent résultats pour les composés particulaires. De plus, sa moindre hydrophobicité lui permet de retenir des composés polaires. Ces observations sont confirmées également pour les HAP et PCB, dont les plus lourds sont mal retenus sur la résine XAD®-2. La mousse de SiC étant le capteur le plus versatile, elle est préférée à la résine.

L'utilisation de mousses SiC greffées a permis d'augmenter la surface spécifique de ce matériau, et donc sa capacité à adsorber les composés volatiles. Il a été montré que pour toutes les familles de polluants considérés, la N-CNT permet d'adsorber une plus grande quantité de produit, mais sa forte hydrophobicité empêche les produits les plus apolaires d'être extraits, principalement les HAP. C'est donc la mousse N-C SiC qui lui est préférée : ses performances sont comparables à celles de la résine XAD®-2 pour les composés volatils, et elle a donné les meilleurs résultats pour les composés particulaires. Sa plus faible hydrophobicité lui permet également de retenir des molécules polaires, elle est donc le matériau le plus versatile de tous ceux qui ont été testés durant cette étude.

Chapitre 4 : Calcul des débits d'échantillonnage

Méthodes de calcul

L'un des inconvénients des capteurs passifs est le manque d'informations directes sur leurs débits d'échantillonnage. Cependant, deux méthodes existent pour les déterminer.

L'une est la comparaison directe avec un échantillonneur actif, en utilisant l'équation suivante :

$$\mathrm{SR} = \frac{\mathrm{M_{PAS}}}{\mathrm{C_{air}} \times \mathrm{t}} \qquad (\mathrm{Eq.\,1})$$

SR est le débit d'échantillonnage en m^3 j^{-1} ou m^3 h^{-1}, M_{PAS} la masse de polluant sur le capteur passif en ng, C_{air} la concentration de ce polluant dans l'air obtenue par échantillonnage actif en ng m^3, et t la durée d'échantillonnage en jours (j) ou en heures (h).

L'autre méthode consiste à utiliser des composés de dépuration (DC), qui sont des produits non présents dans l'atmosphère, principalement des deutérés. Ils sont déposés sur le capteur passif en début de mesure, et leur décroissance pendant la campagne est proportionnelle à l'adsorption des polluants sur le capteur. L'équation reliant décroissance et adsorption est la suivante :

$$\mathrm{SR} = \frac{-\ln\frac{\mathrm{C_{DC}}}{\mathrm{C_{DC,0}}} \times \mathrm{K_{PAS-A}} \times \rho_{\mathrm{PAS}} \times \mathrm{V_{PAS}}}{\mathrm{t}} \qquad (\mathrm{Eq.\,2})$$

SR est le débit d'échantillonnage en m^3 j^{-1} ou m^3 h^{-1}, C_{DC} la concentration d'un DC dans le capteur passif à la fin de l'échantillonnage en ng $capteur^{-1}$, $C_{DC,0}$ la concentration d'un DC dans le capteur passif au début de l'échantillonnage en ng $capteur^{-1}$, $K_{PAS\text{-}A}$ le coefficient de partage capteur/air d'un polluant donné en m^3 $g^{-}1$, ρ_{PAS} la masse volumique du capteur passif en g m^3, V_{PAS} le volume du capteur passif et t la durée d'échantillonnage en jours (j) ou en heures (h).

Ces deux méthodes ont été testées pour déterminer les débits d'échantillonnage de la mousse de SiC, basées sur deux campagnes de mesure au jardin botanique de Strasbourg.

Comparaison entre échantillonnage actif et passif

Les précédents calculs de débit pour les mousses de SiC avaient donné des résultats cohérents, mais la comparaison avait été faites entre de la mousse de SiC comme capteur passif et de la PUF comme échantillonneur actif. Il a donc été décidé de faire une campagne de mesure utilisant la mousse de SiC dans des échantillonneurs actifs afin d'avoir une comparaison plus fiable avec les systèmes passifs.

La campagne s'est déroulée sur dix semaines entre juin et septembre 2015 par périodes d'une semaine. Chaque semaine, deux SiC greffées étaient placées à l'extérieur à proximité d'un échantillonneur actif utilisant une mousse de même greffage. La première semaine des N-C SiC ont été utilisées, puis des N-CNT, en alternant chaque semaine. Les quatre premières semaines, le préleveur actif utilisait une mousse suivie d'un GFF ; les six dernières, un deuxième préleveur actif a été utilisé avec uniquement une mousse de SiC. The deuxième appareil devait servir à déterminer si un filtre était nécessaire ou si la SiC retenait autant de particules. Ces systèmes actifs étaient des "bas débit" pompant 2,3 m^3 h^{-1}.

Sur l'ensemble de la campagne, presque tous les HAP, PCB et OCP ont été détectés, particulièrement durant les quatre dernières semaines. Mais contrairement à ce qui était attendu, les débits calculés grâce à l'équation 1 étaient très supérieurs à ceux calculés durant les campagnes ASPA. Pour l'ensemble de ces composés, qu'il s'agisse de ceux récoltés sur N-C SiC ou N-CNT SiC, les débits d'échantillonnages calculés étaient compris entre 0,4 et 1371,8 m^3 j^{-1}, avec des

moyennes entre 50 et 100 m^3 j^{-1} selon les produits. Sur 534 débits calculés, seuls 127 (24 %) étaient inférieurs à 10 m^3 j^{-1}, valeur limite arbitraire.
Les pesticides de GC ont donné des résultats similaires, allant de 0,3 à 85,9 m^3 j^{-1} avec une moyenne de 23,5 m^3 j^{-1} et 52 % de résultats inférieurs à 10 m^3 j^{-1}. Le même schéma est observé avec les pesticides de LC dont les débits sont compris entre 7,4 et 597,9 m^3 j^{-1}, avec une moyenne de 138,0 m^3 j^{-1} et 10 % de résultats inférieurs à 10 m^3 j^{-1}.

Plusieurs hypothèses ont été émises pour expliquer ces résultats : mélange des mousses entre actives et passives, contamination des échantillons, mais elles ont été écartées. Les résultats étant systématiques, l'erreur ou la contamination devrait être systématique et toujours sur les mêmes mousses, ce qui n'est pas réaliste sur dix semaines de mesure.
La dernière hypothèse est que la mousse de SiC n'est pas adaptée à l'échantillonnage actif. Son réseau de macro- et mésopores laisse facilement passer le flux d'air, ce qui est une qualité recherchée pour un capteur passif. Au contraire, dans un appareil muni d'une pompe, cela signifie que le temps de séjour de l'air dans la mousse est trop court et qu'il n'y a pas assez de perte de charge. Cela conduit donc à sous-estimer la quantité de polluants dans l'air, ce qui augmente artificiellement les débits d'échantillonnage des capteurs passifs.
Cette possibilité n'avait pas été envisagée avant cette campagne ; il n'a donc pas été possible d'en refaire une pour tester différentes mousses de SiC dans des échantillonneurs actifs. Les possibilités sont l'utilisation d'une mousse avec de plus petites fenêtres en surface, ou d'une mousse à porosité plus fermée.

Finalement, comme les résultats de cette campagne étaient inutilisables, la technique des composés de dépuration a été utilisée dans l'étude suivante.

Utilisation de composés de dépuration

Tout d'abord, 14 molécules deutérées ont été choisies comme composés de dépuration : quatre HAP, 8 pesticides de GC et 2 pesticides de LC.
Huit mousses de SiC normales ont été dopées avec 100 µL d'une solution à 10 mg L^{-1} des composés sélectionnés. Elles ont ensuite été placées en même temps au jardin botanique de Strasbourg. Une mousse a été récupérée après une semaine, la seconde après deux semaines, et les SiC restantes ont été enlevées tous les trois ou quatre jours.

Les mousses de SiC récupérées étaient extraites par ASE : deux cycles de 10 mn à 150 °C et 1500 psi avec 100 % d'acétonitrile. L'extrait a été évaporé jusqu'à la goutte à l'évaporateur rotatif, puis resolubilisé dans 1 mL d'acétonitrile. Afin de dériver les pesticides ayant une fonction –OH, 50 µL de M*t*BSTFA ont été ajoutés à la solution, qui a alors été chauffée à 80 °C et agitée pendant une heure. De l'atrazine a été ajoutée comme étalon interne, et la solution a été injectée par injection liquide automatique dans le GC couplé à la MSMS.

Pour tous les composés deutérés, une décroissance quadratique a été observée. Certains composés plus volatils étaient complètement désorbés avant la fin de l'étude, comme le naphtalène d8 et le nitrophénol d4. La valeur de t dans l'équation 2 a donc été modifiée en conséquence. De ces observations, $C_{DC,0}$ et C_{DC} ont été notées. ρ_{PAS} et V_{PAS} étant connus, il ne restait qu'à calculer $K_{PAS\text{-}A}$.

Il existe dans la littérature une équation pour $K_{PUF\text{-}A}$, le coefficient de partage d'un composé entre la PUF et l'air. La PUF ayant été une bonne approximation de la SiC dans les campagnes ASPA, le $K_{PUF\text{-}A}$ a été utilisé plutôt que de calculer un $K_{SiC\text{-}A}$.

Une fois cette valeur calculée, des débits d'échantillonnage ont été calculés pour les composés de dépuration eux-mêmes. Ceux-ci étaient compris entre 2,50 et 5177,4 m^3 j^{-1} avec une moyenne de 573,42 m^3 j^{-1}. Ce genre de valeurs est plus de l'ordre des échantillonneurs actifs "haut débit" que des capteurs passifs.

Après plusieurs tentatives de correction, en n'utilisant que les DC ayant subi moins de 80 % de perte durant la campagne ou en changeant de base de donnée pour obtenir d'autres valeurs pour les équations, le problème restait le même. La conclusion a été que l'utilisation de $K_{PUF\text{-}A}$ n'était pas une bonne approximation de $K_{SiC\text{-}A}$, et qu'il fallait donc déterminer ce dernier.

Il faut tout d'abord comprendre comment un $K_{PAS\text{-}A}$ est calculé. Il est proportionnel au K_{OA} (coefficient de partage octanol-air) d'un polluant, et le but est de trouver la relation linéaire reliant K_{OA} à $K_{PAS\text{-}A}$. La littérature propose un calcul expérimental de $K_{PAS\text{-}A}$, réalisable uniquement après une campagne de mesure :

$$K_{PAS-A} = \frac{C_{PAS}}{C_A} \qquad \text{(Eq. 3)}$$

$K_{PAS\text{-}A}$ est le coefficient de partage capteur passif-air d'un polluant en m^3 g^{-1}, C_{PAS} est la concentration de ce polluant dans le capteur passif en ng g^{-1} et C_A la concentration du polluant dans l'air, déterminée par échantillonnage actif, en ng m^{-3}.

Les valeurs de $K_{PAS\text{-}A}$ ainsi calculées peuvent être placées en ordonnée d'un graphe ayant les K_{OA} des polluants considérés en abscisse, et une relation peut être trouvée entre les deux. Un exemple est donné dans la Figure 11 ci-dessous. Les données utilisées pour C_{PAS} et C_A proviennent de la campagne précédente faite au jardin botanique. Les seuls résultats utilisés pour tracer des courbes sont ceux ayant donné des débits d'échantillonnage inférieurs à 10 m^3 h^{-1}.

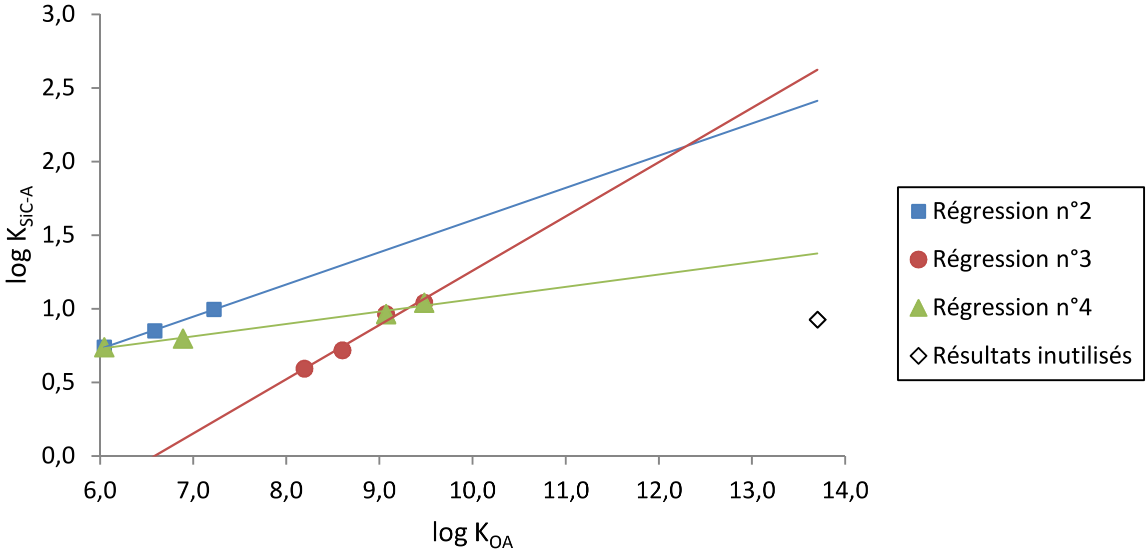


Figure 11 – Régressions linéaires utilisant les résultats HAP de la 7^e semaine de mesure

Au total, douze courbes de régression ont pu être tracées en utilisant les résultats de la campagne précédente. A chaque courbe correspondait une équation reliant $K_{SiC\text{-}A}$ à K_{OA}.

De nouveaux débits d'échantillonnage ont été calculés pour les DC en utilisant chaque équation pour $K_{SiC\text{-}A}$. Les résultats étaient bien plus cohérents avec ce qui était attendu. Une équation a permis de n'obtenir aucun débit supérieur à 10 m^3 j^{-1}, une n'avait qu'un résultat supérieur à cette valeur, et trois autres n'avaient que deux résultats au-dessus de cette limite. Lorsque cette limite était dépassée, il s'agissait toujours des mêmes produits : mécoprop d3 et nitrophénol d4 principalement, suivis du 2,4-D d3 et du métolachlore d6. Les trois premiers sont des pesticides nécessitant une dérivation : il est possible que leurs résultats d'analyse soient moins précis que pour les autres produits puisqu'ils dépendent du succès de la dérivation ; de plus, les équations utilisées n'ont pas forcément été optimisées pour les composés polaires, puisqu'ils sont mal adsorbés par les capteurs actuels. Le métolachlore donnait déjà des débits d'échantillonnage élevés durant les campagnes de l'ASPA : il est peut-être simplement très bien adsorbé sur la mousse de SiC, ou il peut y avoir un biais dans son analyse.

En-dehors de ces valeurs plus élevées, les débits d'échantillonnage étaient compris entre 0,74 et 9,94 $m^3 j^{-1}$, avec une moyenne de 2,55 $m^3 j^{-1}$. Ce sont des valeurs comparables à ce qui avait été calculé pour les mousses de SiC durant les campagnes de l'ASPA ; cette méthode des composés de dépuration semble donc être efficace.

Conclusion

Deux méthodes de calcul ont été utilisées pour déterminer les débits d'échantillonnage de la mousse de SiC.

La comparaison directe entre préleveurs actifs et passifs a donné des résultats bien trop élevés pour être probables, dans les centaines de mètres cubes par jour. Ces résultats ont été attribué à la porosité de la SiC permettant à un flux d'air forcé de passer trop facilement à le matériau. D'autres campagnes de mesure devraient être réalisées pour voir s'il est possible de remédier à cet inconvénient.

Suite à cette observation, une autre méthode de calcul a été utilisée. L'utilisation de composés de dépuration n'implique pas d'échantillonneur actif, ce sont des produits déposés sur le capteur passif en début de campagne dont la décroissance est proportionnelle à l'adsorption de polluants atmosphériques. Cette méthode a donné des résultats cohérents avec de précédentes campagnes, bien que les débits calculés n'aient été que ceux des DC. Une campagne future devrait être mise en place pour les utiliser comme ils sont sensés l'être : déposés en début de campagne et servant à calculer les débits de produits non deutérés adsorbés.

Conclusion générale

Dans cette étude exploratoire, la mousse de SiC a été choisie comme adsorbant alternatif à la PUF ou la résine XAD®-2 pour servir de capteur passif de polluants atmosphérique.

Le choix s'est fait sur les caractéristiques physique de la mousse de SiC : de larges pores et une porosité ouverte permettant de capter des particules, une surface spécifique moyenne pouvait être augmentée par greffage de carbone ou CNT permettant une bonne adsorption des composés gazeux, et hydrophobicité moindre que les adsorbants actuels permettant de retenir des composés polaires.

Une méthode d'analyse combinant ASE, SPE et SPME a été développée et optimisée pour quantifier des HAP, PCB, OCP et autres pesticides dans les mousses de SiC. Le couplage de ces trois techniques permet de préparer les échantillons rapidement, avec peu de solvants organiques et sans évaporation agressive. Les étapes de purification et concentration successives permettent d'atteindre de faibles limites de détection et quantification pour les composés recherchés.

Plusieurs campagnes de mesure ont été réalisées pour comparer la mousse de SiC à la résine XAD®-2 actuellement utilisée. Les résultats montrent que la mousse est toujours plus efficace que la résine pour le piégeage des composés particulaires et polaires. De plus, la SiC peut être greffée avec du carbone ou des nanotubes de carbone pour augmenter sa surface spécifique, ce qui la rend également plus performante pour l'adsorption de composés volatils. La SiC N-C 450 °C est l'adsorbant recommandé car elle conserve tous les avantage de la SiC classique – porosité ouverte, moindre hydrophobicité – tout en ayant une plus grande surface spécifique. Ces caractéristiques en font un excellent capteur pour une large gamme de composés.

Enfin, les débits d'échantillonnage moyens de la mousse ont été calculé de deux manières différentes : par comparaison avec des préleveurs actifs et par observation de la décroissance de composés de dépuration. Les résultats étaient comparables entre eux et sont dans le même ordre de grandeur que ceux donnés dans la littérature pour la résine XAD®-2. A l'avenir, les composés de dépuration pourront donc être utilisés pendant des campagnes de mesure pour permettre de calculer les débits d'échantillonnage de la mousse de SiC.

Introduction

Monitoring semi-volatile organic compounds

Semi-volatile organic compounds (SVOC) can be air pollutants and they are found in both the particulate and gaseous phase of the atmosphere. Such pollutants include polycyclic aromatic hydrocarbons (PAH), polychlorinated biphenyls (PCB), polybrominated diphenyl ethers (PBDE), phtalates and pesticides. Those that were monitored in this study are PAH, PCB and pesticides. The latter family was divided between organochlorine pesticides (OCP) and non-OCP.

Polycylic aromatic hydrocarbons are emitted to the atmosphere mostly from anthropogenic sources. They are a product of the incomplete combustion of organic matter, meaning there are multiple emission sources, both domestic and industrial. PAH are mainly produced from automobile fuel combustion, domestic heating and cooking with coal or wood, waste incineration, industrial aluminium or steel manufacturing and petrochemistry (Ravindra et al., 2008). Smoking also contributes to atmospheric emission of PAH, though mostly in indoor air (Choi et al., 2010).

They were included in the Aarhus protocol in 1998, binding the signatory parties to reduce their PAH emission by 1995. Currently, domestic sources are not regulated, but there have been efforts to reduce automobile sources by using catalytic converters for both gasoline and diesel engines (Ravindra et al., 2008). Twenty-six suspected or confirmed carcinogenic and genotoxic PAH have been listed by several organizations: the US Environmental Protection Agency (US-EPA), the US Agency for Toxic Substances and Disease Registry (US-ATSDR), and the European Food Safety Authority (EFSA). Seventeen of these PAH were monitored in this study, and a complete list can be found in Annex I.

Polybrominated biphenyls have been prohibited in France since 1987, and cannot be manufactured or sold. They were one of the first twelve priority pollutants listed in the Stockholm convention on persistent organic pollutants in 2001. Their main use was as insulators in transformers and capacitors, which are closed systems and cannot emit PCB during their normal use. Contamination from such electrical equipment comes from discarded material, no longer used or properly maintained. PCB used as coolants or hydraulic fluids can more easily be transmitted to the environment, but it is mainly when used as additives that they can be released outside. Such uses include plasticizers, paints, adhesives and industrial oils. (Erickson & Kaley, 2011)

PCB emission in air may come from direct volatilization, or from revolatilization of PCB accumulated in soil. It has been showed, however, that outdoor air contamination mainly comes from indoor air, rather than soil (Jamshidi et al., 2007). Differences have also been noted between lighter molecular weight PCB that are mainly in the gas phase and can thus travel far from their emission sources, and heavier molecular weight PCB that are mainly adsorbed in soil (Li et al., 2010) and whose transport is slower. Twenty-two PCB covering the whole range of molecular weights were monitored during this study. They are listed in Annex I.

Organochlorine pesticides are a special subset of pesticides. They are the chlorinated insecticides listed for elimination in the Stockholm convention on persistent organic pollutants. Nine were present in the first list in 2001: aldrin, chlordane, dichlorodiphenyltrichloroethane (DDT), dieldrin, endrin, heptachlor, hexachlorobenzene, mirex and toxaphene. Four more were added in 2009 (α-hexachlorocyclohexane, β-hexachlorocyclohexane, chlordecone, lindane) and one in 2011 (endosulfan). They are all prohibited in France and can be neither manufactured nor sold. Outside of their persistence, their behaviour is similar to other pesticides.

There are several families of pesticides, not all of which are used on plants or in agriculture. Insecticides are commonly used in private houses to repel mosquitoes, and some are made to protect pets from parasite. However, the most common use for pesticides is as plant protection products.

Pesticides can be emitted to the atmosphere by three different mechanisms: spray drift, volatilisation and re-suspension due to wind erosion. (Scheyer, 2004) Drift occurs when pesticides are sprayed over crops, and only some of the product reaches plants or soil. The finest drops are caught in the wind and stay suspended or are transported away. Volatilisation occurs after spraying, when pesticides are deposited on plants or soil. From there, the more volatile compounds can evaporate and stay in the gaseous phase. Finally, re-suspension concerns less volatile pesticides that are adsorbed on soil particles. When these particles are swept by the wind, adsorbed pesticides are carried with them. (Figure 1)

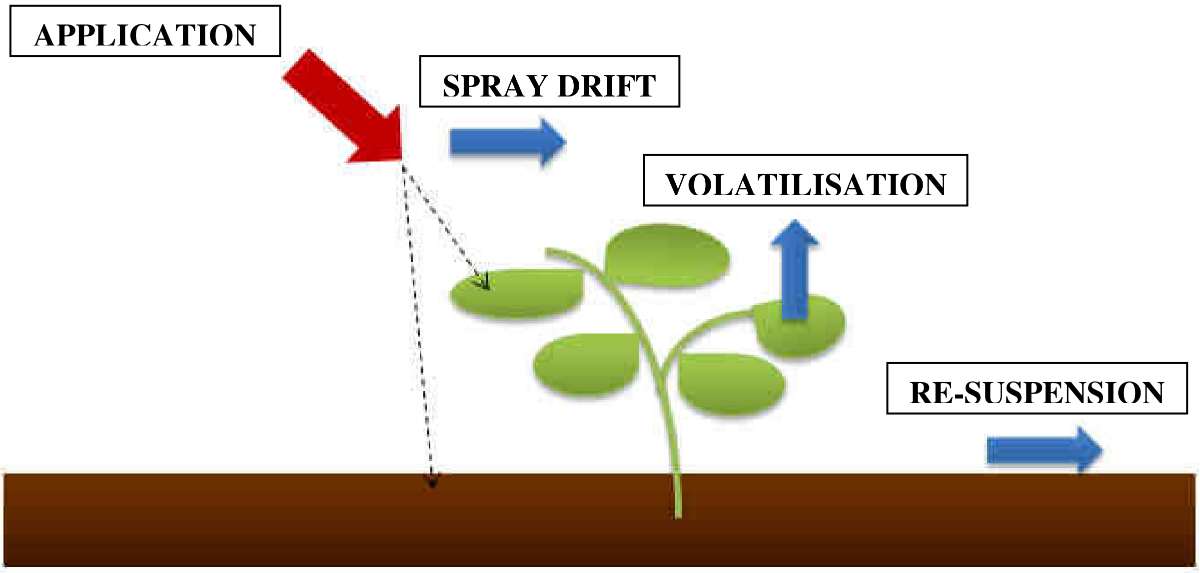


Figure 1 – Emission mechanisms of pesticides

For this study, monitored pesticides were separated in three categories: 21 OCP, including chlorinated pesticides that are not in the Stockholm convention, 68 volatile pesticides analysed in GC –referred to as GC pesticides– and 33 less volatile pesticides analysed in LC –

referred to as LC pesticides–. There are some pesticides in common in the OCP and GC pesticides lists, and all compounds are listed in Annex I.

Active sampling

Several methods exist to determine SVOC concentrations in air, both indoors and outdoors.
Currently, active sampling is the most widespread air sampling technique. Active sampling makes use of active air samplers (AAS), which are machines equipped with a pump that allows a fixed amount of air to pass through a filter then an adsorbent. The filter can be either a quartz or glass fibre filter (GFF), while the most common adsorbents are polyurethane foam (PUF) and XAD®-2 resin. Particulate pollutants are trapped on the filter and gaseous pollutants retained on the adsorbent. When specific information needs to be gathered about particles, the sampler's sampling head can be equipped with an impactor. The impactor allows to discriminate particles based on size and to only trap PM_{10} (particle diameter < 10 µm) or $PM_{2.5}$ (particle diameter < 2.5 µm). This might be of interest when the health impact of pollutants is measured, as these fine particles are the ones that penetrate the deepest into the respiratory system. When no discrimination is made, the sampling is called TSP (total suspended particles).
Active samplers are divided between high-volume samplers (HVS) and low-volume samplers (LVS). HVS pump air at a flow generally comprised between 15 and 30 $m^3\ h^{-1}$, while LVS pump between 0.5 and 3 $m^3\ h^{-1}$. This difference means they are not meant to function for the same durations; HVS are generally used for one-day sampling, while LVS can run for up to two weeks. (Association française de normalisation, 2007) As a result, LVS are less susceptible to punctual variations in air concentration and are used to monitor ambient air pollution, while HVS give information about a precise point in time.

Active sampling has several advantages that justify its continuous use. First, because samplers pump a know amount of air, precise air concentrations can be calculated. Second, being able to program the pump gives a definite start and end time to the sampling period, which can then be closely compared to meteorological information. Third, using both a filter and an adsorbent allows a distinction to be made between particulate and gaseous phase contribution. (Hayward et al., 2010)
However, these samplers have a number of drawbacks that limit the scope of their use. The first is that they are expensive to buy and to maintain. When in use, they are noisy due to their use of a pump, which limits their use near habitations. They also require electricity to function, which restricts the number of sites where they can be deployed. Moreover, most of them are bulky and require more than one person to transport, so it is difficult to place them in remote locations. (Figure 2) Finally, operators have to be trained to use and maintain the machines. (Harner et al., 2006 ; Schummer et al., 2012)

Figure 2 – Leckel active sampler in use (left) and open (right)

Because of these drawbacks, passive sampling has been developed as an alternative to the active sampling of SVOC.

Passive sampling

Passive samplers are based on the free diffusion of air through an adsorbent, without forcing the flow by using a pump. Airborne pollutants are then accumulated by the sampler until they reach equilibrium between air and adsorbent. At present, passive samplers are routinely used to monitor gases like NO_x in air (Harner et al., 2006), but not yet SVOC.

Most passive samplers consist of an adsorbent fixed inside a protective housing. This housing regulates the flow of air passing through the sampler, and protects the adsorbent from rain and direct sunshine. Currently, the most commonly used adsorbents are the same as active sampling, PUF and XAD®-2 resin (Schummer et al., 2012). PUF is usually shaped into a disk and is protected by stainless steel domes, while XAD®-2 is put in a meshed tube and housed in a PVC cylinder for protection.

These passive samplers are cheaper than active machines, easy to handle and to use, and can be put anywhere as they do not depend on an energy source (Schummer et al., 2012). They have also proven to be effective at trapping SVOC and have been used for years. However, they have several drawbacks that limit their effectiveness.

First, since air passively diffuses through the adsorbent, there is no data on the actual volume of air sampled. This makes quantification difficult since the mass of pollutant on the sampler cannot be converted to air concentration. There are methods to determine the sampling rate of passive samplers, either by comparison with active samplers or by using reference compounds spiked on the passive adsorbent. But passive sampling rates can change depending on meteorological conditions, most notably wind speed, so they have to be calculated for each campaign. (Moeckel et al., 2009)

Another issue is that while the currently used passive samplers are well suited to adsorb gaseous pollutants, they are not optimised for particles collection. PUF does not have a large surface area, and its domed protection makes access difficult for large particles. This shortcoming has been noticed and there are examples of new samplers that improve particles deposition on PUF disks, but it leaves the adsorbent more exposed to the weather (Eng et al., 2014). XAD®-2 resin has a greater surface area than PUF, but it is not easily accessible. Since the resin is packed in a meshed cylinder, the mesh is an obstacle for particles. Moreover, XAD®-2 beads have nanoscopic pores that cannot adsorb most of the airborne particles. This is a known fact, as it has been calculated that passive sampling rates for particulate compounds are much lower than those for gaseous compounds (Tao et al., 2007).

PUF and XAD®-2 resin are also hydrophobic materials that are rarely used to trap polar compounds. This limits the range of pollutants that can be monitored, and especially pesticides.

Goal of the study

The goal of this thesis work was to find a material to use as a passive sampler that would remedy to these drawbacks. This material was required to be equally efficient at trapping gaseous and particulate pollutants. Desired characteristics were a large specific surface area and pores wide enough to collect particles, as well as being as easy to handle as the current passive samplers. Carbon nanotubes (CNT) -based foams, having already been used as passive samplers in several matrices, were the first material considered.

Graphite felt and silicium carbide (SiC) foam were also investigated, and SiC foam was selected due to having all the required characteristics and being able to trap polar compounds.

An analytical method was developed and optimised to retrieve PAH, PCB, OCP and other pesticides from SiC foam. This method combines accelerated solvent extraction (ASE), solid phase extraction (SPE) and solid phase microextraction (SPME) in order to reach low limits of detection and quantification to be reached for all compounds of interest. Additionally, coupling these three extraction techniques reduces the quantity of solvent needed and avoids evaporation steps that could result in loss of volatile analytes.

Several sampling campaigns took place to compare the efficiency of SiC foam and XAD®-2 resin. SiC foam had consistently better results than the resin for particulate and polar compounds in every family of pollutants monitored. Moreover, SiC foam can be grafted with carbon or carbon nanotubes (CNT) to increase its specific surface area. While these grafted SiC foams retain their ability to trap particles and polar compounds, they are also more efficient than XAD®-2 resin at adsorbing volatile compounds.

Finally, SiC foam's sampling rates were calculated by comparison with active sampling and by using reference compounds. The results are in agreement and are comparable to the values reported in the literature for XAD®-2 resin.

The structure of this dissertation follows the steps developed above.

First, the process leading to the choice of SiC foam as a passive sampler will be explained, supported by laboratory tests and an outdoors sampling campaign.
Second, the development of the analytical method will be reported.
Third, three sampling campaigns comparing various adsorbents will be detailed. SiC foam will be compared to XAD®-2 resin, then to grafted SiC foams, and finally the two grafted SiC foams will be compared.
Finally, different calculation methods will be tested to determine several compounds' sampling rates on SiC foam.
Each chapter will include the relevant bibliography. Afterwards, a general conclusion will be drawn.

References

Association française de normalisation (2007). *Air ambiant – Dosage des substances phytosanitaires (pesticides) dans l'air ambiant – Prélèvement actif.* Norme XP X 43-058. La Plaine Saint-Denis : Association française de normalisation.

Choi H., Harrison R., Komulainen H., Delgado Saborit J., *WHO Guidelines for Indoor Air Quality: Selected Pollutants*, **2010**, Geneva: World Health Organization, p.289-345, Polycyclic aromatic hydrocarbons

Eng A., Harner T., Pozo K., **2010**, "A prototype passive air sampler for measuring dry deposition of polycylic aromatic hydrocarbons", *Environmental Science & Technology*, *1*, 77-81

Erickson M. D., Kaley II R. G., **2011**, "Applications of polychlorinated biphenyls", *Environmental Science and Pollution*, *18*, 135-151

Harner T., Bartkow M., Holoubek I., Klanova J., Wania F., Gioia R., Moeckel C., Sweetman A. J., Jones K. C., **2006**, "Passive sampling for persistent organic pollutants: Introductory remarks to the special issue", *Environmental Pollution*, *144*, 361-364

Hayward S. J., Gouin T., Wania F., **2010**, **"**Comparison of four active and passive sampling techniques for pesticides in air", *Environmental Science & Technology*, *44*, 3410-3416

Jamshidi A., Hunter S., Hazrati S., Harrad S., **2007**, "Concentrations and chiral signatures of polychlorinated biphenyls in outdoor and indoor air and soil in a major U. K. conurbation", *Environmental Science & Technology*, *41*, 2153-2158

Li Y-F., Harner T., Liu L., Zhang Z., Ren N-Q., Jia H., Ma J., Sverko E., **2010**, "Polychlorinated biphenyls in global air and surface soil : Distributions, air-soil exchange, and fractionation effect", *Environmental Science & Technology*, *44*, 2784-2790

Moeckel C., Harner T., Nizzetto L., Strandberg B., Lindroth A., Jones K. C., **2009**, “Use of depuration compounds in passive air samplers: results from active sampling-supported field deployment, potential uses, and recommendations”, *Environmental Science & Technology*, *43*, 3227-3232

Ravindra K., Sokhi R., Van Grieken R., **2008**, “Atmospheric polycyclic aromatic hydrocarbons: Source attribution, emission factors and regulation”, *Atmospheric Environment*, *42*, 2895-2921

Scheyer A., Développement d’une méthode d’analyse par CPG/MS/MS de 27 pesticides identifiés dans les phases gazeuse, particulaire et liquide de l’atmosphère. Application à l’étude des variations spatio-temporelles des concentrations dans l’air et dans les eaux de pluie, Thesis, Strasbourg University, 2004

Schummer C., Tuduri L., Briand O., Appenzeller B. M., Millet M., **2012**, “Application of XAD-2 resin-based passive samplers and SPME-GC-MS/MS analysis for the monitoring of spatial and temporal variations of atmospheric pesticides in Luxembourg”, *Environmental Pollution*, *170*, 88-94

Tao S., Liu Y., Xu W., Lang C., Liu S., Dou H., Liu W., **2007**, “Calibration of a passive sampler for both gaseous and particulate phase PAH”, *Environmental Science & Technology*, *41*, 568-573

Chapter 1: Selection of a new adsorbent

I/ Introduction: Currently used adsorbents

Currently, the most widely used adsorbents for both active and passive air sampling are polyurethane foam (PUF) and XAD®-2 resin (Armstrong et al., 2013).

1. Polyurethane foam

PUF is a cheap material and easily handled, making it an attractive adsorbent. It has a surface area of 1-2 m² g^{-1} (Truong Huu, 2011), which is lower than other adsorbents and limits its capacity to adsorb high quantities of pollutants. On its surface are pores of 200 to 250 µm in diameter, meaning it can collect airborne particles (Eng et al., 2014).
PUF used in active sampling are cylinders cut to fit the samplers' dimensions. There can be as few as one or as much as a series of four (Association française de normalisation, 2007). PUF used in passive sampling are disks of varying diameter and thickness. PUF disks require a protective housing when put outside, in order to prevent rain and direct sunlight from damaging the matrix and adsorbed pollutants (Klánová et al., 2008). The design of the housing is also made to regulate the flow of air passing through the adsorbent. The most common protection for PUF disks is the 'flying saucer' housing (Tuduri et al., 2006). It is made of two stainless steel domes of different diameters, the largest being the upper one (Figure 1-1).

Figure 1-1 – Stainless steel 'flying saucer' protecting a PUF disk

On the lower dome, a PUF disk is kept in place between stainless steel circles or bars with as much surface as possible unobstructed (Figure 1-2).

Figure 1-2 – Placement of a PUF disk inside its housing

When this system is placed outside, air flows inside the housing via the space between the upper and lower domes (Figure 1-3).

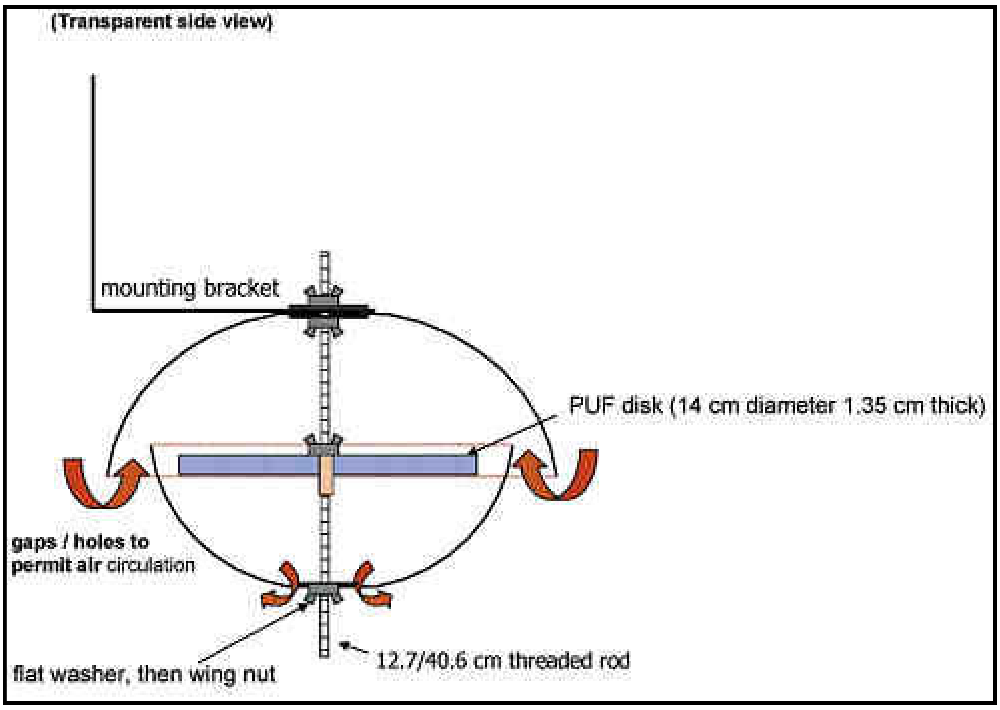


Figure 1-3 – Schematic drawing of a PUF housing, from Jaward et al., 2004

There are concerns that this housing is preventing the PUF from efficiently collecting heavier particles (Tuduri et al., 2006 ; Eng et al., 2013). However, this configuration is still the most used one.

PUF can sample a wide variety of compounds. It is often used to monitor PCB and PBDE (Hazrati & Harrad, 2007), but it can also adsorb PAH (Klánová et al., 2008) and OCP (Jaward et al., 2004).

2. XAD®-2 resin

XAD®-2 resin is a hydrophobic styrene/divinylbenzene copolymer. Its appearance is that of small, hard, white beads. While difficult to handle, XAD®-2 resin is a popular adsorbent due to its high specific surface area of 300-350 m² g^{-1} (Wania et al., 2003 ; Sigma Aldrich) that can accumulate great quantities of pollutants.

In order to be used as an active or passive sampler, XAD®-2 beads have to be put in a container. Active samplers have a cylindrical chamber made to house any adsorbent, and XAD®-2 passive samplers are meshed stainless steel tubes filled with resin beads (Figure 1-4). These tubes have to be protected from rain and direct sunlight just like PUF, and housings are designed to also regulate the flow of air around the sampler. These protective housings are made out of PVC in two parts: a large cylinder circling the tube, and a roof with a hook on which the sampler can be hanged (Figure 1-5).

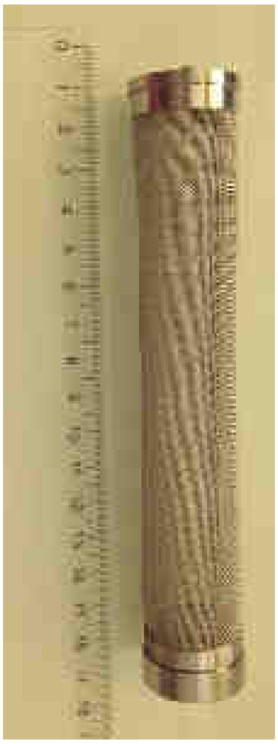


Figure 1-4 – Meshed cylinder to be filled with XAD®-2 resin

Figure 1-5 – PVC housing for the XAD®-2 tube

There are holes inside the roof through which air can pass, but most of the air flow comes from the opening at the bottom of the cylinder (Figure 1-3).

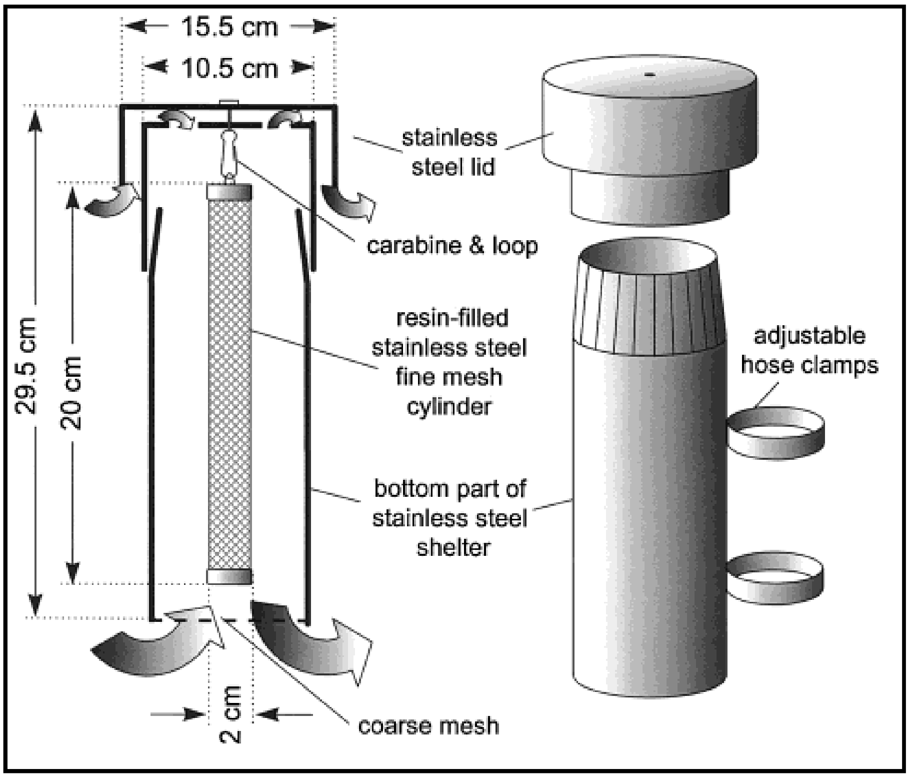


Figure 1-6 – Schematic drawing of a XAD®-2 tube housing, from Wania et al., 2003

This design, that is most widely open under the sampler, is not well suited to collecting heavier particles. In addition to that, the XAD®-2 tube is a tightly meshed cylinder and the resin itself has nanoscopic pores (Wania et al., 2003 ; Sigma Aldrich). All in all, this matrix is best suited to adsorbing volatile, gaseous compounds than particulate ones.

XAD®-2 resin has been majoritarily used to monitor pesticides (Gouin et al., 2008 ; Schummer et al., 2010), but it can also sample PCB and PBDE (Wang et al., 2010 ; Guéguen et al., 2013).

PUF and XAD®-2 resin can be used together as a hybrid sampler, or made into a PUF-XAD®-PUF 'sandwich' (Dobson et al., 2006 ; Hayward et al., 2009). These configurations have only been tested in active samplers where the flow of air can be directed through the different layers successively. They may lose their efficiency when used as passive samplers since the flow of air would be less homonegous.

3. Other adsorbents

Outside of PUF and XAD®-2 resin, several other matrices are used as active or passive samplers.

Semi-permeable membrane devices (SPMD) have been used since the 90s to sample hydrophobic compounds in air and water (Shoeib & Harner, 2002 ; Namieśnik et al., 2005). Their membrane is usually made of low-density polyethylene and filled with the heavyweight triolein, allowing the accumulation of hydrophobic molecules for long periods of time, up to several months. SPMD have been used to monitor PCB (Shoeib & Harner, 2002), PAH (Lohmann et al., 2001) and OCP (Prest & Jacobson, 1995), among others.

Solid phase micro-extraction (SPME) is ordinarily used for sample preparation as a concentration tool. SPME uses a fused silica fibre coated with a polymer acting as an adsorbent. When in contact with a given matrix, it adsorbs compounds until equilibrium is established. Adsorption kinetics varies depending on fibre coating and target compounds. However, using an SPME fibre as a passive sampler requires linear adsorption kinetics (Wang et al., 2009) in order to accurately determine concentration based on a sampled quantity. SPME fibres have been used as passive samplers for a wide variety of matrices: air, water, soil, food, biological samples. The most common coatings are polydimethylsiloxane (PDMS), polyacrylate (PA), divinylbenzene (DVB) and Carboxen (CAR), as well as mixed coatings like PDMS/DVB or CAR/PDMS. This variety allows sampling of a wide range of analytes: pesticides, PAH, PCB, chlorinated compounds, alcohols, phenols, etc… (Namieśnik et al., 2005)

More recently, carbon-based foams have been tested in monitoring environmental pollutants. In particular, carbon nanotubes (CNT) foams are attractive adsorbents due to their high specific surface area which can go above 1000 $m^2 g^{-1}$ (Peigney et al., 2001).
This is why they were the first adsorbent selected for the present study. Other carbon-based foams were considered, with properties close to CNT foam but different three-dimensional structures. In the end, three materials were tested in this study: CNT foam, graphite felt and silicon carbide (SiC) foam.

II/ Characteristics of the three pre-selected materials

1. Carbon nanotubes (CNT) foam

CNT-based adsorbents have proven to be efficient in determining pesticides concentrations in water (Shuo et al., 2007 ; Quingxiang et al., 2009) and other matrices like soil (Asensio-Ramos et al., 2009), plants (Ahmadkhanih et al. a, 2012) or fruits (Shu-Xia et al., 2011). Most often, CNT are used in SPE cartridges. Such cartridges have been tested on water samples (Wang et al., 2007) and soil extracts (Asensio-Ramos et al., 2009), and compared to the currently used C_{18} cartridges (El-Sheikh et al., 2008 ; Hadjmohammadi et al., 2010). While CNT cartridges seem to be the optimal sorbent for SPE, their cost limit their use for routine analysis. Some development has also been done to use CNT as SPME fibres. Compared to PDMS fibres, they appear to have a greater thermal stability and longer lifespan, as well as a higher extraction capacity for OCP. They have been tested in water samples (Lü et al., 2007) and plant extracts (Ahmadkhaniha et al., 2012) in order to determine OCP concentrations in these matrices.
There are reports of CNT being used to trap VOC in air, either by themselves (Li et al., 2004) or supported on another matrix (Hu et al., 2013). CNT adsorbents seem to have a better adsorption capacity than existing samplers, and their performance is not affected by ambient humidity. They have also been used to adsorb dioxin (Long & Yang, 2001), SO_2 (Sun et al., 2013) and CO_2 (Jin et al., 2013) from industrial sources to avoid atmospheric contamination.

More recently, their adsorption capacity has also been tested for PAH and PCB in water and sediments (Velzeboer et al., 2014).

The present study used CNT foam, synthesised as described by Liu et al. (2013a). First, 1 g of CNT is mixed with 6 g of citric acid and 2 g of dextrose. Citric acid acts as a polymerisation agent while dextrose is used as a carbon source. After this step, a given amount of ammonium carbonate is added, usually 10 % in weight. Since ammonium carbonate decomposes during heating, it leaves pores in the otherwise rigid structure of the foam. The mixture is put in a beaker with the desired shape, and then placed in an oven for 5 h at 130 °C. The following step is calcination at 450 °C under air flow for 3 h, and finally annealing in helium at 900 °C for 2 h. This last heating phase is what makes the foam hydrophobic. It graphitises the initially amorphous carbon by removing the surface oxygen functions. While this greatly improves the CNT’s affinity with most pollutants, it does decrease its capacity to adsorb polar compounds.

CNT adsorbents generally have a high specific surface area, which means they can adsorb important quantities of gas. In this study, we used CNT foams that were about 450 m² g^{-1}, but they can range from 50 to 1315 m² g^{-1} (Peigney et al., 2001).

However, CNT foam has pores ranging from 50 to 100 nm in diameter. This means they will only be able to trap the smallest airborne particles, since particles can be as wide as 10 µm in diameter. It is possible to increase the foam’s pore size by using more ammonium carbonate during synthesis, but this would make the foam more brittle (Liu et al., 2013a).

CNT adsorbents are both rigid and resistant, meaning they can be placed outside with no other protection than their housing. (Figure 1-7)

Figure 1-7 – Different sizes of CNT foam, from Liu et al., 2013a

2. Graphite felt

Graphite felt is a hydrophobic material often used as a support for macroscopically shaping nanoscopic materials, like carbon nanofibers or nanotubes (Shen et al., 2016) or metallic catalysts (El-Kacemi et al., 2015). Its other main use is as a cathode in redox batteries (Park & Kim, 2015) or more generally electrochemical systems (Rabbow et al., 2015).

Both of these functions have been exploited in water treatment. Grafted with carbon nanofibers, graphite felt has been an efficient adsorbent (Shen et al., 2016), and as a cathode it has supported reactions to clean wastewaters (Jiang et al., 2015 ; Yu et al., 2015).

However, graphite felt is almost never used on its own. It has a low specific surface area that does not exceed 2 m² g^{-1} (Park & Kim, 2015) and is on average around 1 m² g^{-1} (Rabbow et al., 2015), which limits its use as an adsorbent and explains the need for grafting. Its limited electrochemical activity (Jiang et al., 2015 ; Park & Kim, 2015) is the reason why it is used in composite electrodes in electrochemical systems.

Despite these drawbacks, graphite felt has several advantages. First, its low cost and ease of acquisition, but also its large external surface (Park & Kim, 2015 ; Yu et al., 2015) well suited to grafting. Its high mechanical strength (Jiang et al., 2015 ; Yu et al., 2015) and resistance to corrosion (Jiang et al., 2015 ; Park & Kim, 2015) make it an interesting sampler choice, as it can withstand meteorological variations and laboratory extraction procedures without damage. Moreover, its open porosity can allow particulate compounds to be trapped inside.

Graphite felt can also be thermally treated in order to become hydrophilic (El-Kacemi et al., 2015 ; Rabbow et al., 2015), which is useful when trying to adsorb polar pollutants. Finally, due to graphite felt being softer than the rigid CNT and SiC foams, it is less likely to break and is very easy to handle (Figure 1-8).

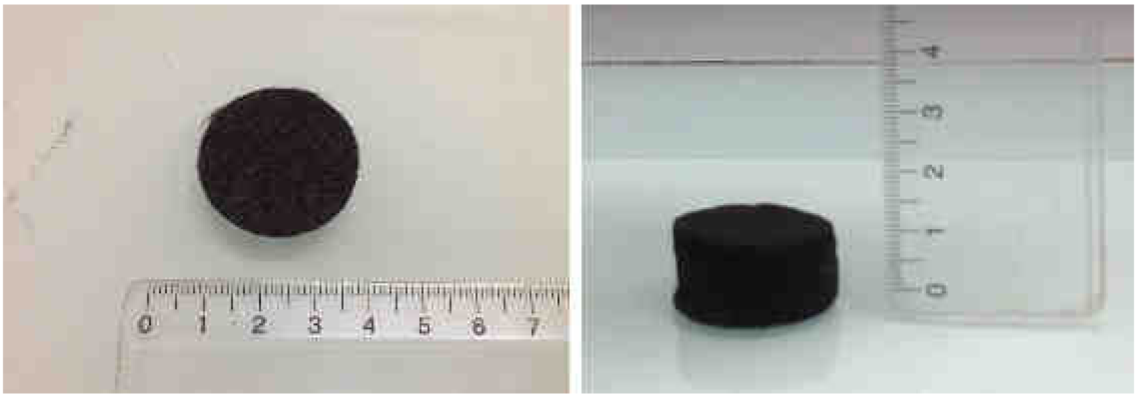


Figure 1-8 – Graphite felt from above and the side

3. Silicon carbide (SiC) foam

SiC foam is a material currently used as a catalyst support (Nguyen & Pham, 2011 ; Duong-Viet et al., 2016). Its macroscopic three-dimensional structure and open porosity make it an ideal support for nanoscopic or metallic catalysts (Vanhaecke et al., 2008 ; Liu et al., 2013b), which are often powdered and hard to shape. The most common of these catalysts include CNT, carbon nanofibers, SiC nanofibers, zeolites, cobalt, and titanium dioxide (Duong-Viet et al., 2016). Outside of catalysis, this open structure of SiC foam can make it a good adsorbent, as it increases the contact surface between the sampled medium (air, water) and the sampler.

However, despite a large surface area, SiC foam's specific surface area is in the medium range, varying between 10 and 100 m² g^{-1} (Nguyen & Pham, 2011), with an average of 30 m² g^{-1} (Kouamé et al., 2011 ; Liu et al., 2013b) which is what was used in the present study. This may limit its ability to adsorb pollutants over long periods or in great quantities, requiring grafting a material with a higher specific surface area on its surface.

Several methods exist to synthesise SiC foam. One of these, called shape memory synthesis, was developed by Ledoux et al. (1988). The first step of the synthesis is to mix solid silicon with solid silicon dioxide in order to produce gaseous silicon monoxide. This gas then reacts with solid carbon and produces solid SiC and gaseous carbon monoxide. Another method was developed by Moene et al. (1995) and is based on a solid-gas reaction. Solid carbon reacts with dihydrogen to produce methane, which then reacts with gaseous silicon tetrachloride to produce solid SiC and hydrogen chloride.

More recently, Nguyen & Pham (2011) proposed a variation of Ledoux's method. Silicon monoxide reacts with carbon to produce SiC and carbon monoxide, which then reacts with silicon to produce SiC and silicon monoxide.

Once synthesised, SiC foam can be further enhanced by deposition of nitrogen-doped CNT on its surface (Figure 1-9). These N-CNT SiC foams are currently used as metal-free catalysts, and their specific surface area can exceed 100 $m^2 g^{-1}$ and be as high as 150 $m^2 g^{-1}$. (Su et al., 2013 ; Duong-Viet et al., 2014) The same process can be used to deposit nitrogen-doped carbon on the foam's surface, making it N-C SiC foam.

Figure 1-9 – SiC foam (left) and N-CNT SiC foam (right)

One physical property of SiC foam that makes it a useful catalyst support and an interesting potential passive air sampler is its macro- and mesoporosity. On its surface are windows ranging from 510 (Liu et al., 2013b) to 4000 µm (Kouamé et al., 2011), leading to an internal porous network. It is useful in catalysis in order to avoid pressure drops and improve mass transfers (Vanhaecke et al., 2008 ; Liu et al., 2013b). In a passive air sampler, it is an ideal structure to trap atmospheric particles. This has been confirmed in a study by Vanhaecke et al. (2008) in which SiC foam grafted with SiC nanofibers was used as an efficient filter for Diesel particles.

Additionally, SiC foam is a rigid and resistant material, which is useful in a wide variety of catalytic reactions and allows it to be put outside as a sampler with only its housing as protection. It has high resistance to oxidation (Vanhaecke et al., 2008) and corrosion (Lacroix et al., 2011), high thermal stability (Kouamé et al., 2011) and great mechanical strength (Yuan et al., 2013). These properties will allow SiC foam to be extracted and cleaned at high temperatures and pressures without affecting its structure.

Finally, it has been observed that SiC foam is chemically inert (Lacroix et al., 2011 ; Duong-Viet et al., 2016). This is important for samplers that should not degrade or interact with the pollutants trapped in it. Such phenomenon has been observed by Armstrong et al. (2013) for organophosphorous pesticides (OPP) on XAD®-2 resin. This matrix tended to transform OPP into their oxygen analogs. This observation was made when using active samplers, but it could be more of a concern for passive samplers that stay in the field for longer periods of time.

III/ Laboratory tests

Tests were performed in the laboratory to evaluate each sampler's capacity to adsorb pollutants and find a suitable extraction method.

1. Materials and methods

Reagents

Standards of individual pesticides of Pestanal® quality (> 99 % purity), PAH and PCB were purchased from Fluka (Sigma Aldrich, St. Quentin Fallavier, France), Dr Ehrenstorfer GmbH (Cluzeau Info Labo, Ste Croix la Grande, France) or Riedel de Haën (Sigma Aldrich, St. Quentin Fallavier, France).

Acetonitrile, ethyl acetate, methylene chloride, n-hexane and toluene of HPLC quality were purchased from Sigma-Aldrich (St. Quentin Fallavier, France).

Stock solutions of individual pollutants and internal standards at 1 g L^{-1} were prepared in acetonitrile. A working solution at 10 mg L^{-1} was prepared in acetonitrile from stock solutions of PAH, PCB and OCP. In addition, a 10-mg L^{-1} internal standard solution was prepared with naphthalene d8.

Machines

All extractions were done by accelerated solvent extraction (ASE) and performed on a DIONEX® ASE 300 with 34 mL stainless steel cells.

PAH, PCB and OCP were analysed on a TRACE™ 1300 GC equipped with a split/splitless injector (splitless for 3 min) and an Optima® XLB capillary column (60 m × 0.25 mm, DF = 0.25 µm, silarylene phase), coupled to an ITQ™ 900 ion trap mass spectrometer. It was used to perform MSMS in electron ionisation (EI) mode. The transfer line was heated to 300 °C and the ion source at 210 °C. The oven ramp was programmed as follows: start at 50 °C (hold 3 min), increase to 240 °C at a rate of 40 °C min^{-1}, then increase to 255 °C at a rate of 1.5 °C min^{-1} (hold 5 min), and increase to 300 °C at a rate of 20 °C min^{-1} (hold 25 min). High purity (≥ 99.999 %) helium was used as the carrier gas flowing at 1 $mL.min^{-1}$ (hold 30 min) then increased to 1.5 mL min^{-1} at a rate of 0.250 mL min^{-1} (hold 22 min).

Adsorbents

CNT foam and graphite felt were synthesised by the Institute of Chemistry and Processes for Energy, Environment and Health (Strasbourg, France). SiC foam was purchased from SICAT (Strasbourg, France).

Adsorbents were synthesised or cut in order to fit within the ASE extraction cells, which are 5.1 cm long cylinders with a 3.0 cm diameter.

SiC foams were cut as 5.0 cm long cylinders with a 2.8 cm diameter.

CNT foam and graphite felt could not be made this long. They were made into 1.5 cm long cylinders with a 2.8 cm diameter.

Prior to use, each adsorbent was cleaned by ASE using one 10 min cycle at 100 °C and 1500 psi with a 50/50 (v/v) hexane/dichloromethane solution.

Experiment

Each adsorbent – CNT foam, graphite felt and SiC foam – was spiked with 100 µL of a 10 mg L^{-1} solution of PAH, PCB and OCP. These compounds were the only ones tested at first since they are the most commonly monitored. Making sure they worked with the chosen matrix was a priority.

Spiking was done as evenly as possible over the adsorbents' surface. They were then extracted by ASE over three 15 min cycles at 150 °C and 1500 psi with 100 % acetonitrile.

The extracts were concentrated by Rotavap to a drop, then re-solubilised in 1 mL acetonitrile.

Briny water (1.5 % NaCl) was added to the acetonitrile to make a 20-mL aqueous solution in which 20 µL of naphthalene d8 were added.

Manual SPME was performed on this solution. The extraction was done with a PDMS fibre at 80 °C for 40 min while stirring. Afterwards, the fibre was manually inserted and desorbed into the GC's injector.

2. Results

Results were expressed using the compounds' relative peak areas. These relative areas are obtained by dividing a compound's peak area by the internal standard's peak area.

For each pollutants family, results are summarised in two figures. The first shows the results of the three matrices, and the second focuses only on CNT foam and graphite felt in order to better reflect their differences.

Results showed that SiC foam was much better extracted than the others materials. Looking at chromatograms, pollutants extracted from SiC foams have much higher relative peak areas than pollutants from the other materials.

PAH results

The difference between the three adsorbents was especially striking for PAH, whose results are summarised in Figures 1-10 and 1-11.

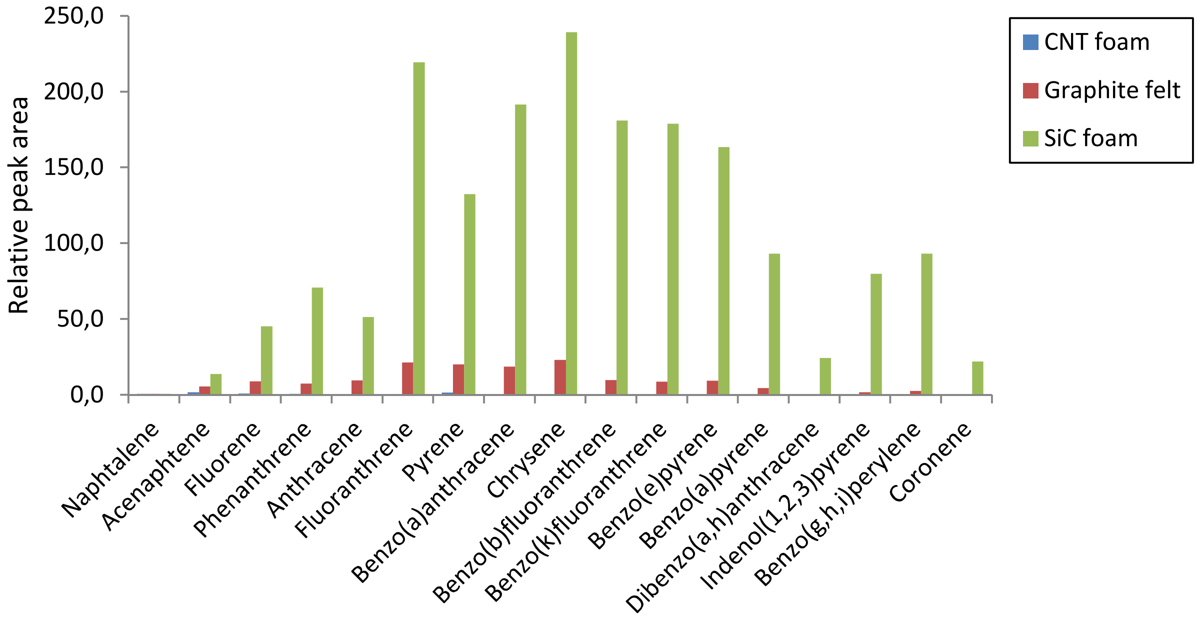


Figure 1-10 – Relative peak areas of PAH for CNT foam, graphite felt and SiC foam

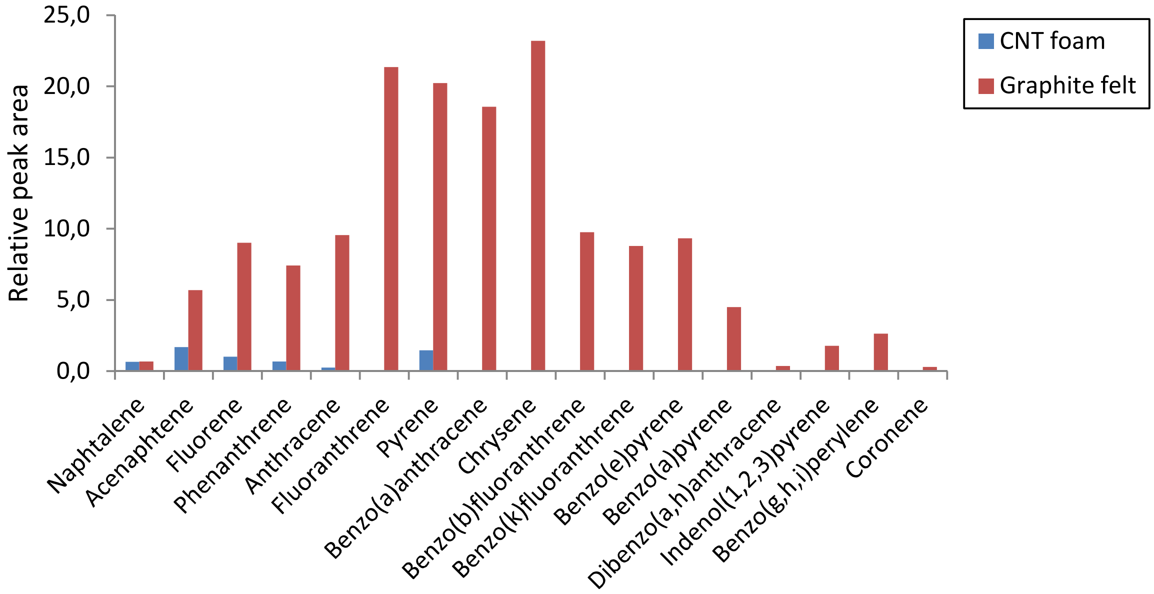


Figure 1-11 – Relative peak areas of PAH for CNT foam and graphite felt

Peak areas from SiC foam extracts were up to 10 times higher than those from graphite felt extracts, which in turn were 10 times higher than those from CNT foam extracts. Relative areas from SiC foam ranged between 0.7 and 239.1, averaging at 105.9. Those from graphite felt were between 0.3 and 23.2, averaging at 9.0. And those from CNT foam were between with 0.4 and 2.5 with an average of 1.4. In addition to these small peak areas, next to no PAH were found in this matrix: 6 out of 17 PAH were detected, while all of them were extracted from SiC foam and graphite felt. Those that were detected were the lighter PAH, from naphthalene to anthracene, and pyrene.

PCB results

The same trend is observed for PCB, whose results are summarised in Figures 1-12 and 1-13.

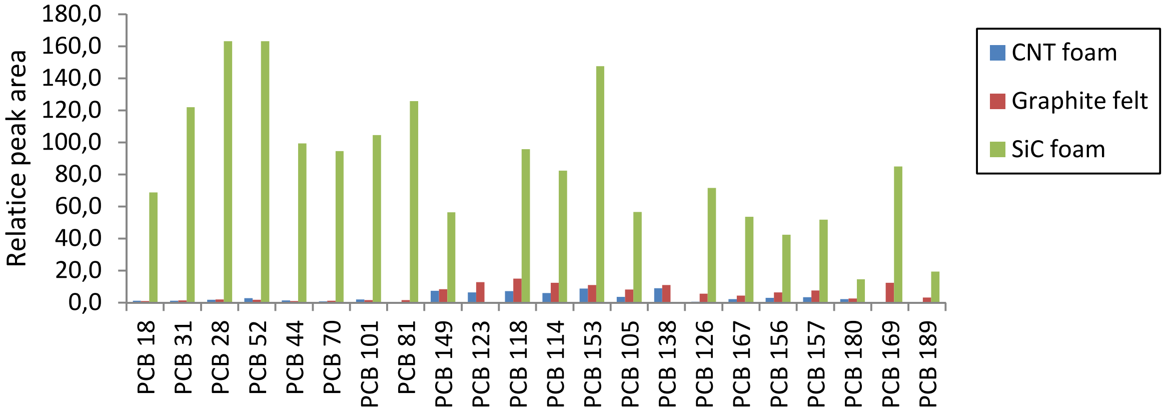


Figure 1-12 – Relative peak areas of PCB for CNT foam, graphite felt and SiC foam

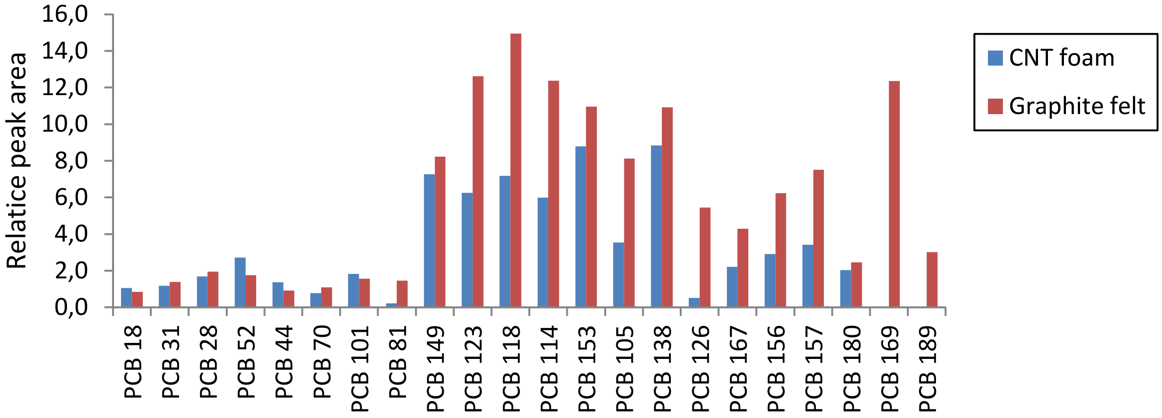


Figure 1-13 – Relative peak areas of PCB for CNT foam and graphite felt

Peak areas from SiC foam extracts were 10 times higher than those of graphite felt and CNT foam extracts. SiC foam gave relative peak areas between 14.5 and 163.2 with an average of 85.9. Graphite felt had peak areas between 0.8 and 14.9, averaging at 5.9. And areas for CNT foam ranged from 0.2 to 8.8 with an average of 3.5. The latter two gave comparable results, but relative peak areas for CNT foam extracts steadily decreased with increasing PCB molecular weight. The last two PCB, PCB 169 and PCB 189, were not even detected on this adsorbent.

OCP results

For OCP too SiC foam gave the highest relative peak areas and graphite felt and CNT foam results were close to each other. Relative peak areas are shown in Figures 1-14 and 1-15.

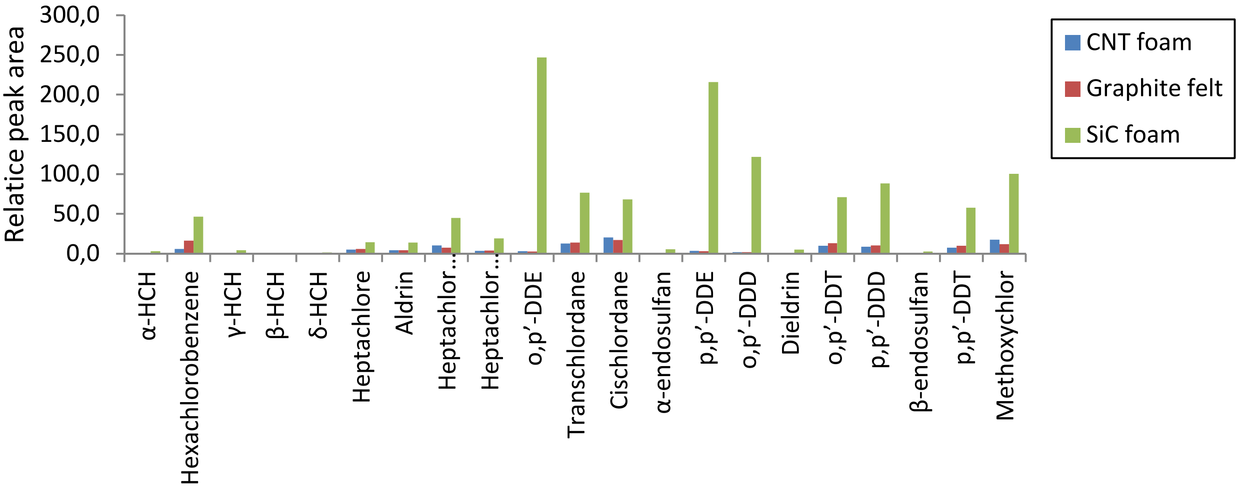


Figure 1-14 – Relative peak areas of OCP for CNT foam, graphite felt and SiC foam

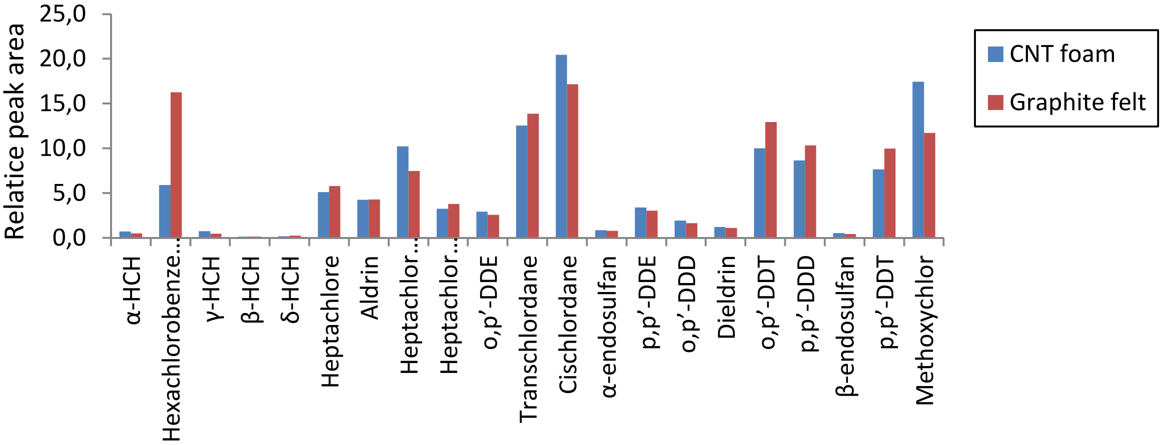


Figure 1-15 – Relative peak areas of OCP for CNT foam and graphite felt

SiC foam extracts had relative peak areas 10 times higher than those of the other matrices. Its peak areas ranged between 0.8 and 246.2 with an average of 57.5. For graphite felt, peak areas were between 0.1 and 17.2, averaging at 5.9. And CNT foam had peak areas between 0.1 and 20.4 with an average at 5.6.

For these molecules, graphite felt and CNT foam are on the same order of magnitude for every compound and all of them were detected in each adsorbent.

Comparison between standard solutions and extracted samples

Since blanks were run before each injection, contamination was ruled out as a reason for explaining the high peak areas obtained for SiC foam. Different SiC foams than those used for the experiment were spiked and extracted, giving the same results.

Two hypotheses were emitted to explain the lower results obtained for graphite felt and CNT foam: either the pollutants, especially the heavier ones, were too strongly adsorbed on the foam and could not be extracted by the current method, or there was an interference from the matrix. In order to test this, another experiment was carried out as follows:

Clean CNT foams and graphite felts were extracted by ASE using the same method as the previous test. The obtained extract was then spiked with 100 µL of the 10 mg L^{-1} solution of PAH, PCB and OCP. Finally, the solution was concentrated and injected like previously. If results for these solutions were higher than the previous ones, it would mean that pollutants are simply strongly retained on the adsorbents.

The resulting relative surface areas are shown for PAH in Figures 1-16 and 1-17.

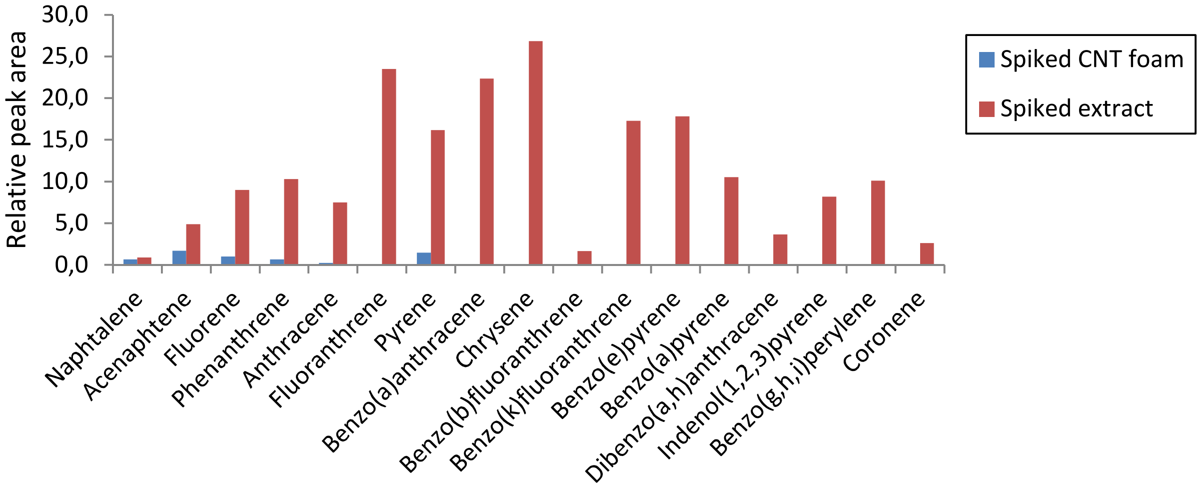


Figure 1-16 – Relative peak areas of PAH for spiked CNT foam and a spiked CNT extract

There is a clear difference between PAH extracted from CNT foam and PAH added to a clean extract. This seems to indicate that these compounds, once adsorbed onto the foam, cannot be efficiently extracted by this ASE method.

No significant difference was observed for PCB and OCP.

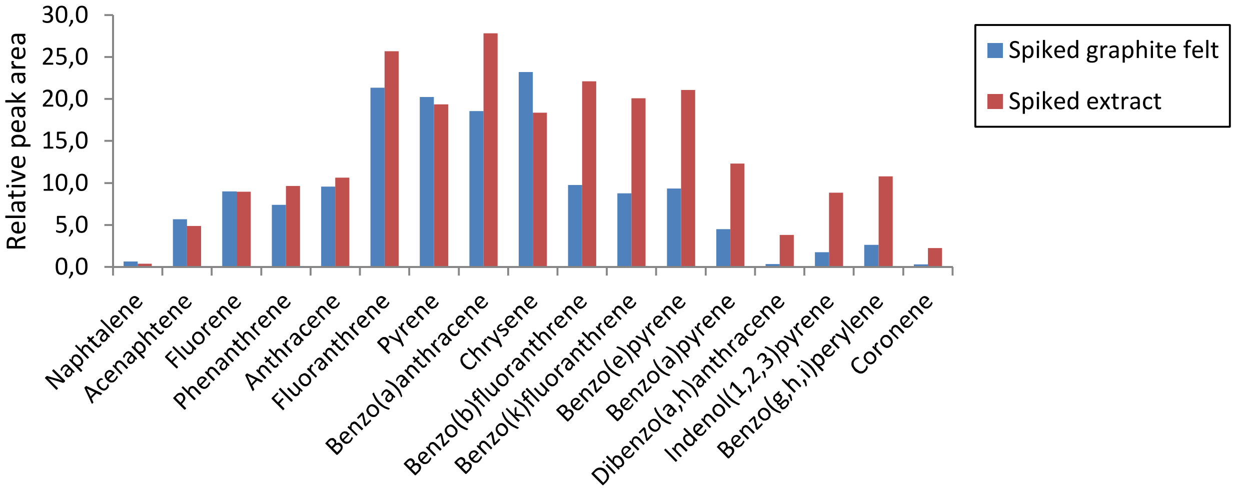


Figure 1-17 – Relative peak areas of PAH for spiked graphite felt and a spiked graphite extract

While a difference was observed between PAH extracted from graphite felt and PAH added to a clean extract, it could fall within analytical incertitude given that the samples were manually extracted and injected. However, for the heaviest PAH from benzo(b)fluoranthene to coronene, relative peak areas from the spiked extract were twice as high as those from the felt extract. It could mean that these PAH are harder to extract from graphite felt than the lighter ones.

No significant difference was observed for PCB and OCP.

It was concluded that PAH were indeed better extracted from SiC foam than the other adsorbents. However, since PCB and OCP seem to be completely extracted from graphite felt and CNT foam, there is currently no explanation regarding the consistently higher peak areas obtained with SiC foam.

Discussion

Overall, SiC foam appeared to be the better material to recover pollutants from. However, this observation posed the question whether SiC foam would be capable of retaining these same pollutants when placed outside. Here, spiking was done with liquid solutions and extraction took place about 30 min afterwards. When left outside for one or two weeks, would SiC foams efficiently adsorb pollutants, or would they be desorbed just as fast due to the wind?

These concerns were addressed by holding a short exterior sampling campaign, which will be discussed in the next section.

Graphite felt and CNT foam, while not behaving in exactly the same way, gave comparable results. Both had relative peak areas ten times lower than those from SiC foam, and both showed great affinity for PAH, even if only the heavier PAH for graphite felt.

Pollutants extracted from graphite felt had similar relative peak areas, but for CNT foam an increase in peak area was noticed with decreasing pollutant hydrophobicity. Areas were between 1 and 2 for PAH, 1 and 9 for PCB and 1 and 20 for OCP.

This would be coherent with what we know of the materials. CNT foam was treated to be hydrophobic, and as such has the greatest affinity with hydrophobic molecules, hence why they would be difficult to extract. Graphite felt is hydrophobic and so follows the same pattern, albeit to a lesser degree. And SiC foam synthesised from silicon and amorphous carbon is the least hydrophobic of the three, which is why it shows little difference between the three pollutants families.

Not being able to extract PAH from CNT foam was a major drawback that justified not selecting it as the adsorbent to study. In addition to this problem, the foam also proved difficult to synthesise to the desired dimensions. Above 1.5 cm in height, it started to crack during thermal treatment. Consequently, it was decided that this material would not be studied further, and testing continued with graphite felt and SiC foam.

IV/ Sampling campaign comparing graphite felt, SiC foam and XAD®-2 resin

After the laboratory tests, a short sampling campaign was held in Strasbourg's botanical garden to compare graphite felt and SiC foam to the currently used XAD®-2 resin.

1. Materials and methods

Reagents

In addition to PAH, PCB and OCP, non chlorinated pesticides were also analysed by GC. Standard solutions for PAH, PCB and OCP were the same as those described in section III.1. Stock solutions of individual GC pesticides and internal standards at 1 g L^{-1} were prepared in acetonitrile. A working solution at 10 mg L^{-1} was prepared in acetonitrile from stock solutions, and a 10-mg L^{-1} internal standard solution was prepared with trifluralin d14 and nitrophenol d4.

Machines

PAH, PCB and OCP were analysed on the same GC as described in section III.1.
Non chlorinated pesticides were analysed on a TRACE^{TM} GC Ultra equipped with a split/splitless injector (splitless for 3 min) and a TRACE^{TM} TR-50MS capillary column (60 m × 0.25 mm, DF = 0.25 µm, silphenylene phase), coupled to an ITQ^{TM} 700 ion trap mass spectrometer. It was used to perform MSMS in electron EI mode. The transfer line was heated to 300 °C and the ion source at 210 °C. The oven ramp was programmed as follows: start at 50 °C (hold 3 min), increase to 220 °C at a rate of 10 °C min^{-1}, then increase to 250 °C at a rate of 3 °C min^{-1} (hold 9 min), and increase to 300 °C at a rate of 3 °C min^{-1} (hold 22 min). High purity ($\geq$ 99.999 %) helium was used as the carrier gas flowing at 1 mL min^{-1}.

Adsorbents

Amberlite® XAD®-2 resin was purchased from Sigma-Aldrich (St. Quentin Fallavier, France). After reception, it was cleaned by ASE using one 10 min cycle at 100 °C and 1500 psi with a 50/50 (v/v) hexane/dichloromethane solution. It was then kept in the laboratory oven at 40 °C.

SiC foams were purchased from SICAT (Strasbourg, France), and were not cleaned before use.

Experiment

The campaign took place between April 11th and April 29th 2014 in Strasbourg's botanical garden. Each week, one SiC foam, one graphite felt and one XAD®-2 resin cylinder were hung on a tree close to each other. Each sampling period lasted one week.

After collection, samplers were extracted by ASE as described in the previous section. Sample preparation was also the same, with Rotavap concentration and manual SPME.

2. Results

Results are presented by pollutants families for each of the two sampling weeks. Relative peak areas are used for comparison between adsorbents.

PAH results

Relative peak areas of detected PAH varied between 0.1 and 8.8 the first week, and 0.1 and 63.5 the second. Every PAH but coronene was detected at least once each week. Results are summarised in Figure 1-18 for the first week and Figure 1-19 for the second week.

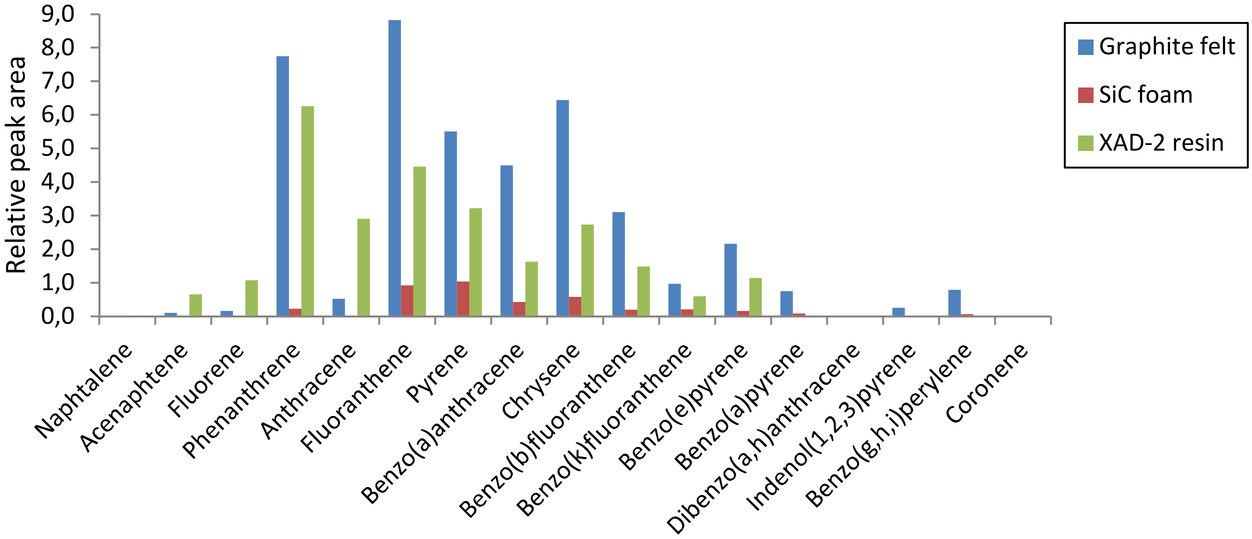


Figure 1-18 – Relative peak areas of PAH between April 11th and 22nd

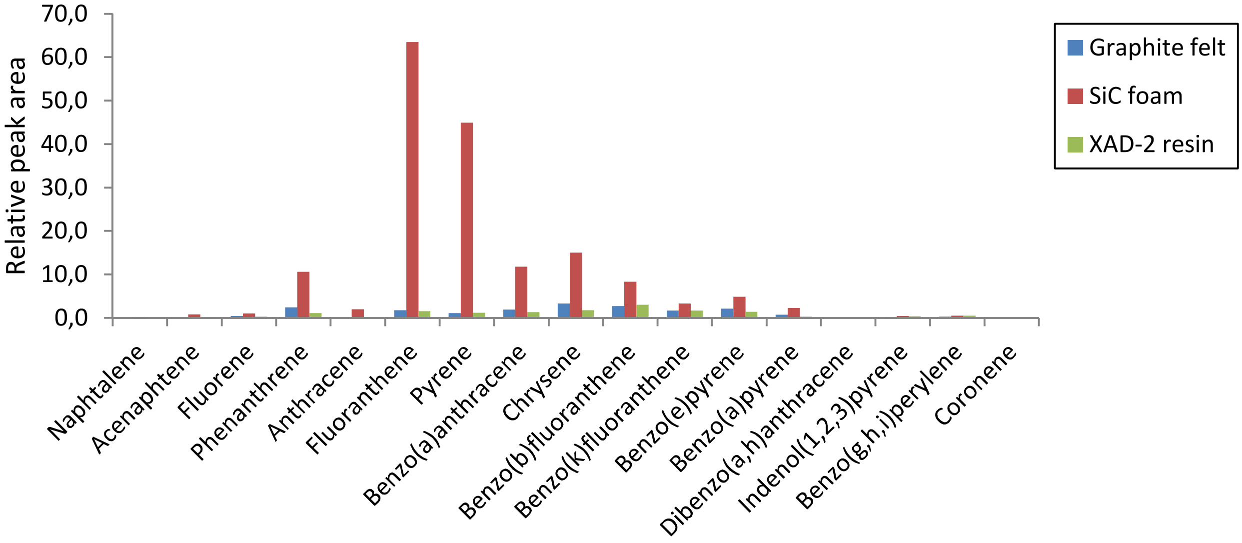


Figure 1-19 – Relative peak areas of PAH between April 22nd and 29th

The first and second week gave opposite results for PAH. The first week, graphite appeared to be the most sensitive sampler, followed by XAD®-2 resin, but the second week SiC foam had the best results by far. Whether this was due to actual quantities adsorbed on the foam or to a problem during sample preparation is unknown at the moment.

In both cases, however, decreasing quantities of PAH were detected with increasing molecular weight, indicating that all three samplers may have had difficulties capturing particles. The low levels detected for the first three PAH might be due to revolatilisation, as these compounds are the most volatile.

PCB results

Nineteen PCB were detected the first week, with relative peak areas varying between 0.2 and 1.8. All twenty-two PCB were detected the second week, and relative areas were between 0.1 and 6.7. Results are summarised in Figure 1-20 for the first week and Figure 1-21 for the second. The lack of detection from PCB 114 to 138 was probably due to the programming of the GC/MSMS method. Several pollutants had close retention times, so their detection was programmed during the same time window. However, trying to detect too many compounds at the same times lowers the analysis' sensitivity.

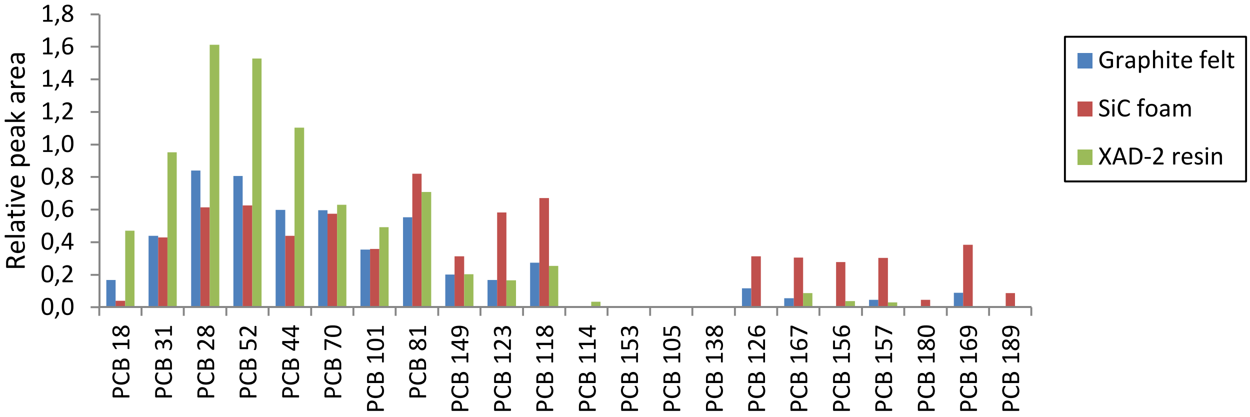


Figure 1-20 – Relative peak areas of PCB between April 11th and 22nd

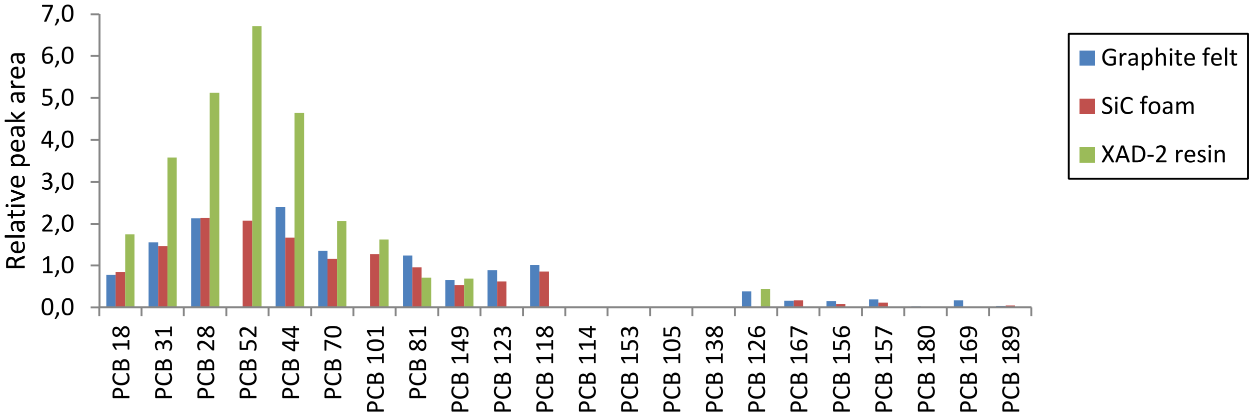


Figure 1-21 – Relative peak areas of PCB between April 22nd and 29th

PCB results were similar between the two sampling weeks. XAD®-2 resin was the most efficient sampler for lighter, more volatile PCB, while graphite and SiC foam were better suited for heavier, particulate PCB. In general, graphite and SiC foam results were very close. SiC foam only had substantially better results than graphite during the first week for the heaviest PCB.

OCP results

Fourteen out of twenty-one OCP were detected the first week with relative peak areas between 0.1 and 2.4. These results are summarised in Figure 1-22. Fifteen OCP were detected the second week, with areas varying between 0.1 and 5.4. These results are summarised in Figure 1-23.

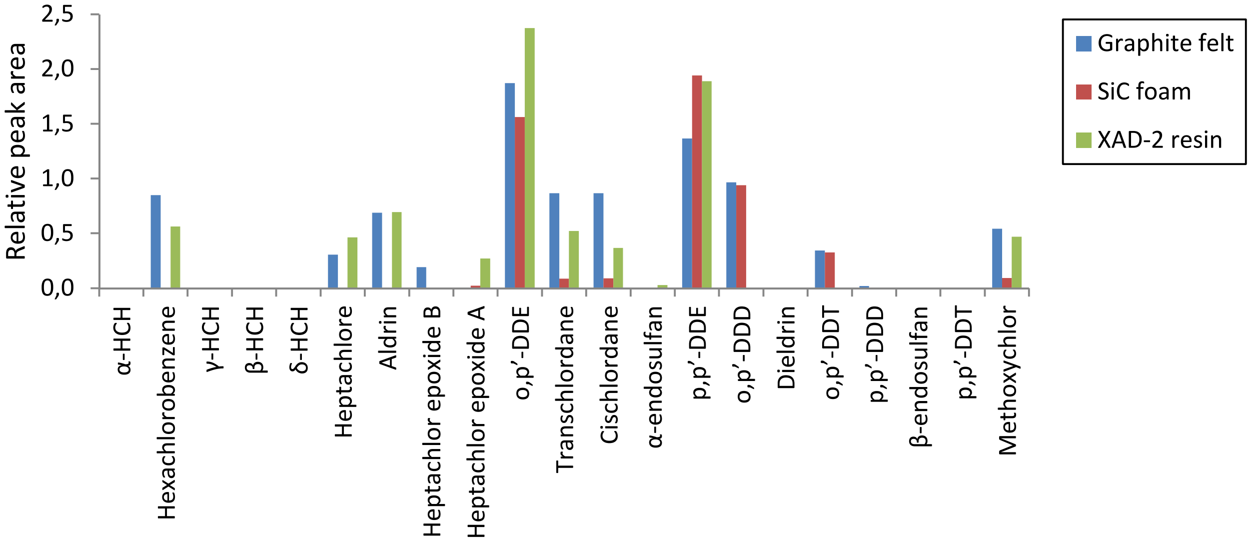


Figure 1-22 – Relative peak areas of OCP between April 11th and 22nd

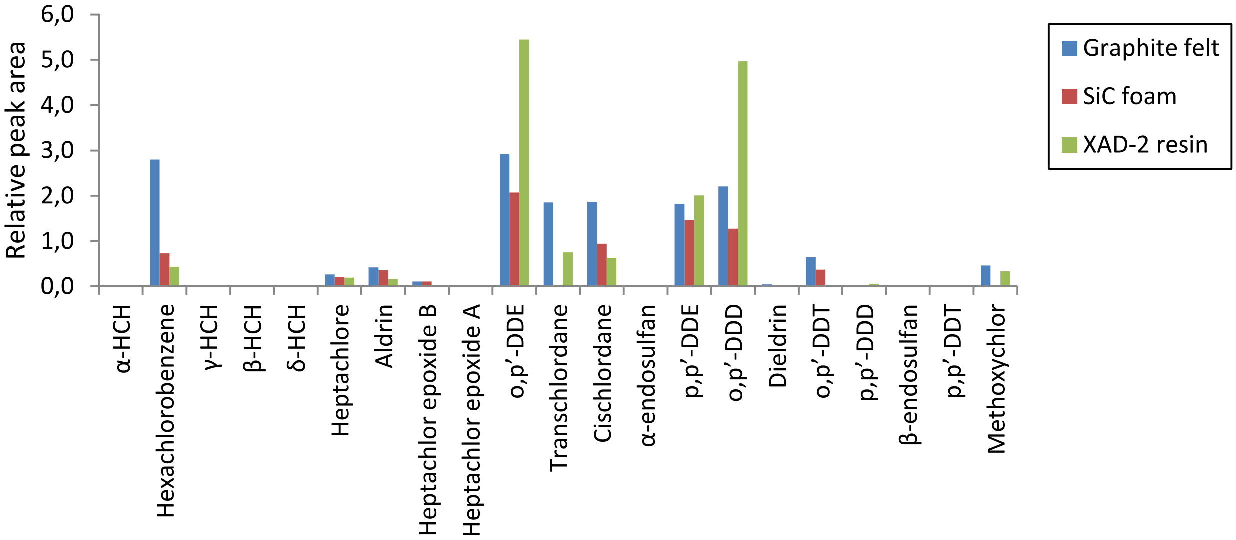


Figure 1-23 – Relative peak areas of OCP between April 22nd and 29th

The two sampling weeks gave similar results for OCP. No sampler was consistently better at trapping these compounds, though SiC foam mostly appears for heavier pesticides.
However, since Strasbourg has a "zero pesticides" policy and these OCP are now forbidden, one can wonder if detecting this many pesticides truly reflects what was in the air. There may have been a contamination of the sample via the SPME fibre, as at this point in the study there

was no systematic cleaning of the fibre. Only later was the memory effect of the fibre discovered.

GC pesticides results

Relative peak areas for these pesticides did not exceed 0.2, which was expected since Strasbourg's policy is not to use pesticides in public spaces. Detected pesticides have probably been transported from surrounding fields and villages. Seventeen pesticides were detected the first week and their results are summarised in Figure 1-24. The second week, twenty pesticides were detected and their results are summarised in Figure 1-25.

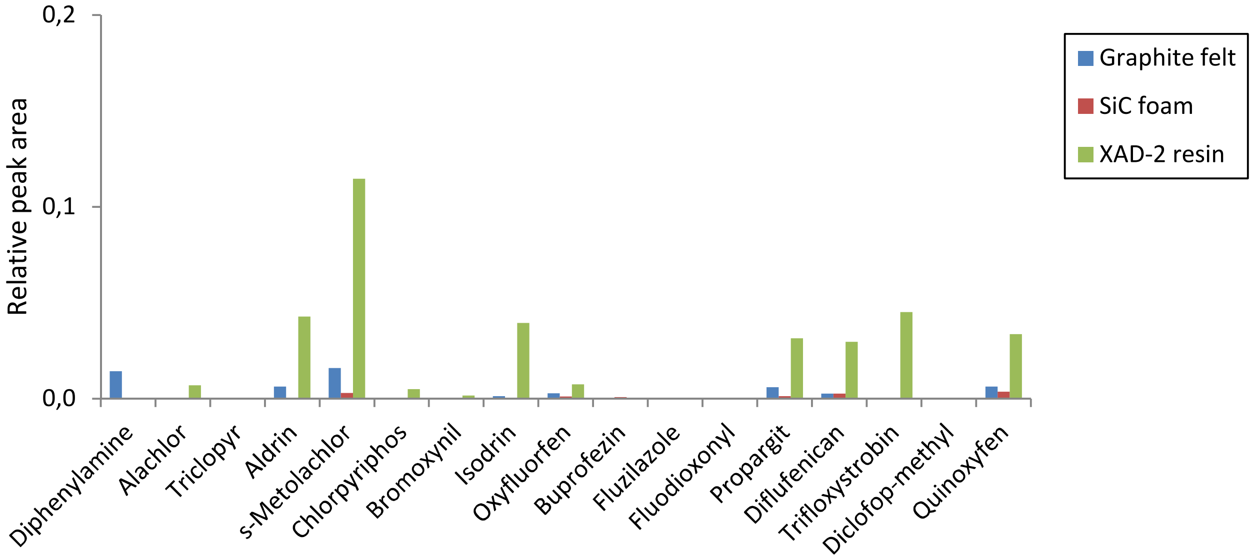


Figure 1-24 – Relative peak areas of non-chlorinated pesticides between April 11th and 22nd

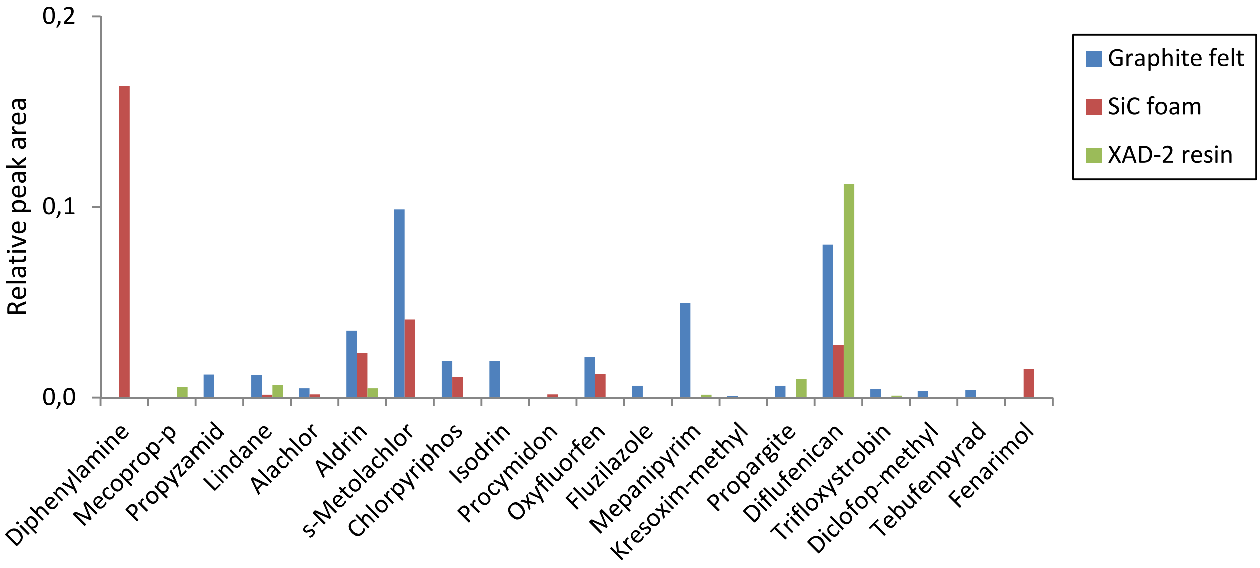


Figure 1-25 – Relative peak areas of non-chlorinated pesticides between April 22nd and 29th

Overall non-chlorinated pesticides, like PAH, gave opposite results depending on the sampling week. At first it seemed like XAD®-2 resin was the superior material for all compounds, but the second week graphite and SiC foam had better results.

However, these results have to be taken with caution, as several pesticides detected have been prohibited for decades and were not used in urban areas (alachlor, aldrin, diclofop methyl, diphenylamine, isodrin, fenarimol, flusilazole, lindane and procymidon). It is possible that there were false positives on the chromatograms, in which case it would explain the apparent randomness in sampler efficiency between the two weeks. But even discarding these pesticides, the conclusion does not change regarding the adsorbents' efficiency.

Discussion

Overall, both graphite felt and SiC foam gave good results and, in certain cases, were more efficient than XAD®-2 resin. This is especially true with heavier compounds, as can be seen with PAH and PCB results, despite the resin still seeming like the best adsorbent for more volatile molecules.

When comparable, graphite felt and SiC foam gave very similar results. In order to choose one of them, other properties had to be considered. Graphite felt, despite its efficiency, has a surface area of 1 to 2 m² g^{-1}. This is hundreds of times smaller than XAD®-2 and tens of times smaller than SiC foam, whose surface areas are respectively 300 m² g^{-1} and 30 m² g^{-1}. In this respect, graphite could be compared to PUF, another currently used material. This means the quantity of pollutants that can be adsorbed over longer periods of time on graphite felt will be very limited.

Moreover, SiC foam is a rigid structure that cannot be deformed, which means its outer windows have a fixed size wide enough to collect particles. Graphite felt is a much softer material that can be bent and deformed. While this makes it less likely to break, it means that pore size can vary. This makes the felt less reliable than SiC foam for particle collection. The hydrophobicity of the material also had to be taken into consideration. While PAH were better extracted from graphite felt than from CNT foam, the heavier ones were extracted in low quantities. The extraction method would need to be adjusted to compensate for this problem. Moreover, this hydrophobicity means that graphite felt would not be able to efficiently adsorb polar compounds, which includes several pesticides of interest.

Therefore, SiC foam was the material selected to be further studied.

V/ Conclusion

Three carbon-based adsorbents were tested in order to determine which one could be developed into a passive air sampler. CNT foam had the advantage of a high specific surface area, graphite felt was the easiest to handle and SiC foam had its macro- and mesoporous network.

Preliminary tests in the laboratory revealed that hydrophobic compounds such as PAH are too strongly adsorbed on CNT foam and cannot be extracted. This, combined with the difficulty to synthesise the foam to desired dimensions, made this material an unsuitable passive air sampler.

During these tests, it also appeared that SiC foam was much better extracted than CNT foam and graphite felt. While these results have been consistently replicated, it is currently unknown why such higher results were obtained.
A two-week sampling campaign was held in order to compare both graphite felt and SiC foam to the currently widely used XAD®-2 resin. While results varied from one week to another, some trends could be found. XAD®-2 resin is definitely the better adsorbent for gaseous pollutants, while graphite felt and SiC foam had better results for more particulate compounds.
In the end, graphite felt was put aside. Despite its good performance, its very low surface area means it will probably not perform as well as SiC foam during longer periods of time. Its hydrophobicity also means it strongly adsorbs compounds like PAH, making them difficult to extract. There are also concerns that its physical structure would be modified over time.

After this preliminary testing phase, SiC foam was the adsorbent selected for further study. Its macroporosity, medium surface area and rigid structure were a good compromise between the three pre-selected materials. SiC foam being less hydrophobic than the others means it is able to adsorb polar compounds that CNT foam and graphite felt could not. It also makes it easier to extract non polar pollutants from.

References

Ahmadkhaniha R., Samadi N., Salimi M., Sarkhail P., Rastkari N., **2012**, "Simultaneous determination of parathion, malathion, diazinon, and pirimiphos methyl in dried medicinal plants using solid-phase microextraction fibre coated with single-walled carbon nanotubes", *The Scientific World Journal*

Armstrong J. L., Fanske R. A., Yost M. G., Tchong-French M., Yu J., **2013**, "Comparison of polyurethane foam and XAD-2 sampling matrices to measure airborne organophosphorous pesticides and their oxygen analogs in an agricultural community", *Chemosphere*, *92*, 451-457

Asensio-Ramos M., Hernández-Borges J., Borges-Miquel T. M., Rodríguez-Delgado M. A., **2009**, "Evaluation of multi-walled carbon nanotubes as solid-phase extraction adsorbents of pesticides from agricultural, ornamental and forestal soils", *Analytica Chimica Acta*, *647*, 167-176

Association française de normalisation (2007). *Air ambiant – Dosage des substances phytosanitaires (pesticides) dans l'air ambiant – Prélèvement actif.* Norme XP X 43-058. La Plaine Saint-Denis : Association française de normalisation.

Dobson R., Scheyer A., Rizet A-L., Mirabel P., Millet M., **2006**, "Comparison of the efficiencies of different types of adsorbents at trapping currently used pesticides in the gaseous phase using the technique of high-volume sampling", *Analytical and Bioanalytical Chemistry*, *386*, 1781-1789

Duong-Viet C., Ba H., Liu Y., Truong-Phuoc L., Nhut J-M., Pham-Huu C., **2014**, "Nitrogen-doped carbon nanotubes on silicon carbide as a metal-free catalyst", *Chinese Journal of Catalysis*, *35*, 906-913

Duong-Viet C., Ba H., El-Berrichi Z., Nhut J-M., Ledoux M. J., Liu Y., Pham-Huu C., **2016**, "Silicon carbide foam as a porous support platform for catalytic applications", *New Journal of Chemistry*, *40*, 4285-4299

El-Kacemi S., Es-Souni Mar., Habouti S., Schopf D., Hamdani M., Es-Souni M., **2015**, "A one-pot synthesis of nanostructured mesoporous TiO_2 films on graphite felt substrates for fast catalysis", *RSC Advances*, *5*, 83115-83121

El-Sheikh A. H., Sweileh J. A., Al-Degs Y. S., Insisi A. A., Al-Rabady N., **2008**, "Critical evaluation and comparison of enrichment efficiency of multi-walled carbon nanotubes, C18 silica and activated carbon towards some pesticides from environmental waters", *Talanta*, *74*, 1675-1680

Eng A., Harner T., Pozo K., **2014**, "A prototype passive air sampler for measuring dry deposition of polycylic aromatic hydrocarbons", *Environmental Science & Technology Letters*, 77-81

Gouin T., Wania F., Ruepert C., Castillo L. E., **2008**, "Field testing passive air samplers for current use pesticides in a tropical environment", *Environmental Science & Technology*, *42*, 6625-6630

Guéguen F., Stille P., Millet M., **2013**, "Persistent organic pollutants in the atmosphere from urban and industrial environments in the Rhine Valley: PCB, PCDD/Fs", *Environmental Science and Pollution Research*, *20*, 3852-3862

Hadjmohammadi M. R., Peyrovi M., Biparva P., **2010**, "Comparison of C18 silica and multi-walled carbon nanotubes as the adsorbents for the solid-phase extraction of chlorpyrifos and phosalone in water samples using HPLC", *Journal of Separation Science*, *33*, 1044-1051

Hayward S. J., Gouin T., Wania F., **2010**, "Comparison of four active and passive sampling techniques for pesticides in air", *Environmental Science & Technology*, *44*, 3410-3416

Hazrati S., Harrad S., **2007**, "Calibration of polyurethane foam (PUF) disk passive air samplers for quantitative measurement of polychlorinated biphenyls (PCB) and polybrominated diphenyl ethers (PBDEs): Factors influencing sampling rates", *Chemosphere*, *67*, 448-455

Hu X., Liu J., Wang L., Zhao P., **2013**, "Application of multi-sorbent tubes filled with modified multi-walled carbon nanotubes for determining volatile organic compounds in a wide range of polarity", *Analytical Methods*, *5*, 4436-4441

Jaward F. M., Farrar N. J., Harner T., Sweetman A. J., Jones K. C., **2004**, "Passive air sampling of PCB, PBDEs, and organochlorine pesticides across Europe", *Environmental Science & Technology*, *38*, 34-41

Jiang X., Lou S., Chen D., Shen J., Han W., Sun X., Li J., Wang L., **2015**, "Fabrication of polyaniline/grapheme oxide composite for graphite felt electrode modification and its performance in the bioelectrochemical system", *Journal of Electroanalytical Chemistry*, *744*, 95-100

Jin Y., Hawkins S. C., Huynh C. P., Su S., **2013**, "Carbon nanotube modified carbon composite monoliths as superior adsorbents for carbon dioxide capture", *Energy & Environmental Science*, *6*, 2591-2596

Klánová J., Èupr P., Kohoutek J., Harner T., **2008**, "Assessing the influence of meteorological parameters on the performance of polyurethane foam-based passive air samplers", *Environmental Science & Technology*, *42*, 550-555

Kouamé N. A., Robert D., Keller V., Keller N., Pham C., Nguyen P., **2011**, "Preliminary study of the use of β-SiC foam as a photocatalytic support for water treatment", *Catalysis Today*, *161*, 3-7

Lacroix M., Dreibine L., de Tymowski B., Vigneron F., Edouard D., Bégin D., Nguyen P., Pham C., Savin-Poncet S., Luck F., Ledoux M-J., Pham-Huu C., **2011**, "Silicon carbide foam composite containing cobalt as a highly selective and re-usable Fischer-Tropsch synthesis catalyst", *Applied Catalysis A: General*, *397*, 62-72

Ledoux M. J., Hantzer S., Pham-Huu C., Guille J., Desaneaux M-P., **1988**, "New synthesis and uses of high-specific-surface SiC as a catalytic support that is chemically inert and has high thermal resistance", *Journal of Catalysis*, *114*, 176-185

Li Q-L., Yuan D-X., Lin Q-M., **2004**, "Evaluation of multi-walled carbon nanotubes as an adsorbent for trapping volatile organic compounds from environmental samples", *Journal of Chromatography A*, *1026*, 283-288

(a) Liu Y., Ba H., Nguyen D-L., Ersen O., Romero T., Zafeiratos S., Begin D., Janowska I., Pham-Huu C., **2013**, "Synthesis of porous carbon nanotubes foam composites with a high accessible surface area and tunable porosity", *Journal of Materials Chemistry A*, *1*, 9508-9516

(b) Liu Y., Edouard D., Nguyen L. D., Begin D., Nguyen P., Pham C., Pham-Huu C., **2013**, "High performance structured platelet milli-reactor filled with supported cobalt open cell SiC foam catalyst for the Fischer-Tropsch synthesis", *Chemical Engineering Journal*, *222*, 265-273

Lohmann R., Corrigan B. P., Howsam M., Jones K. C., Ockenden W. A., **2001**, "Further developments in the use of semipermeable membrane devices (SPMDs) as passive air samplers for persistent organic pollutants: field application in a spatial survey of PCDD/Fs and PAH", *Environmental Science & Technology*, *35*, 2576-2582

Long R. Q., Yang R. T., **2001**, "Carbon nanotubes as superior sorbent for dioxin removal", *Journal of the American Chemical Society*, *123*, 2058-2059

Lü J., Liu J., Wei Y., Jiang K., Fan S., Liu J., Jiang G., **2007**, "Preparation of single-walled carbon nanotubes fiber coating for solid-phase microextraction of organochlorine pesticides in lake water and wastewater", *Journal of Separation Science*, *30*, 2138-2143

Moene R., Kramer L. F., Schoonman J., Makkee M., Moulijn J. A., **1995**, "Conversion of activated carbon into porous silicon carbide by fluidized bed chemical vapour deposition", *Studies in surface science and catalysis*, *91*, 371-380

Namieśnik J., Zabiegala B., Kot-Wasik A., Partyka M., Wasik A., **2005**, "Passive sampling and/or extraction techniques in environmental analysis: a review", *Analytical and Bioanalytical Chemistry*, *381*, 279-301

Nguyen P., Pham C., **2011**, "Innovative porous SiC-based materials: From nanoscopic understandings to tunable carriers serving catalytic needs", *Applied Catalysis A: General*, *391*, 443-454

Park S., Kim H., **2015**, "Fabrication of nitrogen-doped graphite felts as positive electrodes using polypyrrole as a coating agent in vanadium redox flow batteries", *Journal of Materials Chemistry A*, *3*, 12276-12283

Peigney A., Laurent Ch., Flahaut E., Bacsa R. R., Rousset A., **2001**, "Specific surface area of carbon nanotubes and bundles of carbon nanotubes", *Carbon*, *39*, 507-514

Prest H. F., Jacobson L. A., **1995**, "Passive sampling of water and coastal air via semipermeable membrane devices", *Chemosphere*, *30*, 1351-1361

Qingxiang Z., Junping X., Guohong X., Weidong W., Yujie D., Huahua B., **2009**, "Enrichment of pyrethroid residues in environmental waters using a multiwalled carbon nanotubes cartridge, and analysis in combination with high performance liquid chromatography", *Microchimica Acta*, *164*, 419-424

Rabbow T. J., Trampert M., Pokorny P., Binder P., Whitehead A. H., **2015**, "Variability within a single type of polyacrylonitrile-based graphite felt after thermal treatment. Part II: chemical properties", *Electrochimica Acta*, *173*, 24-30

Schummer C., Mothiron E., Appenzeller B. M. R., Rizet A-L., Wenning R., Millet M., **2010**, "Temporal variations of concentrations of currently used pesticides in the atmosphere of Strasbourg, France", *Environmental Pollution*, *158*, 576-584

Shen Y., Li L., Xiao K., Xi J., **2016**, "Constructing three-dimensional hierarchical architectures by integrating carbon nanofibers into graphite felts for water purification", *ACS Sustainable Chemistry & Engineering*, *4*, 2351-2358

Shoeib M., Harner T., **2002**, "Characterization and comparison of three passive air samplers for persistent organic pollutants", *Environmental Science & Technology*, *36*, 4142-4151

Shuo W., Peng Z., Guang M., Guozhen F., **2007**, "Multi-residue determination of pesticides in water using multi-walled carbon nanotubes solid-phase extraction and gas chromatography–mass spectrometry", *Journal of Chromatography A*, *1165*, 166-171

Shu-Xia G., Zhi-Gang Y., Hai-Nan Y., Chun-Hong S., Zeng-Qiang S., Zhi Q., **2011**, "Multi-walled carbon nanotubes as matrix solid-phase dispersion extraction adsorbent for simultaneous analysis of residues of nine organophosphorus pesticides in fruit and vegetables by rapid resolution LC–MS–MS", *Chromatographia*, *73*, 33-41

Sigma Aldrich, *Amberlite XAD-2 Polymeric Adsorbent* [Online] Available at https://www.sigmaaldrich.com/content/dam/sigma-aldrich/docs/Supelco/Product_Information_Sheet/ 4802.pdf [Accessed April 2016]

Su D. S., Perathoner S., Centi G., **2013**, "Nanocarbons for the development of advanced catalysts", *Chemical Reviews*, *113*, 5782-5816

Sun F., Gao J., Zhu Y., Chen G., Wu S., Qin Y., **2013**, "Adsorption of SO_2 by typical carbonaceous material: a comparative study of carbon nanotubes and activated carbons", *Adsorption*, *19*, 959-966

Truong Huu T., Détermination des grandeurs hydrodynamiques et thermiques d'un support à base de mousse alvéolaire β-SiC pour la synthèse de Fischer-Tropsch. De la modélisation vers l'application., Thesis, Strasbourg University, 2011

Tuduri L., Harner T., Hung H., **2006**, "Polyurethane foam (PUF) disks passive air samplers: wind effect on sampling rates", *Environmental Pollution*, *144*, 377-383

Vanhaecke E., Ivanova S., Deneuve A., Ersen O., Edouard D., Winé G., Nguyen P., Pham C., Pham-Huu C., **2008**, “1D SiC decoration of SiC macroscopic shapes for filtration devices”, *Journal of Materials Chemistry*, *18*, 4654-4662

Velzeboer I., Kwadijk C. J. A. F., Koelmans A. A., **2014**, “Strong sorption of PCB to nanoplastics, microplastics, carbon nanotubes, and fullerenes”, *Environmental Science & Technology*, *48*, 4869-4876

Wang S., Zhao P., Min G., Fang G., **2007**, “Multi-residue determination of pesticides in water using multi-walled carbon nanotubes solid-phase extraction and gas chromatography-mass spectrometry”, *Journal of Chromatography A*, *1165*, 166-171

Wang J., Tuduri L., Millet M., Briand O., Montury M., **2009**, “Flexibility of solid-phase microextraction for passive sampling of atmospheric pesticides”, *Journal of Chromatography A*, *1216*, 3031-3037

Wang X-P., Gong P., Yao T-D., Jones K.C., **2010**, “Passive air sampling of organochlorine pesticides, polychlorinated biphenyls, and polybrominated diphenyl ethers across the Tibetan plateau”, *Environmental Science & Technology*, *44*, 2988-2993

Wania F., Shen L., Duan Lei Y., Teixeira C., Muir D. C. G., **2003**, “Development and calibration of a resin-based passive sampling system for monitoring persistent organic pollutants in the atmosphere”, *Environmental Science & Technology*, *37*, 1352-1359

Yu F., Zhou M., Yu X., **2015**, “Cost-effective electro-Fenton using modified graphite felt that dramatically enhanced on H_2O_2 electro-generation without external aeration”, *Electrochimica Acta*, *163*, 182-189

Yuan H., Sun Z., Liu H., Zhang B., Chen C., Wang H., Yang Z., Zhang J., Wei F., Sheng Su D., **2013**, “Immobilizing carbon nanotubes on SiC foam as a monolith catalyst for oxidative dehydrogenation reactions”, *ChemCatChem Communications*, *5*, 1713-1717

Chapter 2: Developing an analytical method

I/ Introduction: Sample preparation

Atmospheric samples can be prepared in a number of ways, depending on the matrix and the pollutants being monitored.

1. Extraction

Airborne pollutants, gathered actively or passively, are trapped on solid adsorbents. Thus the first preparation step is usually a solid/liquid extraction (Tang, 2013).

Soxhlet is a very common extraction method that has been officially recommended in several norms regarding pollutants monitoring (UNEP, 2007 ; US EPA, 2016). It has been used to extract different air sampling matrices like GFF (Tao et al., 2007), PUF (Jaward et al., 2005) and XAD®-2 (Gouin et al., 2008b), but also sediments (Tang et al., 2012) or dust (Kefeni & Okonkwo, 2012). Depending on solvent used, Soxhlet has proven to be able to extract PCB, PBDE, PCDD and OC compounds (Yang et al., 1999 ; Jaward et al., 2005), as well as PAH (Tao et al., 2007) and pesticides (Gouin et al., 2008a). This makes Soxhlet a versatile extraction method, efficient on most of the atmospheric pollutants of interest. However, Soxhlet extraction is a lengthy process that can take hours if not days to complete. It also requires great quantities of solvent that need to be evaporated afterwards, and has been proven to be less effective than other methods, like sonication or ASE (Yang et al., 1999). Soxhlet is now mostly used for pre-cleaning matrices.

ASE is closely related to Soxhlet, but it is faster and uses less solvent. It also has the advantage of being an automated process that can be programmed and thus does not require the user's presence. Using a machine also allows for precise quantities of solvent to be pumped when more than one is used. The most common air samplers can be extracted by ASE: GFF (Mokbel et al., 2016), XAD®-2 (Guéguen et al., 2013) and PUF (Liu et al., 2016); as well as several other matrices like sediments (Duodu et al., 2016), dust (Mercier et al., 2014) and even insects (Lambert et al., 2012). From this wide range of matrices, different families of pollutants can be extracted. ASE is used for extracting pesticides (Schummer et al., 2012) and OCP (Duodu et al., 2016), PAH (Lambert et al., 2012), PCB (Mokbel et al., 2016) or PBDE (Mercier et al., 2014). While these pollutants can be extracted on their own, multi-residue extraction methods are common when using ASE. Solvent quantity varies depending on cell size, matrix dimensions and number of extraction cycles, but the solvent needs to be evaporated in order to concentrate the extracted sample.

In recent years, ultrasound-assisted extraction has gained popularity due to it being a fast extraction method using little solvent, making it both useful and environmentally-friendly. Ultrasonic extraction can be used on its own as the sole extraction method for a given sample, or it can be a complementary method to solid/liquid or liquid/liquid extraction. While initially

developed as a solid/liquid extraction method, sonication can now be used on liquid samples as well (Albero et al., 2015). With the different ways of using ultrasonic waves, a wide range of matrices can be extracted: water (Alberto et al., 2015), sediments (Tölgyessy et al., 2013), food (Pico et al., 2013), dust (Kopp et al., 2012), etc. Regarding air samples, there are examples of GFF (Haraguchi et al., 1994) and XAD®-2 resin (Tavares et al., 2004) being extracted by sonication. SPMD used in polluted water have also been successfully extracted (Bustamante et al., 2013). A great variety of pollutants can be extracted by sonication, both organic and metallic (Pico et al., 2013). Semi-volatile organic compounds are efficiently extracted by this method too: PAH (Tavares et al., 2004), pesticides (Haraguchi et al., 1994), OCP (Alberto et al., 2015), PCB and PBDE (Tölgyessy et al., 2013) extractions are well documented. So sonication is a versatile method applicable to a wide range of samples, but it may need to be combined with another extraction method depending on the sample of interest.
Finally, there is one currently used extraction method that does not rely on solvent. This is thermal desorption, another automated process. It needs to be followed immediately by gas chromatography so the desorbed analytes can be directly analysed. Thermal desorption is mainly used for air samples (Aragon et al., 2013), including dust (Nilsson et al., 2005) and generally particulate matter (Mercier et al., 2012), but there are examples of thermally desorbing soil samples (Mascolo et al., 2013). Air samples are most often trapped on Tenax-TA® tubes (Clément et al., 2000), while particles are collected on a glass or quartz fibre filter (Ho, 2008). The desorption itself can be direct or indirect. A "two-stage" desorption can take place, where the sample is first desorbed in order for the analytes to be trapped on a Tenax tube, which is then desorbed and the GC analysis can take place (Mascolo et al., 2013). Thermal desorption can extract a wide range of compounds, provided they are volatile and thermally stable (Aragon et al., 2013). Pollutants such as PAH, PCB, PBDE and phthalates (Mercier et al., 2012) are often extracted using this technique, and pesticides too have been successfully detected (Clément et al., 2000). This method is quick, easy to use, but is destructive since samples can only be desorbed once.

2. Cleanup

After the extraction step, except in the case of thermal desorption, samples have to be cleaned. Several methods are commonly used, depending on the type of sample.
Solid phase extraction (SPE) is a cleanup method that doubles as concentration step, since compounds adsorbed on SPE cartridges are eluted with little solvent. The most common cartridges are C_{18} silica and hydrophobic-hydrophilic balanced ones (Mogolodi Dimpe & Nomngongo, 2016), and yet there has been an increasing number of reports of magnetic SPE using metallic oxides as sorbents (Wierucka & Biziuk, 2014). SPE is particularly suited to cleaning and concentrating liquid samples, which is why it is a method of choice for water samples. Water samples represent the vast majority of samples cleaned by SPE, but it has also been used for food or biological samples (Wierucka & Biziuk, 2014), and there are some examples of soil (Meghesan-Breja et al., 2015) samples undergoing SPE. Using this technique for air samples is very rare, though there are some reports (Raina-Fulton, 2015). Several pollutants have been successfully extracted by SPE: PAH (Moja & Mtunzi, 2013), PCB (Westbom et al., 2004) and pesticides (Bonansea et al., 2013) are commonly monitored in

water samples, but also PBDE, metals or dyes (Wierucka & Biziuk, 2014). This makes SPE a versatile method, but one rarely used outside of liquid samples and thus almost never coupled to another preparation technique.

Like SPE, SPME is both a cleaning and concentration technique. Additionally, SPME is also an injection step as it is often directly coupled to GC, LC or MS analysis (Piri-Moghadam et al., 2016). Such an extraction can be done on a sample in the laboratory, but also *in situ* (Piri-Moghadam et al., 2016) or even *in vivo* (Souza-Silva et al., 2015a). The main application for SPME is extracting water samples (Piri-Moghadam et al., 2016), but it is also used extensively for food (Xu et al., 2016), soil (Souza-Silva et al., 2015a) and biological samples (Souza-Silva et al., 2015b). However, there are few examples of SPME of atmospheric samples. Schummer et al. (2012) and Raeppel et al. (2014) have successfully used SPME to concentrate atmospheric pesticides extracted from XAD®-2 resin and GFF. From these diverse matrices, a wide variety of compounds can be extracted by SPME, from food flavours (Xu et al., 2016) to medical drugs (Souza-Silva et al., 2015b). Pollutants extracted from environmental samples include OCP, OPP and other pesticides, PCB, PAH, phthalates and BTEX (Souza-Silva et al., 2015a ; Piri-Moghadam et al., 2016). Depending on the volatility of the compounds of interest, the SPME fibre is placed either inside the sample or above, in headspace. The most versatile fibre coating is PDMS, used to extract almost any matrix (Souza-Silva et al., 2015a ; Piri-Moghadam et al., 2016), though PDMS/DVB or DVB/CAR/PDMS are more resilient for food samples (Xu et al., 2016). For pesticides, especially polar ones, PA fibre can also be used (Piri-Moghadam et al., 2016). In the end, SPME has the versatility of SPE, but uses less solvent and can directly be coupled to GC or LC. Like SPE, it is rarely paired with another extraction or pre-cleaning technique.

Despite the efficiency of these two methods, samples are still routinely cleaned via separation on a silica, alumina or Florisil® column (Tang, 2013). While effective, preparative chromatography is a long process that cannot be automated, and requires great quantities of solvent. There have been reports of cleanup taking place in an ASE cell by putting silica gel, alumina, Florisil® or an SPMD inside (Tang, 2013), but these techniques are not widely used and are not suited for all kinds of samples. They do significantly reduce the sample preparation time.

3. Analysis

After samples extractions and cleanup, the analysis can take place. Most analyses of SVOC are currently done by GC, but less volatile compounds are rather injected in LC (Scheyer et al., 2007 ; Tang, 2013).

For detection, mass spectrometry (MS) has become the standard for SVOC. Tandem mass spectrometry (MSMS) is especially popular, with low limits of detection and the ability to single one compound of interest among others.

4. Coupling ASE, SPE and SPME

The method proposed in this study uses classical GC-MSMS and LC-MSMS for analytical purposes. Sample preparation, however, is done by coupling ASE, SPE and SPME. ASE and

SPME have been used in previous works to extract pesticides from XAD®-2 resin (Schummer et al., 2012 ; Raeppel et al., 2014). More recently, Raina-Fulton (2015) used ASE and SPE to prepare atmospheric pesticides samples collected on PUF and GFF. And coupling SPE and SPME has been done for the analysis of pesticides in water samples (Bonansea et al., 2013). Our proposed method links all three methods in order to optimise extraction, cleaning and injection.

Evaporating ASE extracts on a rotary evaporator results in a loss of more volatile compounds like naphthalene, when there are only traces in a sample. Using SPE to treat ASE extracts is a way of concentrating the sample without this drawback. Since SPE is also a way of purifying the solution, this reduces the number of steps before SPME. SPME is an additional concentration of the sample doubling as the injection step. Using these three techniques, the resulting method allows samples to be quickly prepared for injection, with minimal use of solvent and little evaporation needed, and two concentration steps to achieve high sensitivity.

II/ Accelerated Solvent Extraction

1. Fitting samplers into ASE cells

All extractions were performed on a DIONEX® ASE 300, which can be used with 34-, 66- or 100 mL extraction cells. In order to optimise solvent repartition inside the cell, samplers were made to fit exactly inside.

XAD®-2 resin was put in meshed cylinders 15.9 cm long with a 2.9 cm diameter, to match the 100 mL cells which are 16.0 cm long with a 3.0 cm diameter.

SiC foams were cut as 5.0 cm long cylinders with a 2.8 cm diameter, to match the 34 mL cells which are 5.1 cm long cylinders with a 3.0 cm diameter. This smaller size –a third of the resin cylinder– was chosen to save extraction solvent during the preliminary testing phase (Figure 2-1). However, SiC foam was effective enough at these dimensions so they were kept throughout the whole study.

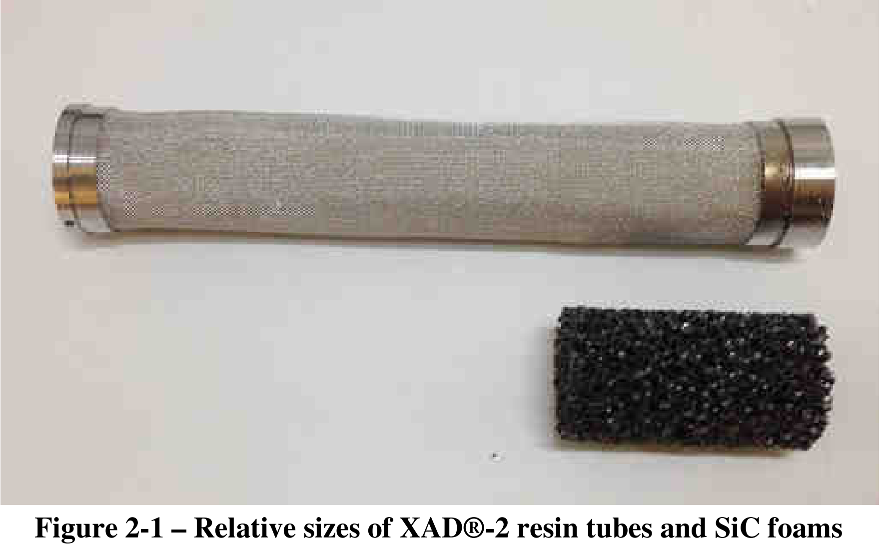


Figure 2-1 – Relative sizes of XAD®-2 resin tubes and SiC foams

2. Cleaning matrices

A method for cleaning samplers by ASE was already in place. They were washed using one 10-min cycle at 80 °C and 1500 psi with a 50/50 (v/v) hexane/dichloromethane solution. This method was used for XAD®-2 resin, but works for SiC foam as well.

XAD®-2 needs to be dried in the laboratory oven (50 °C) after this washing, but SiC foam can be reused immediately.

Both materials are washed once before use, and once after.

3. Optimisation of an existing method

An ASE method already existed for XAD®-2 resin, validated by Schummer et al. (2012). It consisted of three 15 min cycles at 1500 psi and 150 °C with acetonitrile.

This method was tested on SiC foam and XAD®-2 resin spiked with 50 µL of a 10 mg L^{-1} solution of PAH, PCB and OCP. While the extraction was effective, it was overlong when extracting several samplers and used a large quantity of solvent.

Further testing was done to reduce the extraction time without losing efficiency. The cycles' length was reduced from 15 to 10 minutes, which had no discernable effect on the extraction yield. Figures 2-2, 2-3 and 2-4 respectively show the relative peak areas of PAH, PCB and OCP extracted from SiC foam with 15 min cycles and 10 min cycles.

Due to a problem with the mass spectrometer, not all PAH could be detected, but a clear trend can be seen, and this is confirmed with PCB and OCP results.

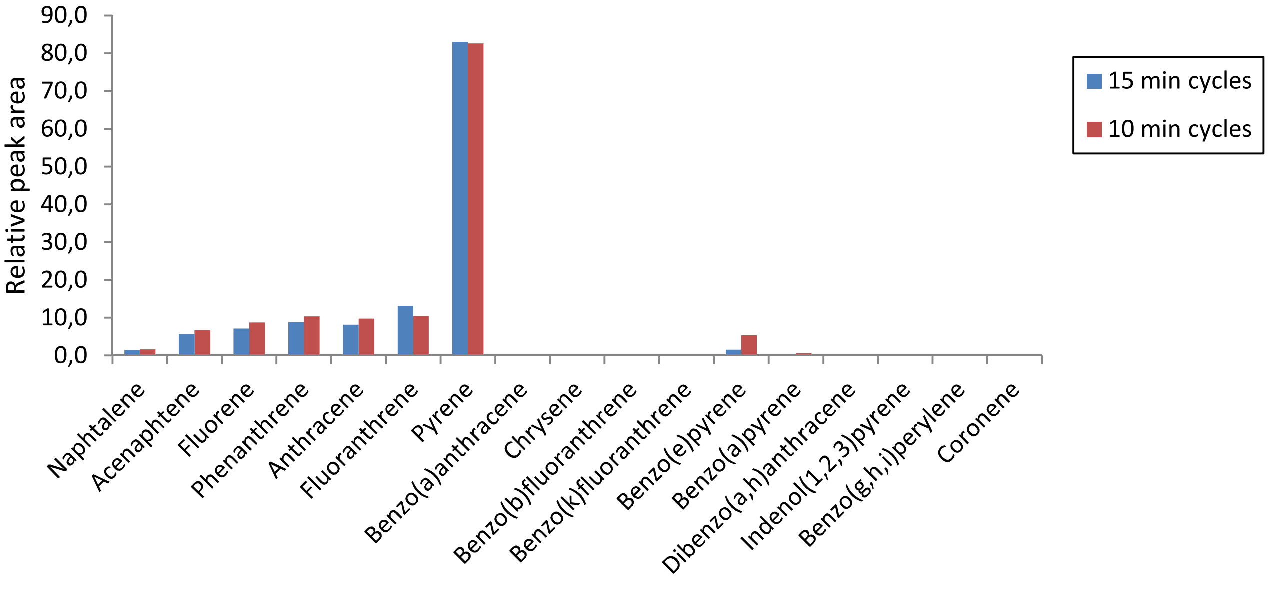


Figure 2-2 – Relative peak areas of PAH extracted from SiC foam with 15- and 10-min ASE cycles

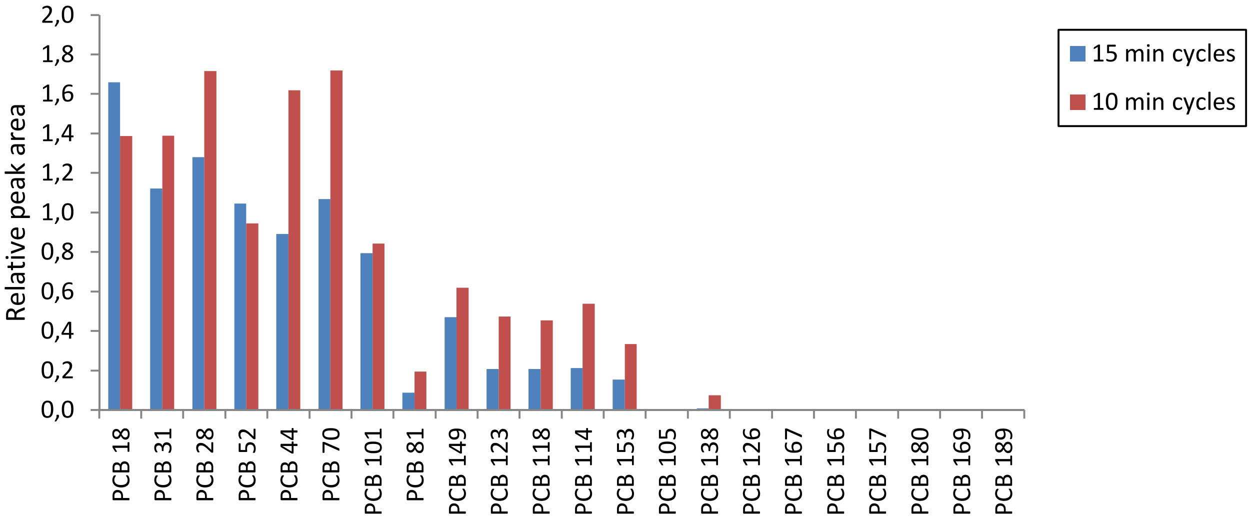


Figure 2-3 – Relative peak areas of PCB extracted from SiC foam with 15- and 10-min ASE cycles

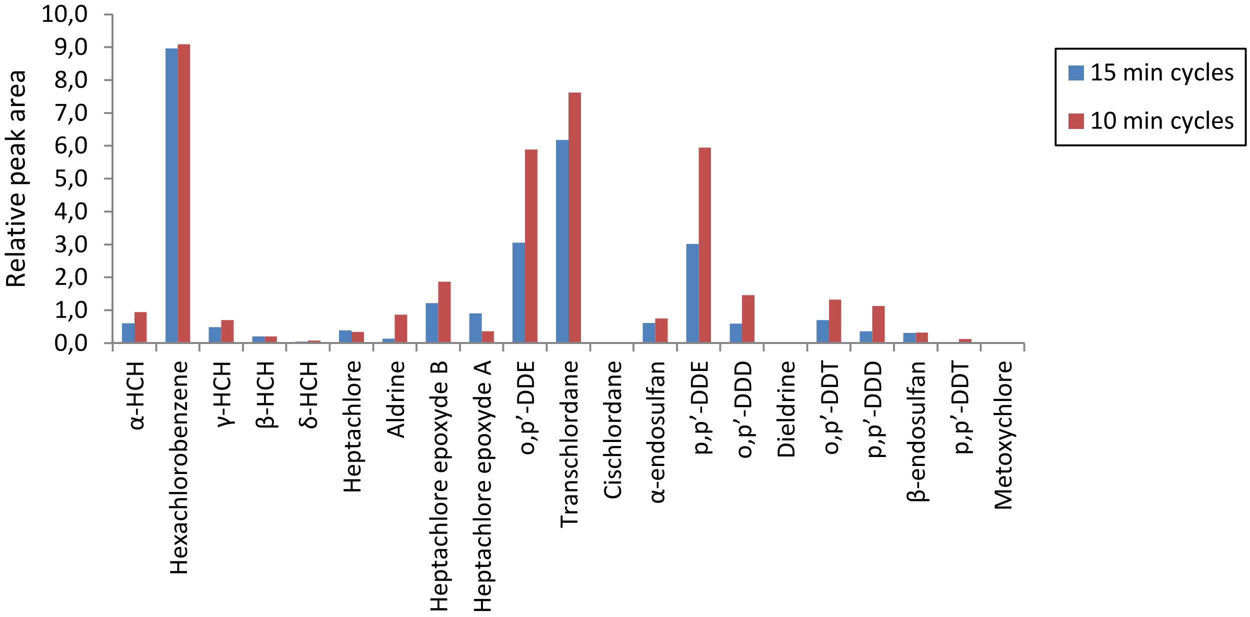


Figure 2-4 – Relative peak areas of OCP extracted from SiC foam with 15- and 10-min ASE cycles

The cycles' length was then fixed at 10 min.

The number of cycles too was reduced, from three to two. Two 10 min ASE cycles are enough to extract most of the pollutants from both SiC foam and XAD®-2 resin.

As in the previous test, not all PAH could be detected, but all gave similar results that were in agreement with results from PCB and OCP.

Only some PAH were detected with a third extraction cycle, as seen on Figure 2-5. Several PCB (Figure 2-6) and OCP (Figure 2-7) are fully extracted with only one cycle, and only one of each (PCB 153 and hexachlorobenzene) was detected in the third cycle.

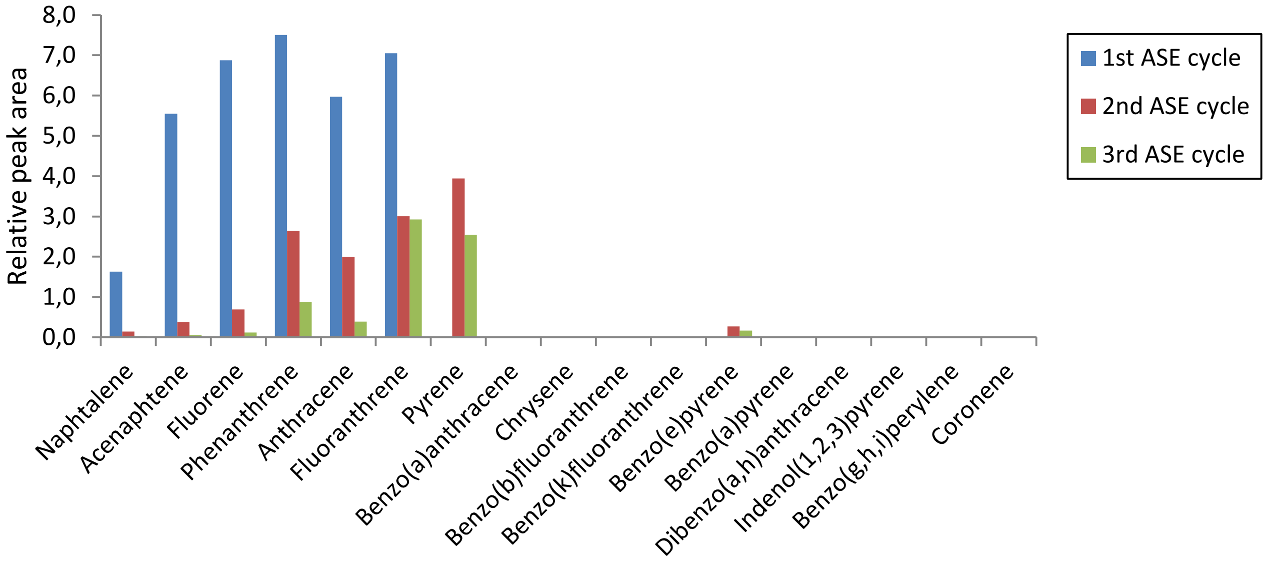


Figure 2-5 – Relative peak areas of PAH extracted from SiC foam after 1, 2 and 3 cycles

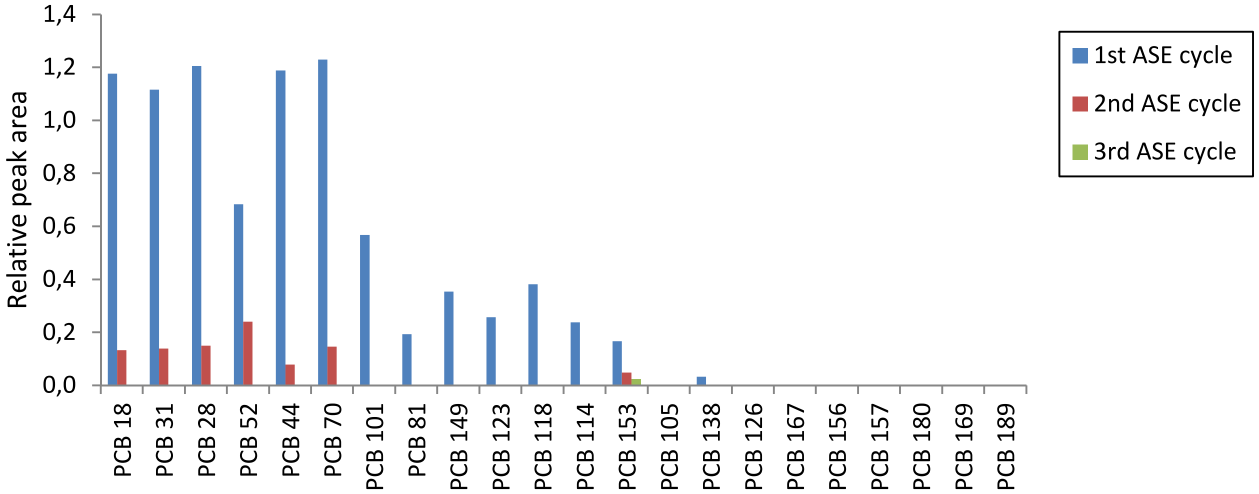


Figure 2-6 – Relative peak areas of PCB extracted from SiC foam after 1, 2 and 3 cycles

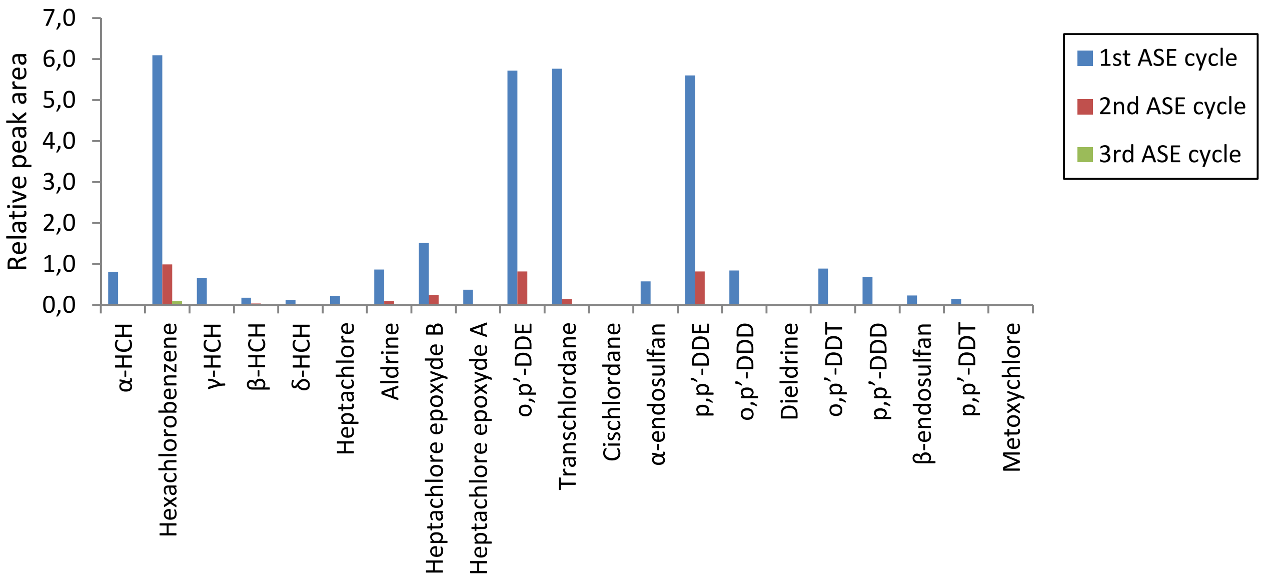


Figure 2-7 – Relative peak areas of OCP extracted from SiC foam after 1, 2 and 3 cycles

Acetonitrile was kept as the extraction solvent. Since the next steps in the preparation of the samples are SPE and SPME, done in water, a solvent miscible in water was needed.

III/ Solid Phase Extraction

ASE was directly followed was SPE in order to avoid concentrating the extract on a rotary evaporator, which results in losses for the most volatile compounds. Moreover, evaporing acetonitrile on a rotary evaporator is a long process. While SPE also takes time, it concentrates and cleans the extracts at the same time, combining two steps into one.

1. Preparation of ASE extracts for SPE

ASE extracts are 100 mL solutions of acetonitrile, using the above method. In order to increase the affinity between the mostly non-polar pollutants and the non-polar SPE cartridge, the extracted solution needs a more polar solvent than acetonitrile. Thus, water is added to the 100-mL extracts to obtain 1-L solutions. The aqueous solution is set at pH 3 by addition of nitric acid, so that the more acidic pesticides will stay protonated and be more easily retained on the SPE cartridges. This pH was chosen due to it having already been used in previous works concerning the SPME of pesticides (Scheyer et al., 2007 ; Raeppel et al., 2014) and phenols (Jaber et al., 2007 ; Schummer et al., 2009).

The volume of the aqueous solution was chosen so that acetonitrile could play the role of a modifier. When extracting PAH via SPE, an organic modifier can be added to the aqueous sample to increase recovery rates. Solvents that can be used as modifiers include 2-propanol (Busetti et al., 2006 ; Kiss et al., 1996), methanol (Sibiya et al., 2012 ; Kiss et al., 1996), acetonitrile (Sibiya et al., 2012) and isopropanol (Urbe & Ruana, 1997). Modifier/sample ratio (v/v) varies from 5 to 25%, but there is often no increase past 10 %, which is considered the optimal ratio (Busetti et al., 2006 ; Urbe & Ruana, 1997).

In this study, with ASE extracts being 100 mL of acetonitrile, SPE samples had to have a volume of 1 L in order for the solvent to make up 10 % of the aqueous solution. According to Sibiya et al. (2012), 10 % acetonitrile is not enough to extract all PAH and 2-propanol or methanol should be used instead. However, solvent-exchanging the sample between ASE and SPE would defeat the purpose of this coupling, which is to reduce preparation steps and solvent usage. Moreover, recovery rates from SPE have been calculated for all compounds, and PAH recovery is above 80 % for all seventeen with the exception of benzo(e)pyrene and coronene (Table 2-1).

2. Parameters of the SPE methods – cartridges and solvents

PAH are most commonly extracted with C_{18} cartridges (Bispo et al., 2011 ; Sibiya et al., 2012). The same applies to PCB which are mostly extracted with C_{18} cartridges (Mahindrakar et al., 2014 ; Wittsiepe et al., 2014) or disks (Westbom et al., 2004 ; Otaka et al., 2004), but they can also be eluted on Strata-X (Zhang & Rhind, 2011) or HLB (Lin et al., 2013) cartridges. Pesticides –OCP or non chlorinated– can be extracted with HLB (Montagner et al., 2014), PSA (Hou et al., 2013 ; Iwafune et al., 2014) or C_{18} (Bonansea et al., 2013 ; Martins et al., 2013) cartridges. There have also been attempts at using graphene (Shi et al., 2014) and multi-walled carbon nanotubes (MWCNT) (Guo & Lee, 2011 ; Ma et al., 2010) cartridges to extract pesticides and PAH. In this study, C_{18} cartridges were chosen as they are an efficient compromise to extract PAH, PCB and pesticides.

Commonly used eluents for PAH are methanol, acetonitrile and acetone (Moja & Mtunzi, 2013 ; Khalili-Fard et al., 2012), but non polar solvents like hexane and dichloromethane can sometimes be used (Kouzaiha et al., 2001 ; Ma et al., 2010). PCB, however, are most often eluted with non polar solvent like hexane (Mahindrakar et al., 2014 ; Wittsiepe et al., 2014), pentane (Westbom et al., 2004) or dichloromethane (Zhang & Rhind, 2011), though acetone (Otaka et al., 2004) seems to be able to elute them. Pesticides, like PAH, are usually eluted with polar solvents such as methanol (El-Osmani et al., 2014), acetonitrile (Hou et al., 2013) and acetone (Shi et al., 2014) or with a mix of polar and non polar solvents (Martins et al., 2013).

Usually only one eluent is used, but there can be two solvents of different polarities (Bispo et al., 2011 ; Montagner et al., 2014) eluting one after the other. The present study uses three solvents of varying polarity to ensure elution of all analytes: ethyl acetate for PAH and pesticides, then toluene for PCB, and finally acetonitrile, as they are all soluble in this solvent.

Recovery rates for a selected number of compounds have been calculated. These compounds were chosen over a wide range of retention times, molecular weights, and for GC pesticides there are both polar and non polar molecules.

Recovery rates were calculated based on the extraction of three 1 L aqueous solutions spiked with 100 µL of 10 mg L^{-1} solutions of pollutants. They are summarised in Tables 2-1 and 2-2. In general, PCB had the best recovery rates while PAH had the lowest.

Table 2-1 – SPE recovery rates for PAH, PCB and OCP

PAH	% recovery	PCB	% recovery	OCP	% recovery
Acenaphtene	95.4	PCB 44	89.3	Aldrin	88.5
Anthracene	82.7	PCB 52	77.2	α-endosulfan	87.3
Benzo(a)anthracene	98.8	PCB 70	88.2	β-HCH	85.2
Benzo(a)pyrene	92.2	PCB 101	91.2	Cischlordane	94.2
Benzo(b)fluoranthrene	97.9	PCB 105	94.2	δ-HCH	78.2
Benzo(e)pyrene	36.7	PCB 114	96.3	γ-HCH	101.2
Benzo(g,h,i)perylene	108.2	PCB 126	98.2	Heptachlor epoxide A	88.1
Benzo(k)fluoranthrene	100.4	PCB 149	84.8	Hexachlorobenzene	78.2
Chrysene	102.0	PCB 156	97.2	p,p'-DDE	88.5
Coronene	28.2	PCB 157	94.3	p,p'-DDT	99.2
Dibenzo(a,h)anthracene	85.9	PCB 169	92.8	Transchlordane	93.2
Fluoranthrene	96.6	PCB 180	95.2		
Fluorene	97.2	PCB 189	99.1		
Indenol(1,2,3)pyrene	88.8				
Naphthalene	84.1				
Phenanthrene	83.7				
Pyrene	100.5				

Table 2-2 – SPE recovery rates for GC and LC pesticides

GC pesticides	% recovery	GC pesticides	% recovery	LC pesticides	% recovery
2,4-MCPA	94.2	Lenacil	101.3	Diflufenican	76.0
Acetochlor	85.5	Mecoprop-p	92.0	Epoxiconazole	91.3
Aclonifen	96.3	Mepanipyrim	98.2	Isoxadifen	89.0
Benoxacor	97.1	Propyzamide	90.1	Penconazole	72.0
Bromoxynil	87.8	Quinoxyfen	97.2	Pendimethalin	94.3
Buprofezin	84.3	s-Metolachlor	78.5		
Captan	89.3	Spiroxamine	85.3		
Clomazone	90.8	Tebutam	95.0		
Fenpropidin	89.1	Tolylfluanid	88.3		
Folpet	97.3	Triclopyr	88.3		
Ioxynil	102.3				

Recovery rates were generally high. Out of 67 compounds tested, 47 (70 %) had recovery rates above 80 %.

Benzo(e)pyrene and coronene had particularly low recovery rates, at 36.7 % and 28.2 % respectively. While this means traces of these pollutants could be lost during SPE, PAH quantities were generally high in the samples gathered during this study.

IV/ Solid Phase Micro Extraction

1. Preparation of SPE extracts for SPME

SPE extracts are evaporated to a drop under a fume hood. Despite being a lengthy process, it is gentler than using a rotary evaporator or evaporation under nitrogen. This way, losses of volatile compounds are prevented.
After evaporation, the extracts are resolubilised in 1 mL acetonitrile, and 100 µL are taken for liquid injection in LC/MSMS. Briny water (1.5 % NaCl) is added to the remaining 900 µL to obtain a 20-mL solution. They are then concentrated by SPME before injection in GC/MSMS.

2. Developing an SPME method for OCP

An SPME method was already in place for PAH and PCB, a 40 min extraction at 80 °C with a 100 µm polydimethylsiloxane (PDMS) fibre immersed in a stirred solution. OCP had to be added to this process.
OCP have been successfully extracted from both water (Derouiche et al., 2007) and soil (Zhao et al., 2006) with 100 µm PDMS fibres, though a more recent study states that PDMS/DVB is a more efficient coating for these compounds (Lu et al., 2011). However, our method being a multi-residue one, a 100 µm PDMS fibre was kept as the most efficient compromise to extract PAH, PCB and OCP.
The temperature was kept at 80 °C. While there were concerns that OCP would be degraded by temperature, it has been showed by Derouiche et al. (2006) that the effectiveness of SPME increased with increasing temperature, and that most OCP could be recovered at 80 °C.
Finally, the 40 min duration was also kept. Both Derouiche et al. (2006) and Zhao et al. (2006) studied the effect of extraction duration. Most OCP reach equilibrium around 60 min. Some, like α- and γ-HCH, show decreased quantities after 40 min while others like DDE or DDT only decrease after 80 min. Since the difference in efficiency between 40 and 60 min is minimal, the shortest duration was favoured in order to save time and energy.

While testing this method, an important carry-over was noticed, especially for PAH. In order to better desorb the PDMS fibre, the desorption time was set at 15 min as advised by Rianawati & Balasubramanian (2009). In addition to this, between each sample pure acetonitrile was extracted for 40 min at 80 °C. This has the double function of cleaning the fibre and making a blank for the next sample.

3. Developing an SPME method for GC pesticides

Non chlorinated pesticides required two different SPME methods depending on whether or not there was a derivatization step (Scheyer et al., 2006 ; 2007). The goal was to find a single extraction method that would work with all pesticides.

Fibre

The first parameter that was tested was which fibre to use. Three different fibre coatings were tested: 85 µm polyacrylate (PA), 65 µm polydimethylsiloxane-divinylbenzene (PDMS-DVB) and 100 µm PDMS. The three extractions were done at 50 °C for 40 min, and the solution was made with acidic (pH 3) briny (1.5 % NaCl) water. Pesticides were present at a concentration of 50 $\mu g\,L^{-1}$. Before the fibre was desorbed, 2 µL of the derivatizating agent MtBSTFTA were injected directly into the injector of the GC. This has been shown to be the most efficient way to derivatize pesticides undergoing SPME (Scheyer, 2004).

The majority of pesticides were missing from the chromatogram after extraction with the PDMS-DVB fibre and its sensitivity was two to four times lower than that of the other fibres, as shown on Figure 2-8. PA and PDMS fibres both allowed to detect all pesticides, but which gave the best response depended on the compound.

A second extraction was done to compare only these two fibres. The results, summarised in Figure 2-9, showed that the PA fibre could be as efficient as or more efficient than the PDMS fibre for nearly all pesticides. It is especially sensitive towards polar molecules: 2,4-D, 2,4-MCPA, bromoxynil, cyproconazol, dicamba, ioxynil, mecoprop-p, triclopyr. Results for these pesticides are showed on Figure 2-10.

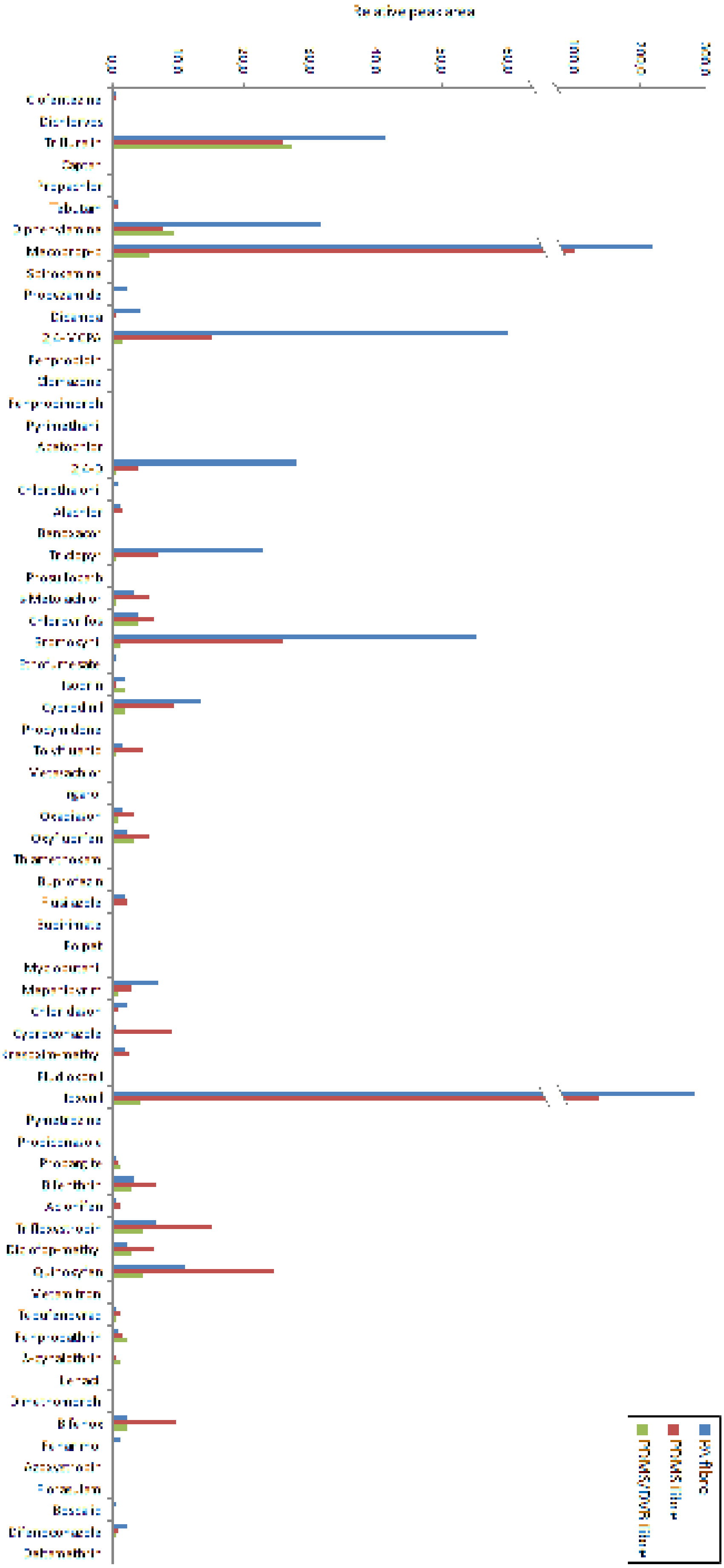


Figure 2-8 – Relative peak areas of pesticides extracted with PA, PDMS and PDMS-DVB fibres

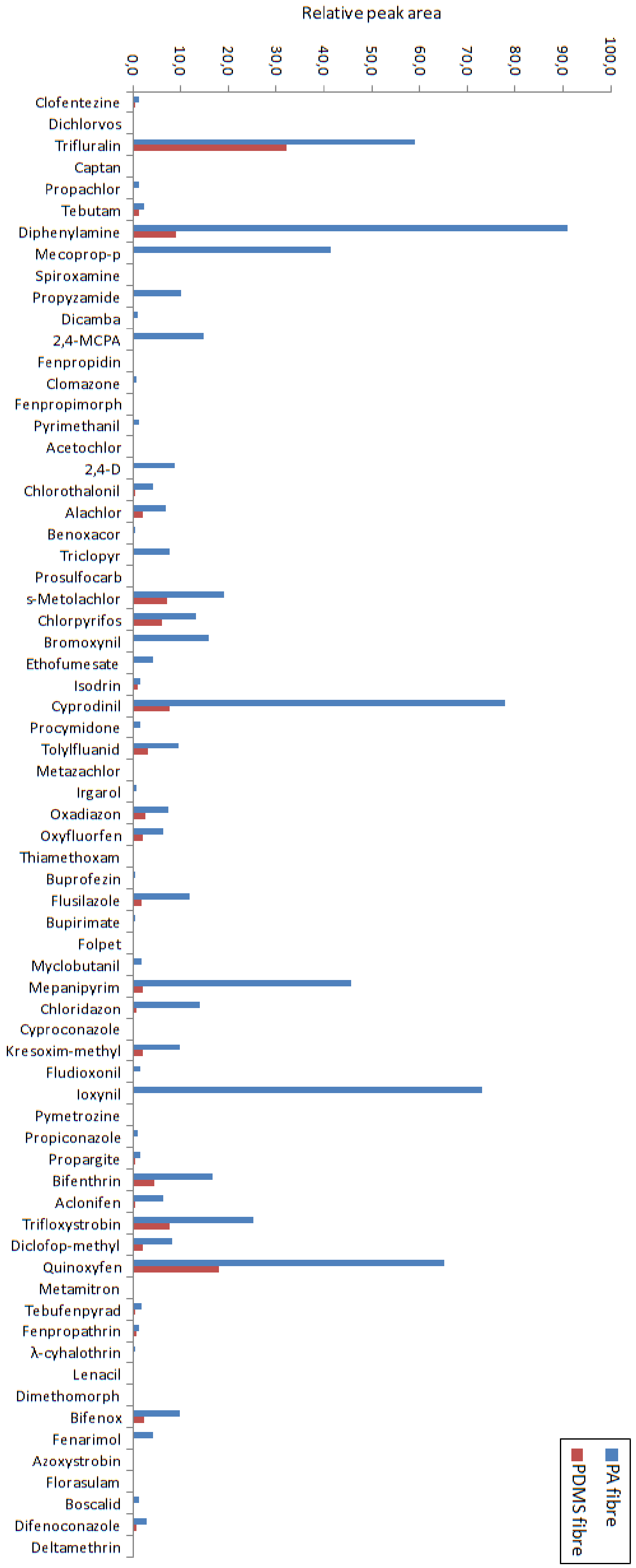


Figure 2-9 – Relative peak areas of pesticides extracted with PA and PDMS fibres

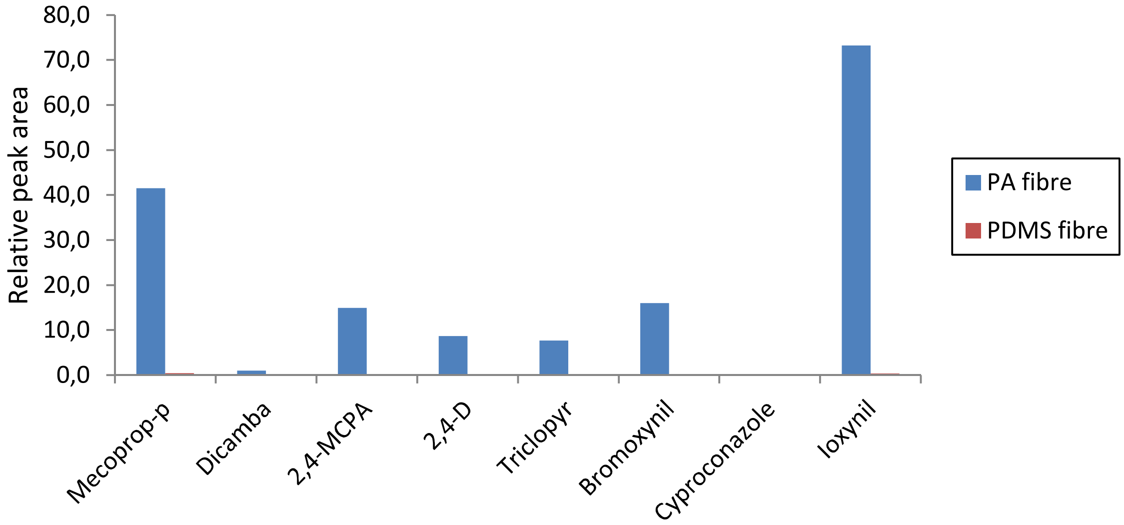


Figure 2-10 – Relative peak areas of polar pesticides extracted with PA and PDMS fibres

pH of the solution

The second test was to see whether or not the aqueous solution needed to be acidic in addition to briny. Pesticides with an –OH function need to be derivatized in order to be detectable, and having a solution at pH 3 ensures that this function is protonated and can be targeted by MtBSTFA. However, these polar pesticides can also be detected in plain distilled water.

Results showed that acidity does increase sensitivity for polar compounds (Figure 2-11), despite not influencing results in a significant way for non polar pesticides (Figure 2-12).
The solution was then always put at pH 3 by addition of nitric acid.

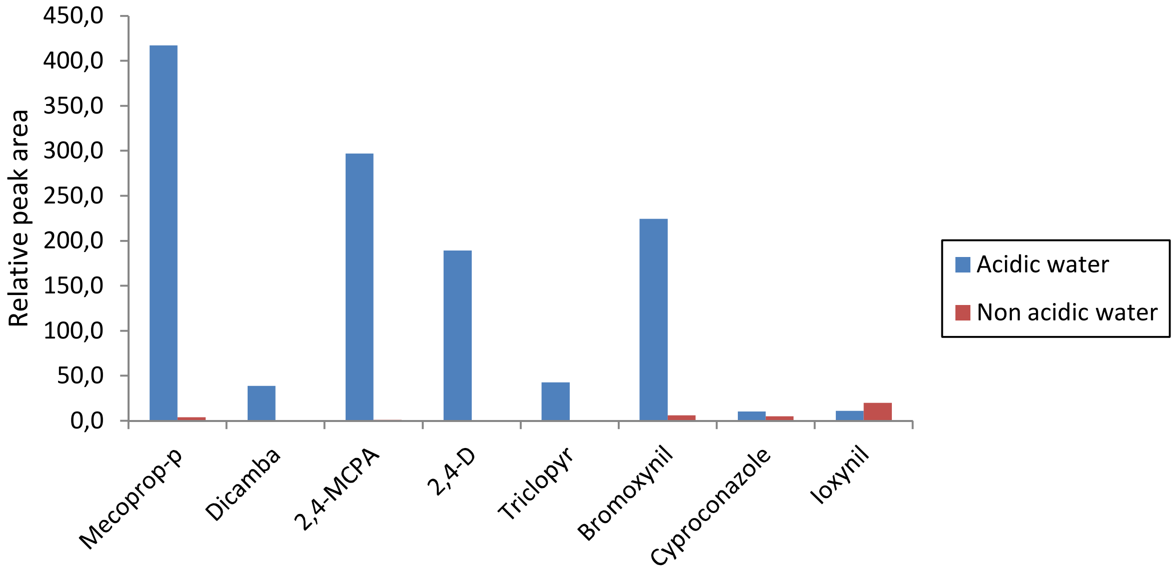


Figure 2-11 – Relative peak areas of polar pesticides extracted in acidic or non acidic water

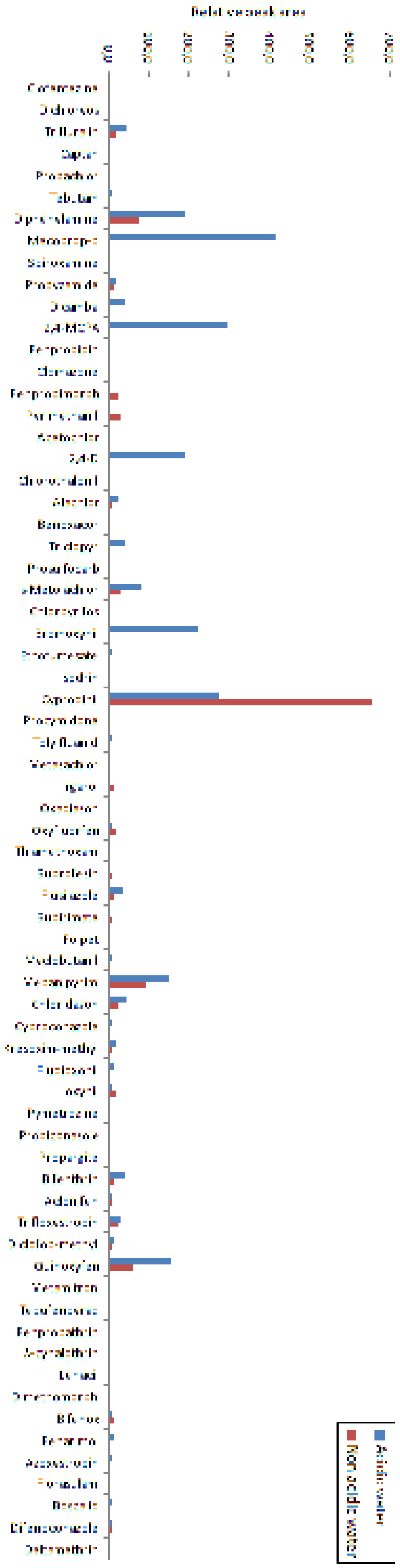


Figure 2-12 – Relative peak areas of pesticides extracted in acidic or non acidic water

Duration

Default extraction time was set at 40 min. A longer extraction time would improve the adsorption on the fibre of pesticides that are slow to reach equilibrium, but it would have the reverse effect on pesticides that quickly reach equilibrium.

A comparison was made between a 40 min extraction and a 60 min extraction. Both were done at 50 °C in acidic briny water with a pesticides concentration of 50 µg L^{-1}. Results showed that the 60 min extraction decreases both sensitivity and the number of pesticides recovered (Figure 2-13).

Therefore, the shorter extraction time was kept.

Temperature

Finally, default extractions were done at 50 °C. A higher temperature tends to improve the mobility of the pesticides, thus improving their extraction. However, heating too much leads to a decrease of the pesticides' distribution constant, thus lowering the quantity adsorbed on the SPME fibre (Derouiche et al., 2007). Moreover, at high temperatures some pesticides could start degrading.

In order to test the influence of temperature, SPME was performed at 30, 40, 50 and 60 °C. These extractions lasted 40 min and were done in acidic briny water with a pesticides concentration of 50 µg L^{-1}.

Overall, results improved with increasing temperature (Figure 2-14) despite some polar molecules (mecoprop-p, 2,4-MCPA, 2,4-D, triclopyr, bromoxynil) being better extracted at 30 °C (Figure 2-15). Above 60 °C pesticides may have started to degrade, which is why the experiment did not go higher. Moreover, most of the pesticides seemed to hit a threshold between 50 °C and 60 °C after which their extraction could not be improved further.

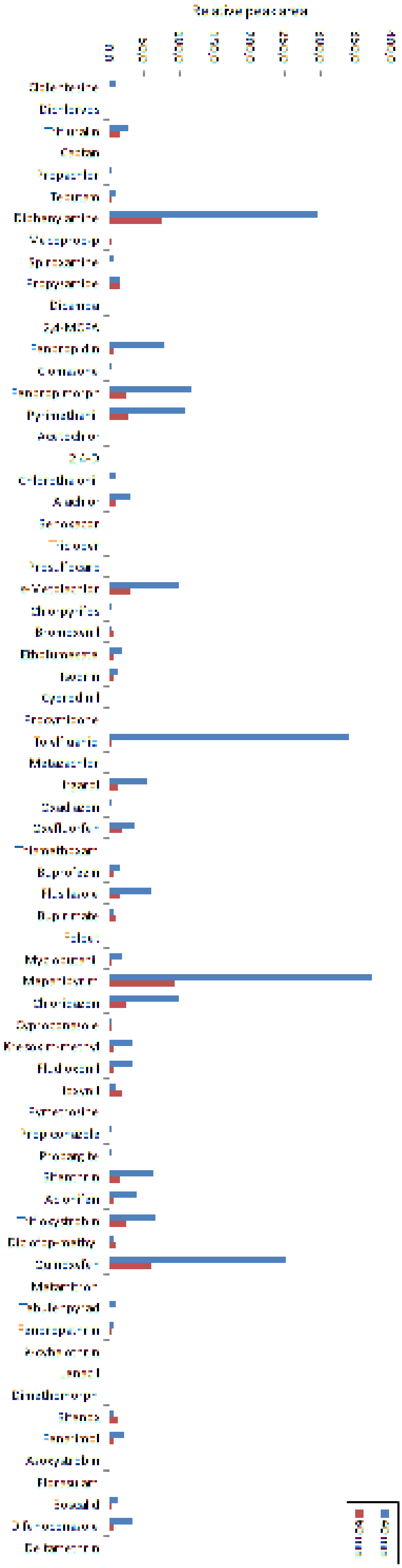


Figure 2-13 – Relative peak areas of pesticides extracted for 40 and 60 min

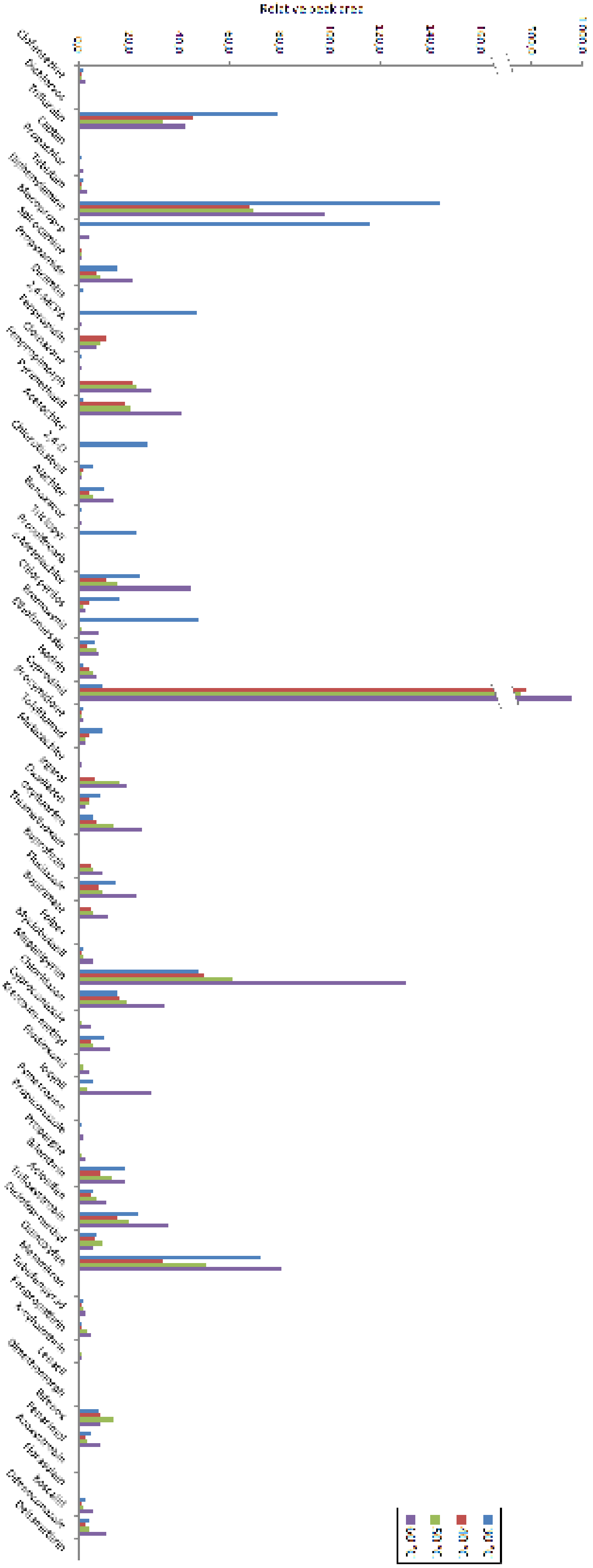


Figure 2-14 – Relative peak areas of pesticides extracted at 30, 40, 50 and 60 °C

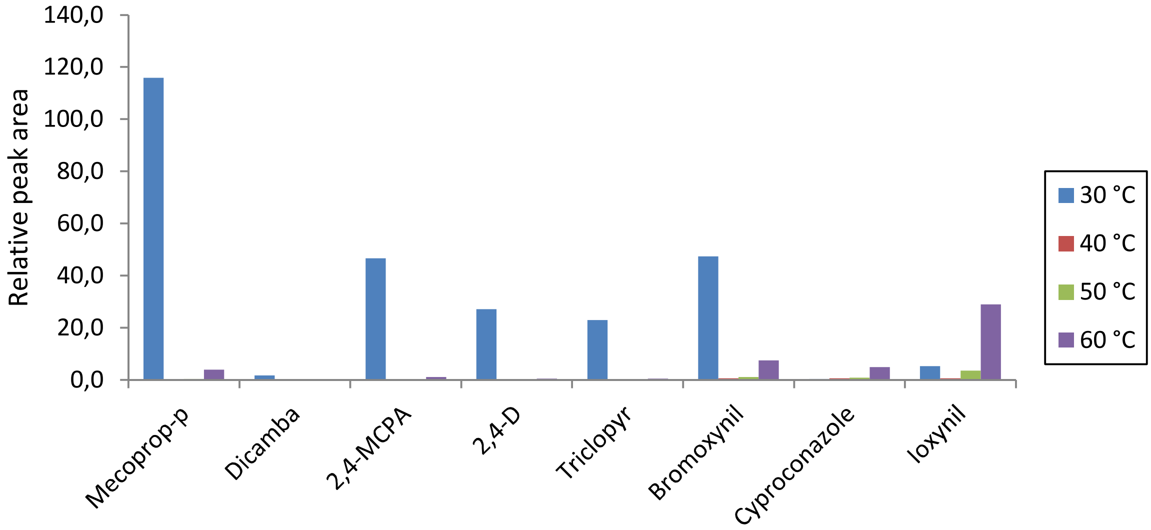


Figure 2-15 – Relative peak areas of polar pesticides extracted at different temperatures

V/ Calibration curves

1. Materials and methods

Using this method, calibration curves were made for SiC foam and XAD®-2 resin. Each matrix was spiked with 15, 30, 50, 100, 500, 1500, 2000, 2500 and 3000 ng of pollutants. Three 10 mg L^{-1} solutions were used: one with PAH, PCB and OCP, one with pesticides to be analysed in GC, and one with pesticides to be analysed in LC.

Three foams and three resin tubes were spiked this way, to obtain three curves by matrix by pollutants type. An average curve was drawn from the three, and was kept as the final calibration curve.

2. Results

Calibration curves for PAH, PCB, OCP and GC pesticides were generally quadratic, while those for LC pesticides tended to be more linear.

This effect could be attributed to SPME, as it is the only step that is present before GC injection and absent before LC injection. SPME relies on a compound's equilibrium between fibre and solution; it is possible that at small concentrations equilibrium is reached faster and the pollutants are successively adsorbed and desorbed from the fibre, explaining the lack of linearity.

Some curves, are given as examples in Figure 2-16 for each family of compounds. They are the final curves averaged from the original three for each compound.

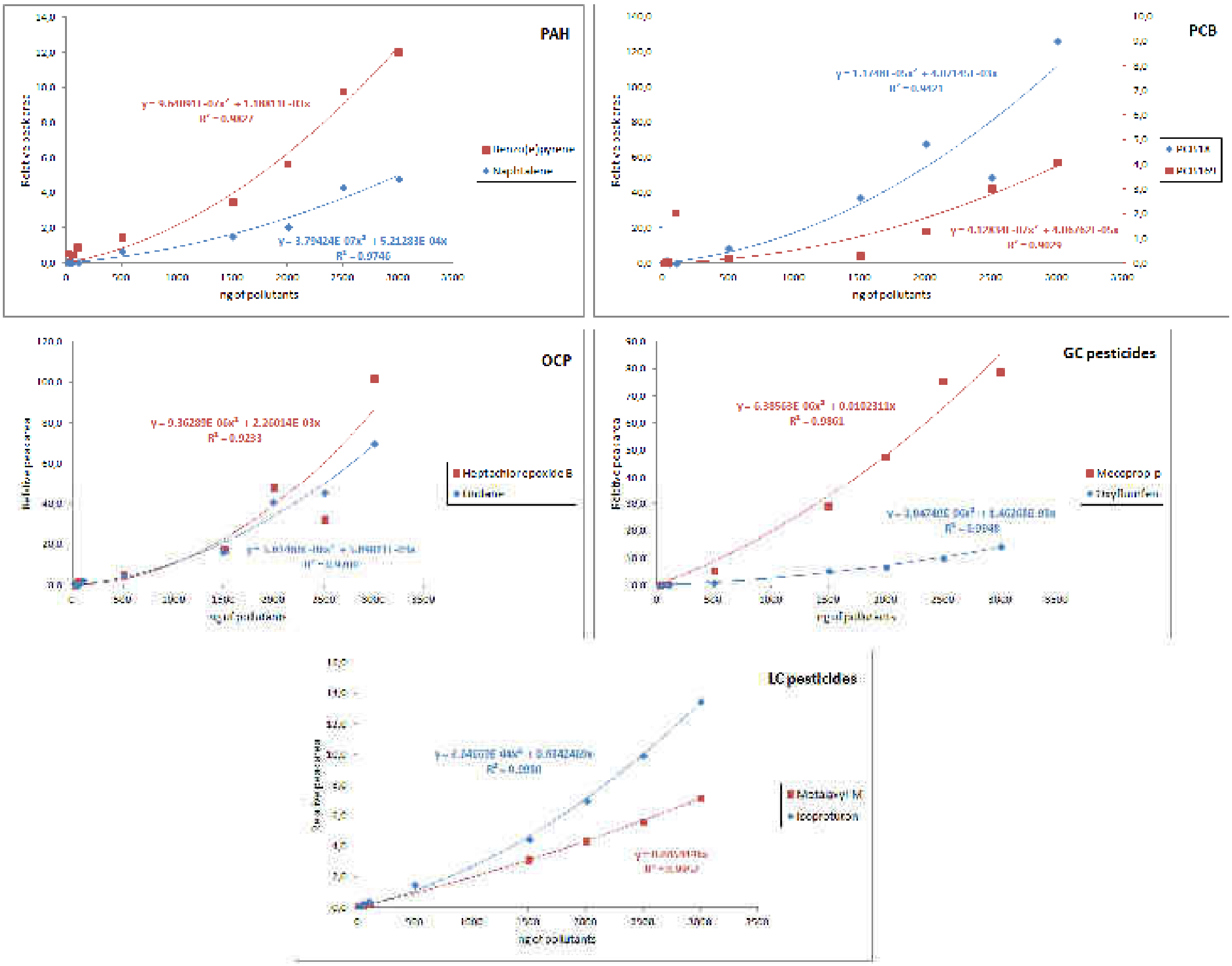


Figure 2-16 – Example of SiC calibration curves for all pollutants families considered

Calibration curves made from XAD®-2 resin extracts generally had a similar profile, quadratic for most and some linear for LC pesticides.

3. Limits of detection and quantification

Limits of detection (LOD) and quantification (LOQ) were calculated using a graph-based method (International Organisation of Vine and Wine, 2000).
Using this method, calculations are made from the noise present in a blank sample and the following relations:

LOD = 3 × h × R
LOQ = 10 × h × R

h: the average or maximum signal height on the chromatogram in a window centred on the peak's retention time. The window's width should be twenty times the peak's mid-height width.
R: the machine's response factor.

LOD and LOQ were calculated using the maximum h: over the selected window, the height between the lowest and highest point is measured. The resulting detection and quantification limits are listed in Annex II and summarised in Table 2-3 for SiC foam and 2-4 for XAD®-2 resin.

Table 2-3 – Minimum and maximum LOD and LOQ for all types of pollutants on SiC foam

	Min. LOD (ng sampler^{-1})	Min. LOQ (ng sampler^{-1})	Max. LOD (ng sampler^{-1})	Max. LOQ (ng sampler^{-1})
PAH	0.2	0.6	9.0	27.0
PCB	0.1	0.3	14.5	43.5
OCP	0.1	0.3	5.8	17.4
GC pesticides	0.1	0.3	1,530.4	4,591.2
LC pesticides	0.1	0.3	5.6	16.8

Table 2-4 – Minimum and maximum LOD and LOQ for all types of pollutants on XAD®-2 resin

	Min. LOD (ng sampler^{-1})	Min. LOQ (ng sampler^{-1})	Max. LOD (ng sampler^{-1})	Max. LOQ (ng sampler^{-1})
PAH	0.1	0.3	40.0	120.0
PCB	0.1	0.3	3.0	9.0
OCP	0.1	0.3	8.5	25.5
GC pesticides	0.1	0.3	29.0	87.0
LC pesticides	0.1	0.3	281.6	844.8

Greater variability in LOD and LOQ was noticed for GC pesticides, due in part to the high number of compounds analysed with this method: 75, which is three to four times more than in other methods. The high LOD and LOQ calculated for these pesticides are mostly due to the polar, derivatized pesticides. Their detection is dependent on the success of the derivatization process, which adds uncertainty to their results.

In general, GC pesticides had the highest LOD/LOQ while PAH and PCB had more stable limits.

The highest detection and quantification limits for PAH are those of benzo(g,h,i)perylene on SiC foam and coronene on XAD®-2 resin. These two compounds are the very last to leave the column, and coronene especially tends to degrade by this time. This makes their detection more difficult than for other PAH.

The same comment can be made for PCB and OCP. On SiC foam, the highest values are those of PCB 180 and o,p'-DDD, both late to exit the column. On XAD®-2 resin, highest values correspond to PCB 105 and p,p'-DDT. While p,p'-DDT is the next to last OCP to exit the GC column, PCB 105 comes out earlier, which might explain its relatively low LOD and LOQ.

The very high limits of 1,530.4 and 4,591.2 ng sampler^{-1} on SiC foam are those of dimethomorph, one of the last pesticides to exit the GC column. At these retention times, pesticides often decompose and cannot be reliably detected. Outside of these extreme values, the highest limits are 63.2 (detection) and 189.6 ng sampler^{-1} (quantification) for boscalid, another slowly eluted pesticide. The highest limits on XAD®-2 resin for GC pesticides are also from one of these late pesticides: azoxystrobin.

For LC pesticides, the opposite phenomenon is usually observed, with the first pesticides eluted being the hardest to detect. This is verified on XAD®-2 resin, whose limits at 281.6 and 844.8 ng sampler^{-1} are those of carbendazim, the second to exist the LC column. However, on SiC foam, it is prothioconazole that has the highest LOD/LOQ despite being one of the last pesticides eluted.

Low extraction yields may play a part in the highest LOD and LOQ calculated. The three preparation steps are extractions that are optimised to yield a maximum of compounds, and are not tailored to individual molecules.

Finally, it should be noted that calculation methods for detection and quantification limits assume that R, the response factor, is linear for the compounds of interest. Most calibrations curves in this study are not linear, especially at small concentrations. In order to calculate limits as close to reality as possible, R was determined from the least concentrated solutions at 15 ng sampler^{-1}.

Some detection limits were found to be lower than 0.1 ng sampler^{-1} but were rounded up. Since the calibration curves did not go below 15 ng sampler^{-1} and the preparation method had three different steps, we felt that calculations could not be precise enough to have more than one significant figure.

4. Repeatability

The repeatability of the different methods was tested.

On the same day, three SiC foams were spiked with 50 ng of pollutants and three with 1500 ng. Extraction, preparation and injection were done at the same time for these six samples. The test was done once per week for three weeks.

Results were considered repeatable if they were within a 30 % margin of the median result. They are summarised in Table 2-5 for the 50 ng samples and Table 2-6 for the 1500 ng samples.

Table 2-5 – Percentage of compounds that had repeatable results in 50 ng samples

	Overall	Week 1	Week 2	Week 3
PAH, PCB, OCP	62.2	-*	62.5	50.0
GC pesticides	41.7	-*	55.0	20.0
LC pesticides	66.7	68.8	87.1	73.3

* not enough data to conclude

Table 2-6 – Percentage of compounds that had repeatable results in 1500 ng samples

	Overall	Week 1	Week 2	Week 3
PAH, PCB, OCP	37.8	82.9	93.0	28.6
GC pesticides	36.9	-*	54.2	62.9
LC pesticides	81.8	93.6	75.0	81.3

* not enough data to conclude

In general, different samples prepared within the same week showed better repeatability than samples from different weeks. The difference could be attributed to the evaporation after SPE, which is done simply under a fume hood. This step is neither automated nor does it require the presence of an operator, and depends entirely on the fume hood's performance. While samples evaporated at the same time evaporate under the same air flow, the exact conditions may not be the same from one day to the other.

Repeatability was consistently better for LC pesticides than for other compounds. This could be explained by LC injections not being preceded by SPME. Because this extraction is based on a compound's equilibrium between the fibre and the solution, it is not as repeatable as a liquid injection. Despite the SPME being performed by an automated sampler, differences in temperature, duration and agitation may still exist.

Despite these issues, SPME is an important step in this preparation method. LOD and LOQ calculated after an SPME injection are twice to ten times lower than those calculated after liquid injection. To give a few examples, pyrimethanil went from 9.8 and 32.6 ng sampler^{-1} to 6.0 and 18.0 ng sampler^{-1} and s-metolachlor went from 6.2 and 20.6 ng sampler^{-1} to 0.3 and 0.9 ng sampler^{-1}. (Leibel, 2015)

VI/ Conclusion

This sample preparation method proposes coupling ASE, SPE and SPME, which is a new process for air samples.

ASE has been optimised in order to use a minimum of solvent and take a minimum of time without losing efficiency. Following this step by SPE allows samples to be concentrated without using a rotary evaporator which could cause volatile compounds to completely evaporate. Further concentration by SPME means that low detection limits can be reached; lower than liquid injection. This process includes two cleaning steps that greatly reduce background noise on the chromatogram.

SPME had to be optimised for different compounds and efficient compromises have been found. However, SPME is also currently a limiting factor in the sample preparation process regarding repeatability. What should be done is a study of the equilibrium times of different compounds at different concentrations in order to find the optimal extraction time.

Despite this inconvenient, the preparation method is a solid process with high extraction yields, low LOD and LOQ, and usable calibration curves that gave coherent results over the course of the study.

References

Albero B., Sánchez-Brunete C., García-Valcárcel A. I., Pérez R. A., Tadeo J. L., **2015**, "Ultrasound-assisted extraction of emerging contaminants from environmental samples", *Trends in Analytical Chemistry*, *71*, 110-118

Aragon M., Borrul F., Marce R. M., **2013**, “Thermal desorption-gas chromatography-mass spectrometry method to determine phthalate and organophosphate esters from air samples”, *Journal of Chromatography A*, *1303*, 76-82

Bispo J. R. L., Navickiene S., Dórea H. S., **2011**, “Method validation for SPE applied to determination of PAH in petroliferous industry effluent water”, *American Journal of Analytical Chemistry*, *2*, 971-978

Bonansea R. I., Amé M. V., Wunderlin D. A., **2013**, “Determination of priority pesticides in water samples combining SPE and SPME coupled to GC-MS. A case study: Suquía River basin (Argentina)”, *Chemosphere*, *90*, 1860-1869

Busetti F., Heitz A., Cuomo M., Badoer S., Traverso P., **2006**, “Determination of sixteen polycyclic aromatic hydrocarbons in aqueous and solid samples from an Italian wastewater treatment plant”, *Journal of Chromatography A*, *1102*, 104-115

Bustamante J., Navarro P., Arana G., de Diego A., Madariaga J. M., **2013**, “Ultrasound assisted dialysis of semi-permeable membrane devices for the simultaneous analysis of a wide number of persistent organic pollutants”, *Talanta*, *114*, 32-37

Clément M., Arzel S., Le Bot B., Seux R., Millet M., **2000**, “Adsorption/thermal desorption-GC/MS for the analysis of pesticides in the atmosphere”, *Chemosphere*, *40*, 49-56

Derouiche A., Driss M. R., Morizur J-P., Taphanel M-H., **2007**, “Simultaneous analysis of polychlorinated biphenyls and organochlorine pesticides in water by headspace solid-phase microextraction with gas chromatography-tandom mass spectrometry”, *Journal of Chromatography A*, *1138*, 231-243

Duodu G. O., Goonetilleke A., Ayoko G. A., **2016**, “Optimization of in-cell accelerated solvent extraction technique for the determination of organochlorine pesticides in river sediments”, *Talanta*, *150*, 278-285,

El-Osmani R., Net S., Dumoulin D., Bigan M., Ouddane B., Baroudi M., **2014**, “An experimental design approach to the optimization of pesticide extraction from water”, *Analytical Methods*, *6*, 6514-6521

(a) Gouin, T., Shoeib M., Harner T., **2008**, “Atmospheric concentrations of current-use pesticides across south-central Ontario using monthly-resolved passive air samplers”, *Atmospheric Environment*, *42*, 8096-8104

(b) Gouin T., Wania F., Ruepert C., Castillo L. E., **2008**, “Field testing passive air samplers for current use pesticides in a tropical environment”, *Environmental Science & Technology*, *12*, 6625-6630

Guo L., Lee H. K., **2011**, "Development of multiwalled carbon nanotubes based micro-solid-phase extraction for the determination of trace levels of sixteen polycylic aromatic hydrocarbons in environmental water samples", *Journal of Chromatography A*, *1218*, 9321-9327

Haraguchi K., Kitamura E., Yamashita T., Kido A., **1994**, "Simultaneous determination of trace pesticides in urban air", *Atmospheric Environment*, *28*, 1319-1325

Ho, S .S. H., Yu J. Z., Chow J. C., Zielinska B., Watson J. G., Sit E. H. L., Schauer J. J., *Journal of Chromatography* A, 2008, 1200, 217-227, "Evaluation of an in-injection port thermal desorption-gas chromatography/mass spectrometry method for analysis of non-polar organic compounds in ambient aerosol samples"

Hou R.-Y., Jiao W.-T., Qian X.-H., Wang X.-H., Xiao Y., Wan X.-C., **2013**, "Effective extraction method for determination of neonicotinoid residues in tea", *Journal of Agricultural and Food Chemistry*, *61*, 12565-12571

International Organisation of Vine and Wine, *Quality assurance in oenological laboratories*, **2000** [Web] OIV-MA-AS1-10 : R2000

Iwafune T., Ogino T., Watanabe E., **2014**, "Water-based extraction and liquid chromatography-tandem mass spectrometry analysis of neonicotinoid insecticides and their metabolites in green pepper/tomato samples", *Journal of Agricultural and Food Chemistry*, *62*, 2790-2796

Jaber F., Schummer C., Al Chami J., Mirabel P., Millet M., **2007**, "Solid-phase microextraction and gas chromatography-mass spectrometry for analysis of phenols and nitrophenols in rainwater, as their *t*-butyldimethylsilyl derivatives", *Analytical and Bioanalytical Chemistry*, *387*, 2527-2535

Jaward F. M., Zhang G., Nam J. J., Sweetman A. J., Obbard J. P., Kobara Y., Jones K. C., **2005**, "Passive air sampling of polychlorinated biphenyls, organochlorine compounds, and polybrominated diphenyl ethers across Asia", *Environmental Science & Technology*, *39*, 8638-8645

Kefeni K. K., Okonkwo J. O., **2012**, "Analysis of major congeners of polybromobiphenyls and polybromodiphenyl ethers in office dust using high resolution gas chromatography-mass spectrometry", *Chemosphere*, *87*, 1070-1075

Khalili-Fard V., Ghanemi K., Nikpour Y., Fallah-Mehrjardi M., **2012**, "Application of sulfur microparticles for solid-phase extraction of polycyclic aromatic hydrocarbons from sea water and wastewater samples", *Analytica Chimica Acta*, *714*, 89-97

Kiss G., Varga-Puchony Z., Hlavay J., **1996**, “Determination of polycyclic aromatic hydrocarbons in precipitation using solid-phase extraction and column liquid chromatography”, *Journal of Chromatography A*, *725*, 261-272

Kopp E. K., Fromme H., Volkel W., **2012**, “Analysis of common and emerging brominated flame retardants in house dust using ultrasonic assisted solvent extraction and on-line sample preparation via column switching with liquid chromatography-mass spectrometry”, *Journal of Chromatography A*, *1241*, 28-36

Lambert O., Veyrand B., Durand S., Marchand P., Le Bizec B., Piroux M., Puyo S., Thorin C., Delbac F., Pouliquen H., **2012**, “Polycyclic aromatic hydrocarbons : Bees, honey and pollen as sentinels for environmental chemical contaminants”, *Chemosphere*, *86*, 98-104

Leibel F., “Analyse de retardateurs de flamme bromés et de certains pesticides par chromatographie gazeuse couplée à de la spectrométrie de masse en tandem”, Report, Strasbourg University, 2015

Lin, Y.-P., Pessah I. N., Puschner B., **2013**, “Simultaneous determination of polybrominated diphenyl ethers and polychlorinated biphenyls by gas chromatography-tandem mass spectrometry in human serum and plasma”, *Talanta*, *113*, 41-48

Lu L. C., Wang C. I., Sye W. F., **2011**, “Applications of chitosan beads and porous crad shell powder for the removal of 17 organichlorine pesticides (OCP) in water solution”, *Carbohydrate Polymers*, *83*, 1984-1989

Ma J., Xiao R., Li J., Yu J., Zhang Y., Chen L., **2010**, “Determination of 16 polycyclic aromatic hydrocarbons in environmental water samples by solid-phase extraction using multi-walled carbon nanotubes as adsorbent coupled with gas chromatography-mass spectrometry”, *Journal of Chromatography A*, *1217*, 5462-5469

Mahindrakar A. N., Chandra S., Shinde L. P., **2014**, “Comparison of solvent extraction and solid-phase extraction for the determination of polychlorinated biphenyls in transformer oil”, *Chemosphere*, *94*, 199-202

Martins M. L., Donato F. F., Pestes O. D., Adaime M. B., Zanella R., **2013**, “Determination of pesticide residues and related compounds in water and industrial effluent by solid-phase extraction and gas chromatography coupled to triple quadrupole mass spectrometry”, *Analytical and Bioanalytical Chemistry*, *405*, 7697-7709

Mascolo G., Bagnulo G., De Tommaso B., Uricchio V., **2013**, “Direct analysis of polychlorinated biphenyls in heavily contaminated soils by thermal desorption/gas chromatography/mass spectrometry”, *International Journal of Environmental Analytical Chemistry*, *93*, 1030-1042

Meghesan-Breja A., Marutoiu C., Cimpoiu C., **2015**, "Multi-residues analysis for 88 pesticides and metabolites from soil by gas chromatography-time - of - flight mass spectrometry", *Revista de Chimie*, *66*, 32-38

Mercier F., Gilles E., Saramito G., Glorennec P., Le Bot B., **2014**, "A multi-residue method for the simultaneous analysis in indoor dust of several classes of semi-volatile organic compounds by pressurized liquid extraction and gas chromatography/tandem mass spectrometry", *Journal of Chromatography A*, *1336*, 101-111

Mercier F., Glorennec P., Blanchard O., Le Bot B., **2012**, "Analysis of semi-volatile organic compounds in indoor suspended particulate matter by thermal desorption coupled with gas chromatography/mass spectrometry", *Journal of Chromatography A*, *1254*, 107-114

Mogolodi Dimpe K., Nomngongo P. N., **2016**, "Current sample preparation methodologies for analysis of emerging pollutants in different environmental matrices", *Trends in Analytical Chemistry*, *82*, 199-207

Moja S. J., Mtunzi F., **2013**, "Application of solid phase extraction (SPE) method in determining polycylic aromatic hydrocarbons (PAH) in river water samples", *Journal of Environmental Chemistry and Ecotoxicology.*, *11*, 278-283

Mokbel H., Al Dine E. J., Elmoll A., Liaud C., Millet M., **2016**, "Simultaneous analysis of organochlorine pesticides and polychlorinated biphenyls in air samples by using accelerated solvent extraction (ASE) and solid-phase micro-extraction (SPME) coupled to gas chromatography dual electron capture detection", *Environmental Science and Pollution Research*, *23*, 8053-8063

Montagner C. C., Vidal C., Acayaba R. D., Jardim W. F., Jardim I. C. S. F., Umbuzeiro G. A., **2014**, "Trace analysis of pesticides and an assessment of their occurrence in surface and drinking waters from the State of São Paulo (Brazil)", *Analytical Methods*, *6*, 6668-6677

Nilsson A., Lagesson V., Bornehag C-G., Sundell J., Tagesson C., **2005**, "Quantitative determination of volatile organic compounds in indoor dust using gas chromatography-UV spectrometry", *Environment International*, *31*, 1141-1148

Otaka H., Shimono H., Hashimoto S., **2004**, "Optimization of solid-phase extraction procedure for determination of polychlorinated dibenzo-*p*-dioxins, polychlorinated dibenzofurans and coplanar polychlorinated biphenyls in humic acid containing water", *Analytical and Bioanalytical Chemistry*, *378*, 1854-1860

Pico Y., **2013**, "Ultrasound-assisted extraction for food and environmental samples", *Trends in Analytical Chemistry*, *43*, 84-99

Piri-Moghadam H., Ahmadi F., Pawliszyn J., **2016**, “A critical review of solid phase microextraction for analysis of water samples”, *Trends in Analytical Chemistry*, Ahead of Print

Raeppel C., Fabritius M., Nief M., Appenzeller B. M. R., Millet M., **2014**, “Coupling ASE, sylilation and SPME-GC/MS for the analysis of current-used pesticides in atmosphere”, *Talanta*, *121*, 24-29

Raina-Fulton R., *Journal of Agricultural and Food Chemistry*, **2015**, “Determination of neonicotinoid insecticides and stobilurin fungicides in particle phase atmospheric samples by liquid chromatography-tandem mass spectrometry”, *63*, 5152-5162

Rianawati E., Balasubramanian R., **2009**, “Optimization and validation of solid phase micro-extraction (SPME) method for analysis of polycyclic aromatic hydrocarbons in rainwater and stormwater”, *Physics and Chemistry of the Earth*, *34*, 857-865

Scheyer A., “Développement d’une méthode d’analyse par CPG/MSMS de 27 pesticides identifiés dans les phases gazeuse, particulaire et liquide de l’atmosphère. Application à l’étude des variations spatio-temporelles des concentrations dans l’air et dans les eaux de pluie.”, Thesis, Strasbourg University, 2004

Scheyer A., Morville S., Mirabel P., Millet M., **2006**, “Analysis of trace levels of pesticides in rainwater by SPME and GC-tandem mass spectrometry”, *Analytical and Bioanalytical Chemistry*, *384*, 475-487

Scheyer A., Briand O., Morville S., Mirabel P., Millet M., **2007**, “Analysis of trace levels of pesticides in rainwater by SPME and GC-tandem mass spectrometry after derivatisation with PFFBr”, *Analytical and Bioanalytical Chemistry*, *387*, 359-368

Schummer C., Groff C., Al Chami J., Jaber F., Millet M., **2009**, “Analysis of phenols and nitrophenols in rainwater collected simultaneously on an urban and rural site in east of France”, *Science of the Total Environment*, *407*, 5637-5643

Schummer C., Tuduri L., Briand O., Appenzeller B. M., Millet M., **2012**, “Application of XAD®-2 resin-based passive samplers and SPME-GC-MS/MS analysis for the monitoring of spatial and temporal variations of atmospheric pesticides in Luxembourg”, *Environmental Pollution*, *170*, 88-94

Shi Z., Hu J., Li Q., Zhang S., Liang Y., Zhang H., **2014**, “Graphene based solid phase extraction combined with ultra high performance liquid chromatography-tandem mass spectrometry for carbamate pesticides analysis in environmental water samples”, *Journal of Chromatography A*, *1355*, 219-227

Sibiya P., Potgieter M., Cukrowska E., Jönsson J. Å., Chimuka L., **2012**, "Development and application of solid phase extraction method for polycylic aromatic hydrocarbons in water samples in Johannesburg area, South Africa", *South African Journal of Chemistry*, *65*, 206-213

(a) Souza-Silva E. A., Jiang R., Rodriguez-Lafuente A., Gionfriddo E., Pawliszyn J., **2015**, "A critical review of the state of the art of solid-phase microextraction of complex matrices I. Environmental analysis", *Trends in Analytical Chemistry*, *71*, 224-235

(b) Souza-Silva E. A., Reyes-Garces N., Gomez-Rios G. A., Boyaci E., Bojko B., Pawliszyn J., **2015**, "A critical review of the state of the art of solid-phase microextraction of complex matrices III. Bioanalytical and clinical applications", *Trends in Analytical Chemistry*, *71*, 249-264

Tang F., Ni Y., Zhang H., Li Y., Jin J., Wang L., Chen J., **2012**, "A new cleanup method of dioxins in sediment using large volume injection gas chromatography online coupled with liquid chromatography", *Analytica Chimica Acta*, *729*, 73-79

Tang H. P.-O., **2013**, "Recent development in analysis of persistent organic pollutants under the Stockholm Convention", *Trends in Analytical Chemistry*, *45*, 48-66

Tao S., Liu Y., Xu W., Lang C., Liu S., Dou H., Liu W., **2007**, "Calibration of a passive sampler for both gaseous and particulate phase polycylic aromatic hydrocarbons", *Environmental Science & Technology*, *41*, 568-573

Tavares M., Pinto J. P., Souza A. L., Scarminio I. S., Solci M. C., **2004**, "Emission of polycylic aromatic hydrocarbons from diesel engind in a bus station, Londrina, Brazil", *Atmospheric Environment*, *38*, 5039-5044

Tölgyessy P., Vrana B., Šilhárová K., **2013**, "An improved method for determination of polychlorinated biphenyls and polybrominated diphenyl ethers in sediment by ultrasonic solvent extraction followed by stir bar sorptive extraction coupled to TD-GC-MS", *Chromatographia*, *76*, 177-185

Urbe I., Ruana J., **1997**, "Application of solid-phase extraction discs with a glass fiber matrix to fast determination of polycyclic aromatic hydrocarbons in water", *Journal of Chromatography A*, *778*, 337-345

US EPA, **2016**, *United States Environmental Protection Agency* [Online] Available at https://www3.epa.gov/ [Accessed 27 July 2016]

UNEP, **2007**, *Guidance on the Global Monitoring Plan for Persistent Organic Pollutants - Preliminary version*

Westbom R., Thörneby L., Zorita S., Mathiasson L., Björklund E., **2004**, "Development of a solid-phase extraction method for the determination of polychlorinated biphenyls in water", *Journal of Chromatography A*, *1033*, 1-8

Wierucka M., Biziuk M., **2014**, "Application of magnetic nanoparticles for magnetic solid-phase extraction in preparing biological, environmental and food samples", *Trends in Analytical Chemistry*, *59*, 50-58

Wittsiepe J., Nestola M., Kohne M., Zinn P., Wilhelm M., **2014**, "Determination of polychlorinated biphenyls and organochlorine pesticides in small volumes of human blood by high-throughput on-line SPE-LVI-GC-HRMS", *Journal of Chromatography B*, *945-946*, 217-224

Yang J. S., Lee S. K., Park Y. H., Lee D. W., **1999**, "Analytical method for dioxin and organo-chlorinated compounds: (II) comparison of extraction methods of dioxins from XAD-2 adsorbent", *Bulleting of the Korean Chemical Society*, *20*, 689-695

Zhang Z., Rhind S. M., **2011**, "Optimized determination of polybrominated diphenyl ethers and polychlorinated biphenyls in sheep serum by solid-phase extraction-gas chromatograph-mass spectroscopy", *Talanta*, *84*, 487-493

Zhao R., Wang X., Yuan J., Jiang T., Fu S., Xu X., **2006**, "A novel headspace solid-phase microextraction method for the exact determination of organochlorine pesticides in environmental soil samples", *Analytical and Bioanalytical Chemistry*, *384*, 1584-1589

Chapter 3: Sampling campaigns and samplers comparison

I/ Introduction: Sampling campaigns

Once SiC foam was selected as the adsorbent to study and the sample preparation method was optimised, field studies could be planned on a larger scale than the neighbouring botanical garden.

There is no standard for sampling campaigns, as the scope and the kind of sampler used depend on the goal of the study. Roughly, three categories of campaigns can be observed: those that compare different samplers, those that focus on monitoring pollutants, and those that optimise a given sampler's performances. While methodologies are similar, decisions regarding sites, samplers and duration vary according to these goals.

1. Comparing several samplers

Comparisons can be made between passive and active samplers (Gouin et al., 2005 ; Hayward et al., 2010). Passive samplers are PUF disks or XAD®-2 tubes while active samplers often use PUF-XAD®-2-PUF sandwiches (Waite et al., 2005 ; Hayward et al., 2010) and a GFF. While these sandwiches are more effective than a single adsorbent at trapping pollutants (Dobson et al., 2006), it is surprising to see them used in comparative studies where the same adsorbent could be used as active and passive sampler. Both kinds of samplers are placed at the same site next to each other for the duration of the sampling campaign. However, sampling duration varies depending on the sampler: low-volume active samplers (LVS) can run for up to two weeks at a time while high-volume samplers (HVS) are designed for one-day uses (Association française de normalisation, 2007 ; Hayward et al., 2010). In the same way, PUF can adsorb less pollutants than XAD®-2 resin (Gouin et al., 2008b), so passive samplers are not always left in the field for the same duration (Hayward et al., 2010). In general, sampling campaigns that use passive samplers can last up to a year (Gouin et al., 2005 ; Hayward et al., 2010), during which the passive adsorbent is not replaced. However, it is impractical to run active samplers for a whole year, even when changing adsorbent regularly. This is why some comparison campaigns last only one or two months (Jaward et al., 2004 ; Waite et al., 2005), changing the active adsorbent every one or two weeks.
Active samplers have also been compared between themselves. For instance, Armstrong et al. (2013) compared PUF and XAD®-2 tubes linked to low-volume pumps with the goal of studying pesticides degradation on each matrix. Dobson et al. (2006) studied the differences between PUF, XAD®-2, and PUF/resin sandwiches in HVS. In the first case, LVS were chosen because the adsorbents were placed next to the pesticides application area so there were no concerns about detection limits. The second study, however, took place at an urban site where pesticides concentrations in the atmosphere were low, so HVS were preferred. In

both cases, using active samplers allowed the sampling campaigns to be much shorter than those using passive samplers. Armstrong's study took place over the course of a day, when pesticides were used; Dobson's lasted two months, sampled two days at a time.

2. Monitoring atmospheric pollutants

Sampling campaigns focused on studying atmospheric pollutants are usually done in order to understand their behaviour depending on meteorological conditions, or under certain climates, and to predict transport trajectories. Such campaigns mostly use a single kind of sampler: either active (Schummer et al., 2010) or passive (Gouin et al., 2008a ; Schummer et al., 2012). Studying the atmospheric behaviour of volatile pollutants requires long studies, which is why passive samplers are used more often than active ones.

The goal of Gouin et al. (2008a) and Wang et al. (2010) was to plot back pollutants trajectories in order to identify emission sources. This exploratory study required a wide variety of sampling sites and long sampling times, so they used passive PUF disks and XAD®-2 resin tubes respectively. Another similar campaign was done by Schummer et al. (2012) to monitor spatial and temporal variations of several atmospheric pesticides.

When general pollutants behaviour is known, sampling campaigns can be shorter to focus on specific periods of interest. This is especially true for pesticides, as seen in the study made by Schummer et al. (2010) in Strasbourg. Sampling lasted for only one month, during the first herbicides treatments in the region. There was only one sampling site, with an active sampler pumping air on a 48-hour basis. This set up worked because the goal was to link variations in pesticides concentrations to meteorological parameters, so several quick sampling periods could be accurately compared to weather conditions. Such short campaigns using passive samplers are rarer, but some have been documented. For instance, Harner et al. (2004) studied PCB and OCP over four months using PUF disks and SPMD. The study was realised over a short period because the goal of the study was to show differences in pollutants concentrations between urban and rural areas, rather than follow the evolution of such pollutants over time.

3. Evaluating one sampler's performances

Finally, there are a few campaigns that focus solely on studying a sampler's performances under certain conditions. For instance, Gouin et al. (2008b) used both passive and active samplers for a one-year study of PUF and XAD®-2 resin's behaviour in a hot and humid environment. In such a study, comparing samplers and finding pollutants sources are secondary results to testing the adsorbents' efficiency.

The sampling campaign realised by Eng et al. (2014) was used to test a new housing system for PUF disks that would allow particles deposition. In this case, the search for pollutants was a mean to compare particles uptake by different samplers. Sampling periods were also chosen specifically for this goal: summer, when there are more pollutants in the gas phase, and winter, when there are more particulate compounds in the atmosphere.

4. Common methodologies

Despite these differences, sampling campaigns in general have methodologies in common.
First, before field deployment, PUF and XAD®-2 resin are generally pre-cleaned with solvent. It can be done by ASE (Schummer et al., 2012) or, more often, by Soxhlet. Solvents of choice include acetone followed by petroleum ether (Pozo et al., 2004 ; Gouin et al., 2005), but hexane and dichloromethane in a 50/50 v/v mix can be used too (Dobson et al., 2006 ; Schummer et al., 2010). Adsorbents for both passive and active samplers are cleaned. There are reports of also cleaning passive samplers' housings (Pozo et al., 2004), and for active samplers GFF are cleaned using the same method as the adsorbent (Dobson et al., 2006 ; Schummer et al., 2010).
Second, in order to correct the results of the study, blanks are made at several points throughout the campaign. Field blanks (Harner et al., 2004 ; Eng et al., 2014) are the most common ones. They are adsorbents treated exactly like the ones actually being used, but simply brought to the field, unwrapped at the sampling site, then wrapped again and brought back to the laboratory (Pozo et al., 2004 ; Gouin et al., 2005). Laboratory blanks can also be made (Jaward et al., 2004 ; Wang et al., 2010) to account for a possible contamination while preparing samples. Rarer than these are the travel blanks (Gouin et al., 2008b). They are handled like field blanks but are not deployed at the sampling location, only transported to and from the laboratory. Blanks are not always used, especially when the pre-cleaning method is validated (Schummer et al., 2010), but they are very common.
Finally, longer campaigns tend to use more sampling sites than short ones. Studies lasting one year can have as many as 15 (Gouin et al., 2005) or 16 (Wang et al., 2010) sites, though more often 5 to 10 sites are sampled (Gouin et al., 2008a ; Schummer et al., 2012). One- or two-month long campaigns usually take place at a single sampling site (Schummer et al., 2010 ; Eng et al., 2014). When several sites are chosen, different typologies are selected: urban, suburban, rural, agricultural, forested… Since all pollutants are not emitted from the same source, their concentration and behaviour differs from environment to environment. Thus, varied sampling sites give more accurate information than several sites with the same typology.

During a sampling campaign, different families of pollutants can be sampled at the same time, often PCB, PBDE and OCP (Pozo et al., 2004 ; Gouin et al., 2005 ; Wang et al., 2010). Non chlorinated pesticides are usually sampled by themselves (Gouin et al., 2008a ; Hayward et al., 2010 ; Schummer et al., 2012). While these are the most common, other pollutants can also be monitored: PAH (Eng et al., 2014), organophophorous pesticides (Armstrong et al., 2013) or polychlorinated dibenzodioxins and dibenzofurans (Guégen et al., 2013).

The campaigns that took place during this study were made to compare different adsorbents. First SiC foam and XAD®-2 resin, then different kinds of SiC foam. Some of these campaigns were done with both passive and active samplers in order to determine the foam's sampling rate.
Pesticides were monitored during every campaign, and PAH, PCB and OCP only during some of them.

Two campaigns lasted four months in five sampling sites throughout Alsace. One site was always an urban one, while others varied between suburban and rural. Shorter campaigns, from two to ten weeks, took place at a single urban site.

II/ First pesticides monitoring campaign – comparison betwen XAD®-2 resin and SiC foam

1. Context of the study

The first large scale study was done in collaboration with the Association for the Monitoring and Study of Atmospheric Pollution in Alsace (ASPA in French). For the second year in a row, they organised a sampling campaign to monitor pesticides levels in the atmosphere in Alsace. This collaboration was a way to have access to a wide range of sampling locations, by placing samplers at the same sites as the ASPA. It also allowed us to compare results.

For the ASPA, this campaign was part of a regional project meant to assess and reduce the impact of phytosanitary products in air (DREAL, 2012), which is why pesticides are the only pollutants analysed. This also means their results are confidential until approved by a regional council: they will not be disclosed in this work.

For the present study, the goal was to compare results from XAD®-2 resin and SiC foam, and to determine their respective sampling rates by comparing their results to those of the ASPA's active samplers. The sampling rate of a given sampler is the volume of air that passes through it per unit of time, which means it is always unknown at first for passive samplers since they do not use a pump to regulate the flow of air.

2. Materials and methods

The campaign took place between April 14th 2014 and August 12th 2014 on four agricultural sites and an urban site, placed on Figure 3-1 below.

They were as follows:

- Field crops site (1) – Ohnenheim, a village in the middle of Alsace, with wheat and maize crops
- Viticulture site (2) – Kintzheim, a village in the middle of Alsace
- Arboriculture site (3) – Sigolsheim, a village in the southern part of Alsace
- Market gardening site (4) – Village-Neuf, a village in the far south of Alsace
- Urban site (5) – Niederau, a school in the Robertsau residential area in Strasbourg

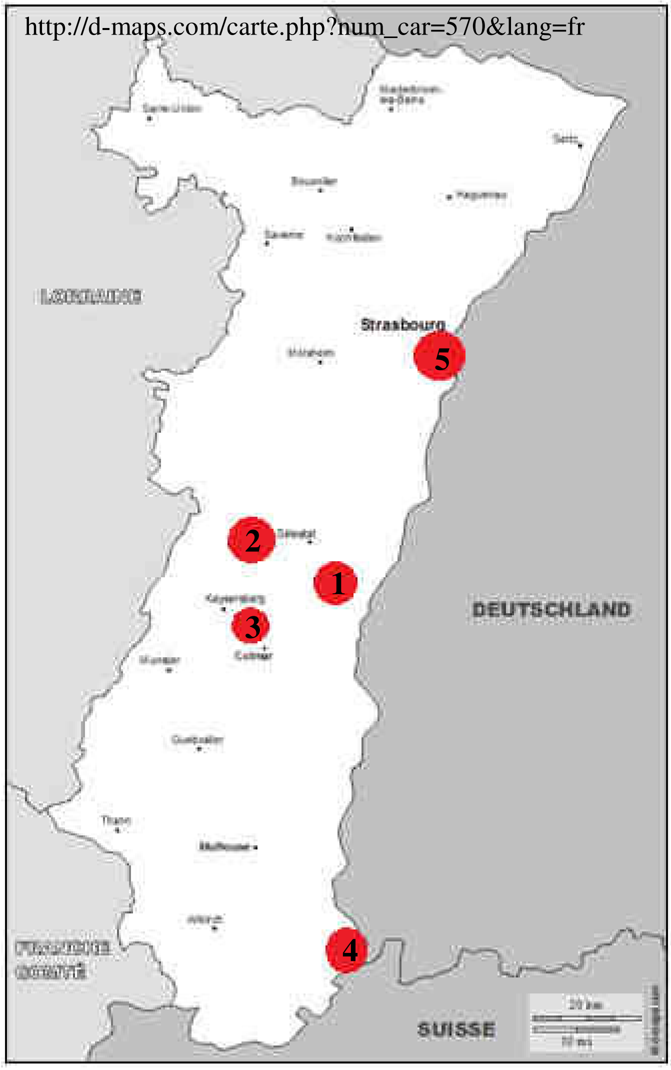

http://d-maps.com/carte.php?num_car=570&lang=fr

Figure 3-1 – Map situating the five sampling locations (2014)

Each site was sampled for five weeks, one or two weeks at a time. This totalled to 16 sampling periods: 9 two-week periods and 7 one-week periods. For each sampling period, one SiC foam and one cylinder filled with XAD®-2 resin were placed close to the active sampler used by the ASPA. Their samplers were low-volume Partisol Plus samplers, pumping air at 1 m^3 h^{-1}. The adsorbent was a series of four PUF (47 × 16 mm) preceeded by a GFF (Ø 47 mm).

The following equation was used to calculate the passive samplers' sampling rates (Persoon & Hornbuckle, 2009):

$$\mathrm{SR} = \frac{\mathrm{M_{PAS}}}{\mathrm{C_A} \times \mathrm{t}} \qquad (\mathrm{Eq.}\ 1)$$

SR: sampling rate in m^3 d^{-1} or m^3 h^{-1}
M_{PAS}: mass of a compound in the passive air sampler, in ng
C_A: concentration of the same compound in air, determined by active sampling, in ng m^{-3}
t: sampling duration in days (d) or hours (h)

3. Results

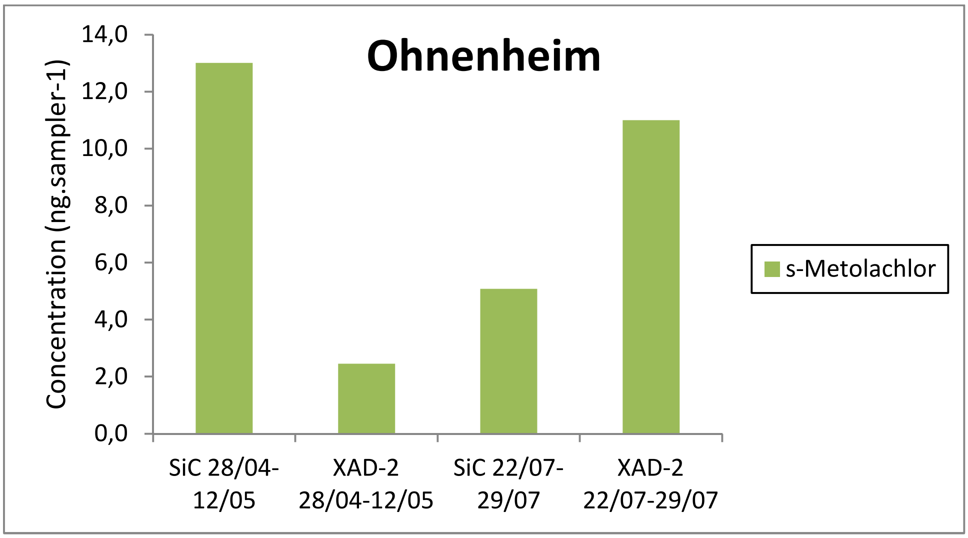
Due to a last-minute schedule change, two sites were not equipped with passive samplers during the month of June. Two weeks are missing at Kintzheim between June 10th and June 24th, and two at Ohnenheim: between June 17th and 24th and between June 29th and July 6th. This is why, instead of having 16 batches of results per matrix, there are only 13.

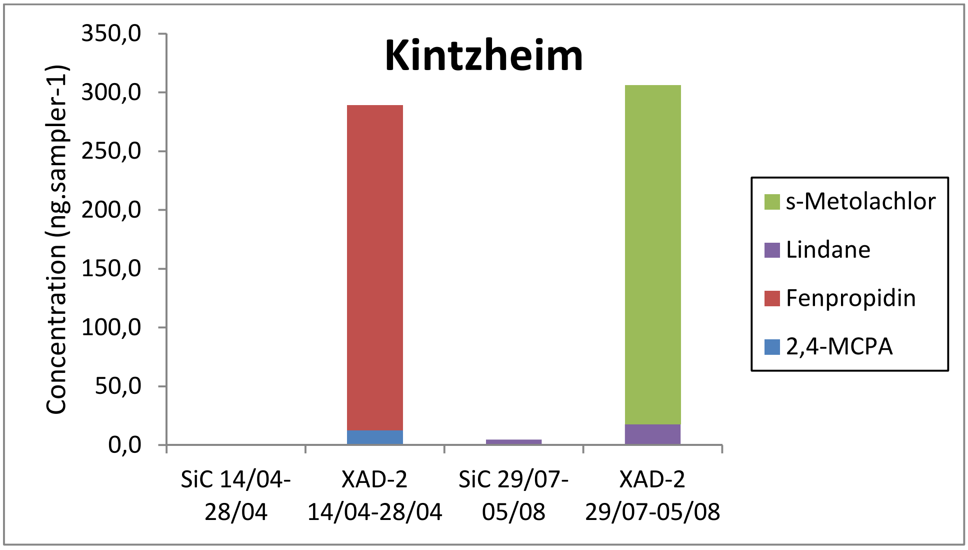
Moreover, due to technical problems, the samples from Kintzheim between April 14th and April 28th could not be analysed in LC. Therefore, there are 13 batches of results per matrix in GC but only 12 in LC.

GC pesticides results

Eighteen pesticides were detected by GC over the campaign, and nine quantified. Fourteen pesticides were detected and seven quantified in XAD®-2 resin while eleven were detected and six quantified in SiC foam.

Results are summarized in the following graphs (Figure 3-2), site by site. A table with detailed results can be found in Annex III.





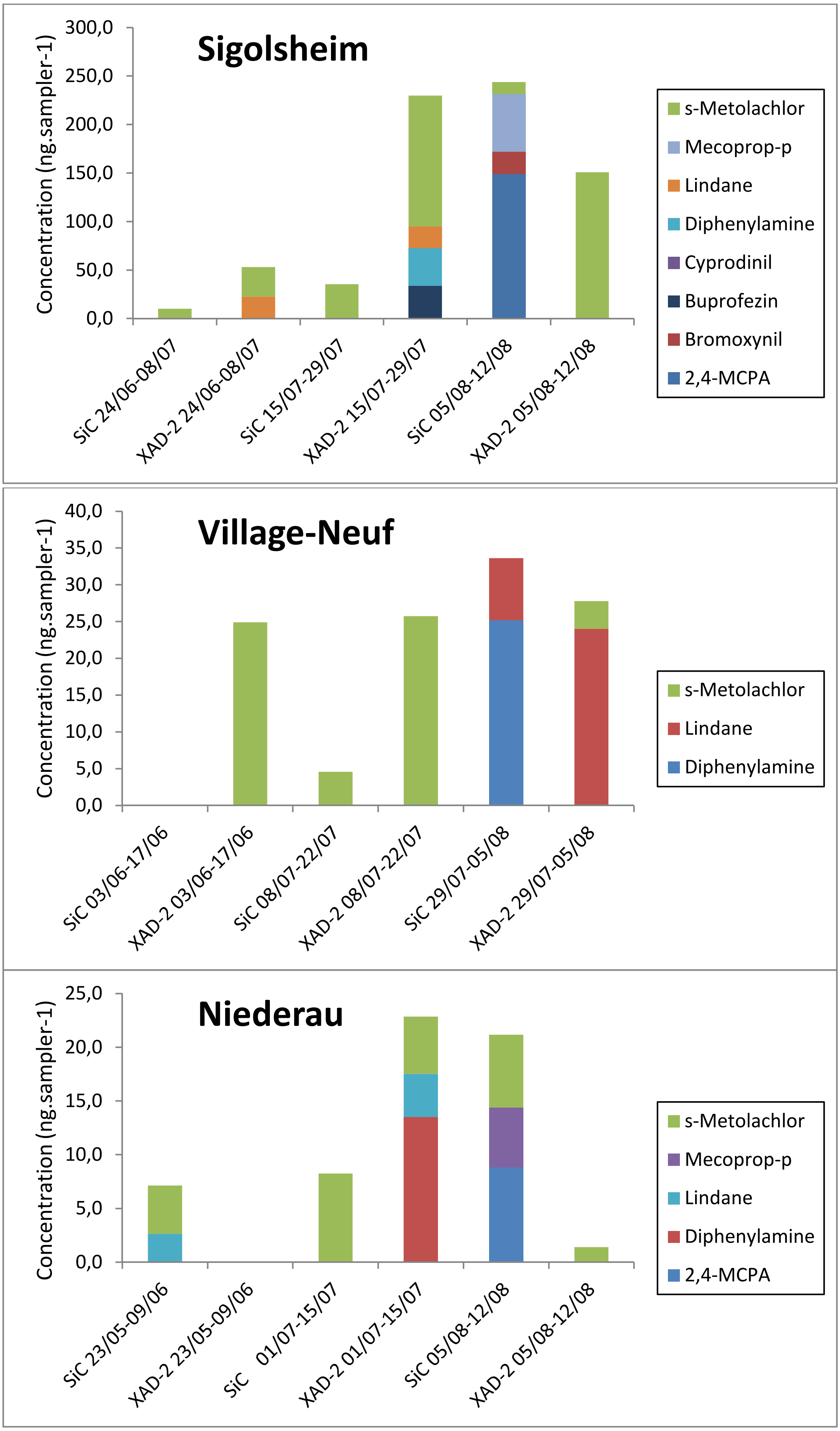


Figure 3-2 – Graphic results for GC pesticides site by site (2014)

One pesticide was found on every site: the herbicide s-metolachlor. It even is the only pesticide detected in Ohnenheim, the field crops site. This omnipresence was expected, as s-metolachlor is used to treat maize, the most abundant culture in Alsace. From these numerous emission sites, s-metolachlor can be transported to nearby locations.

One surprising detection was lindane, found at four of the five sampling sites. This insecticide has been banned from production and use in France since the end of 2007. However, lindane is a very persistent pollutant that can still be detected today. It can be accumulated in soil and resuspended during ploughing, or accumulated in wood and revolatilised when the weather is particularly hot. In this study, the highest lindane quantities (24.0 ng sampler^{-1}) were found in Village-Neuf, the market gardening site. This sampling site is situated about 3 km south from an old lindane production facility whose rehabilitation only started in 2012 (source: Regional Health Agency). The next highest quantities are in Sigolsheim at 22.4 and 22.7 ng sampler^{-1}, then Kintzheim at 17.7 ng sampler^{-1}. Investigations to find these lindane sources are still underway.

Over the course of the campaign, pesticides were detected 37 times and quantified 22 times in XAD®-2 resin, while there were 31 detections and 18 quantifications in SiC foam. XAD®-2 resin also adsorbed greater quantities than SiC foam: out of twelve times when the same pesticide was detected by both samplers at the same time, XAD®-2 resin had a higher quantity nine times. Quantities measured on the resin varied between 0.6 and 288.7 ng sampler^{-1}, averaging at 52.0 ng sampler^{-1}, while on the foam they were between 2.6 and 149.3 ng sampler^{-1} and averaged at 21.5 ng sampler^{-1}.

However, depending on the matrix, different pesticides were detected. The majority of pesticides found in SiC foam were less volatile than those in XAD®-2 resin. This is shown in Table 3-1 and Table 3-2, listing the vapour pressure and Henry's law constant (University of Hertfordshire, 2007) of the pesticides that were detected:

Table 3-1 – Detected pesticides from lowest to highest vapour pressure

Pesticides	Vapour pressure (25 °C) (mPa)	Henry's law constant (25 °C) (Pa m3 mol^{-1})
Trifloxystrobin	3.40E-03	2.30E-03
Propargite	4.04E-03	6.40E-02
Captan	4.20E-03	3.00E-04
Quinoxyfen	1.20E-02	3.19E-02
Acetochlor	2.20E-02	2.10E-03
Diclofop-methyl	2.50E-02	1.05E-05
Buprofezin	4.20E-02	2.80E-02
Triclopyr	1.00E-01	2.90E-03
Bromoxynil	1.70E-01	5.30E-04
Mecoprop-p	2.30E-01	5.70E-05
2,4-MCPA	4.00E-01	5.50E-05
Cyprodinil	5.10E-01	6.60E-03
Diphenylamine	8.52E-01	3.21E-01
Alachlor	2.90E+00	3.20E-03
s-Metolachlor	3.70E+00	2.20E-03
Lindane	5.99E+00	2.96E-01
Aldrin	8.60E+00	1.72E+01
Fenpropidin	1.70E+01	1.07E+01

pesticides in blue are those detected in majority in SiC foam

Table 3-2 – Detected pesticides from lowest to hightest Henry's law constant

Pesticides	Vapour pressure (25°C) (mPa)	Henry's law constant (25°C) (Pa m3 mol^{-1})
Diclofop-methyl	4.00E-01	1.05E-05
2,4-MCPA	4.00E-01	5.50E-05
Mecoprop-p	2.30E-01	5.70E-05
Captan	4.20E-03	3.00E-04
Bromoxynil	1.70E-01	5.30E-04
Acetochlor	2.20E-02	2.10E-03
s-Metolachlor	3.70E+00	2.20E-03
Trifloxystrobin	3.40E-03	2.30E-03
Triclopyr	1.00E-01	2.90E-03
Alachlor	2.90E+00	3.20E-03
Cyprodinil	5.10E-01	6.60E-03
Buprofezin	4.20E-02	2.80E-02
Quinoxyfen	1.20E-02	3.19E-02
Propargite	4.04E-03	6.40E-02
Lindane	5.99E+00	2.96E-01
Diphenylamine	8.52E-01	3.21E-01
Fenpropidin	1.70E+01	1.07E+01
Aldrin	8.60E+00	1.72E+01

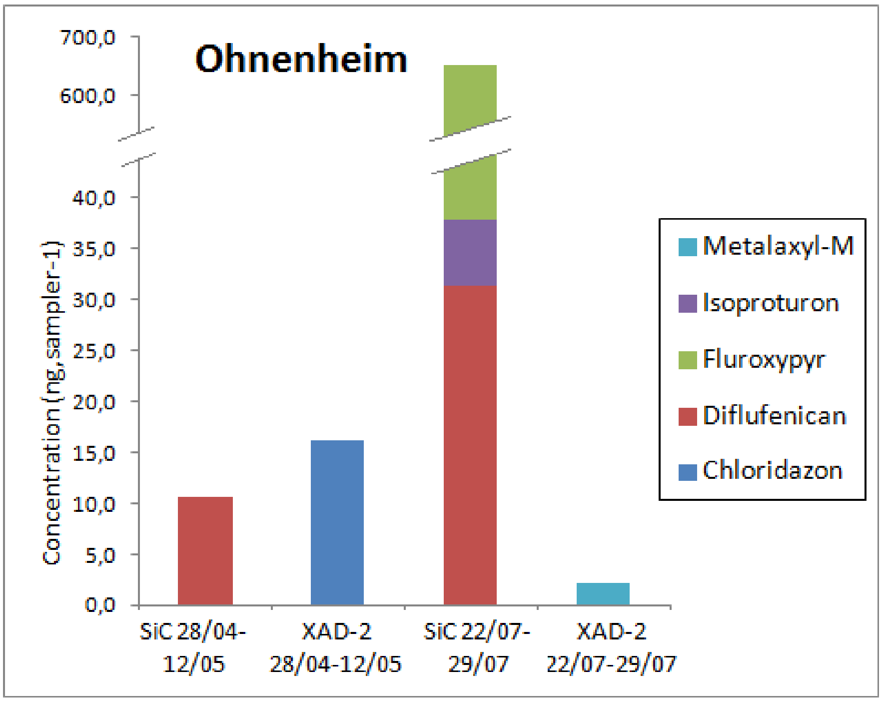
pesticides in blue are those detected in majority in SiC foam

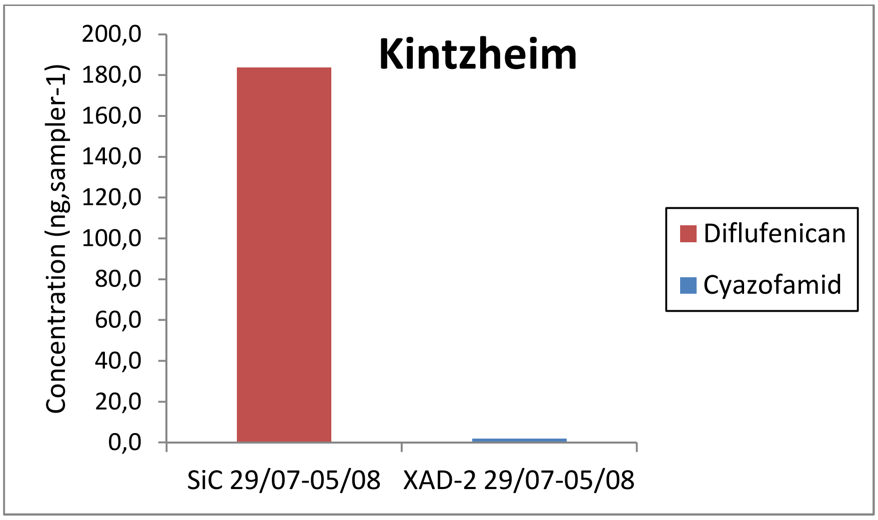
These results are likely due to the resin's high surface area, well-suited to the accumulation of the more volatile gaseous pollutants, while SiC foam is better suited to accumulate less volatile particulate pollutants because of its porous structure.

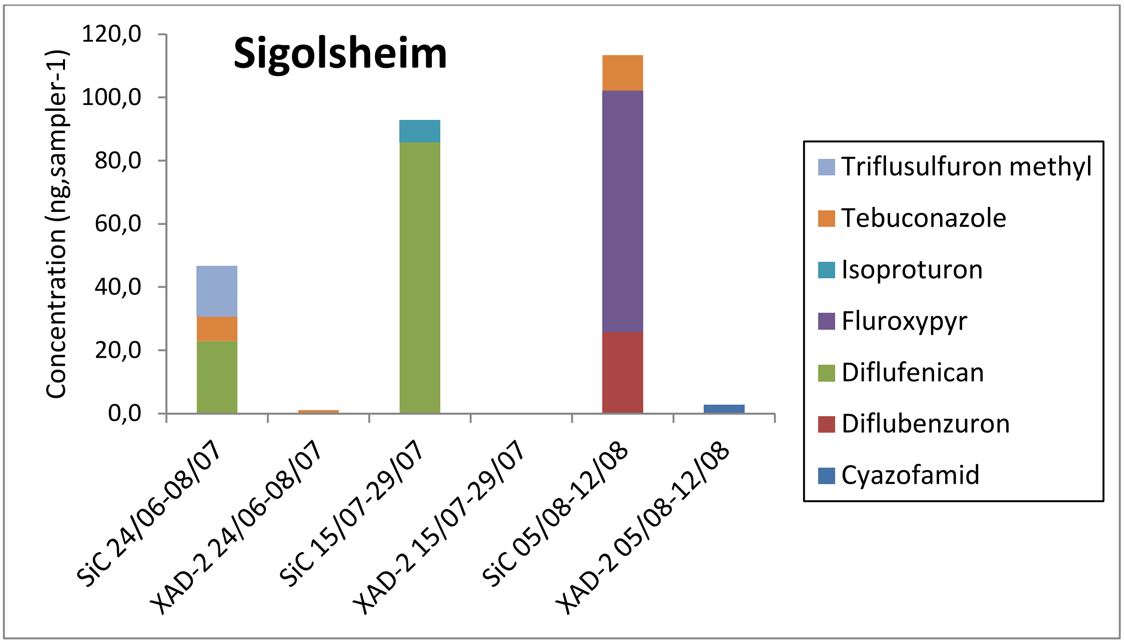
It can also be noted that, out of the seven pesticides detected in majority in SiC foam, four are polar: 2,4-MCPA, bromoxynil, mecoprop-p and triclopyr all have an –OH function. This difference in detection is likely due to SiC foam being less hydrophobic than XAD®-2 resin, thus more likely to adsorb polar compounds.

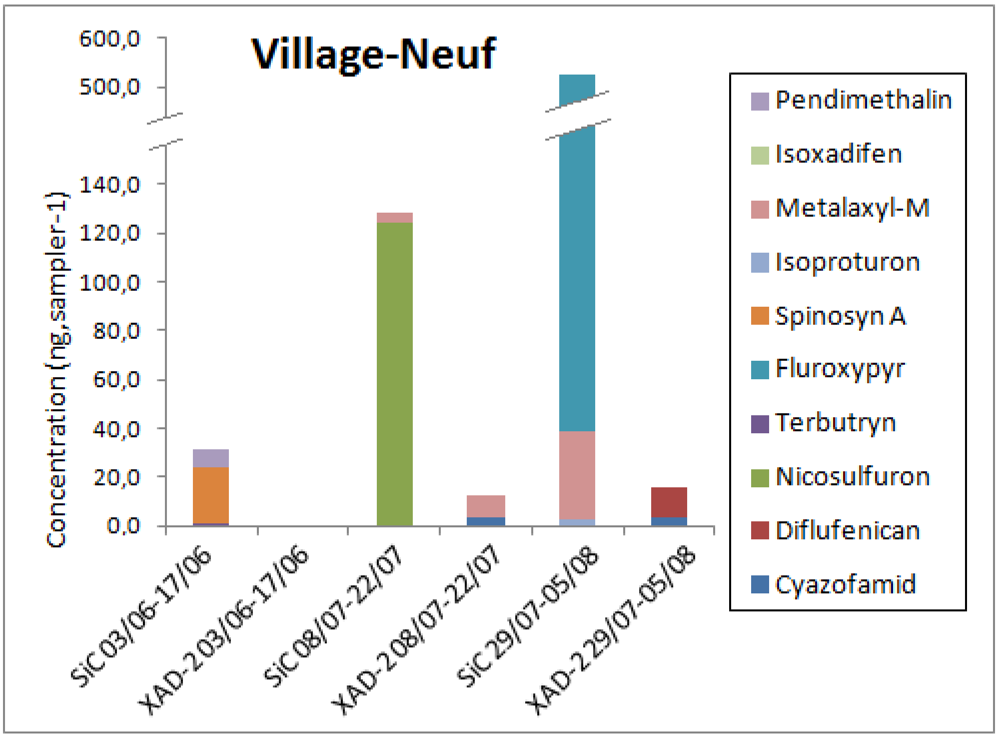
LC pesticides results

Twenty LC pesticides were detected at least once during this study. They were found more often and in greater quantities in SiC foam than in XAD®-2 resin. Results are summarized in the following graphs (Figure 3-3), site by site. A table with detailed results can be found in Annex III.






Sigolsheim
Concentration (ng,sampler-1)
120,0
100,0
80,0
60,0
40,0
20,0
0,0
SiC 24/06-08/07
XAD-2 24/06-08/07
SiC 15/07-29/07
XAD-2 15/07-29/07
SiC 05/08-12/08
XAD-2 05/08-12/08
Triflusulfuron methyl
Tebuconazole
Isoproturon
Fluroxypyr
Diflufenican
Diflubenzuron
Cyazofamid


Village-Neuf
Concentration (ng,sampler-1)
600,0
500,0
140,0
120,0
100,0
80,0
60,0
40,0
20,0
0,0
SiC 03/06-17/06
XAD-2 03/06-17/06
SiC 08/07-22/07
XAD-2 08/07-22/07
SiC 29/07-05/08
XAD-2 29/07-05/08
Pendimethalin
Isoxadifen
Metalaxyl-M
Isoproturon
Spinosyn A
Fluroxypyr
Terbutryn
Nicosulfuron
Diflufenican
Cyazofamid

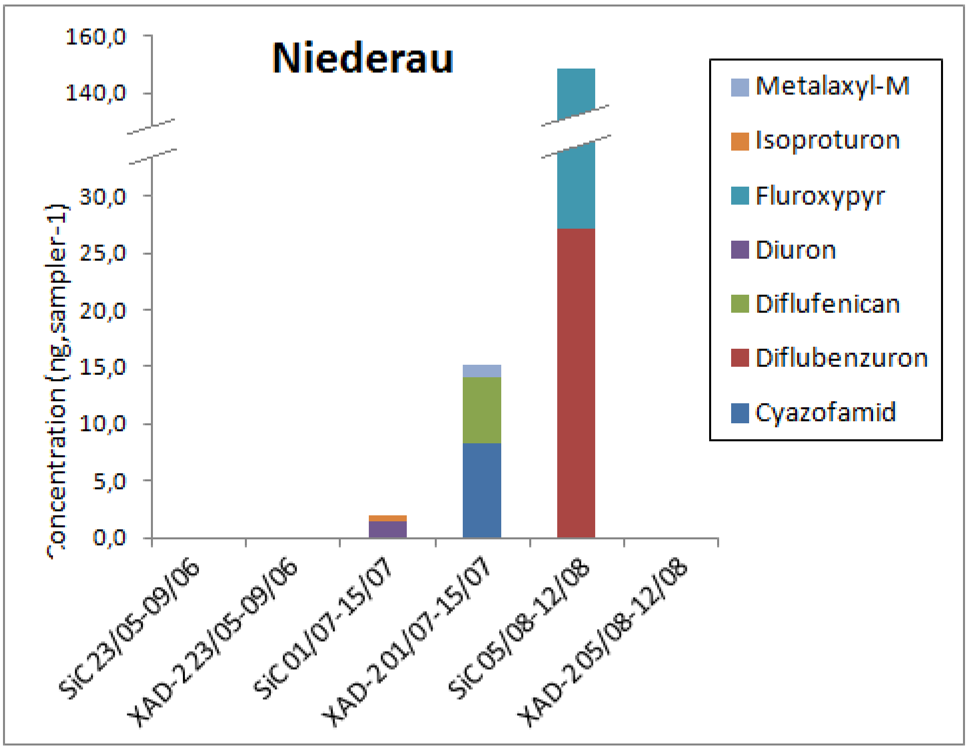


Figure 3-3 – Graphic results for LC pesticides site by site (2014)

One pesticide was found on every site: diflufenican is a herbicide used on field crops, which are the dominant cultures throughout Alsace. This means that not only can diflufenican be found on its source site, but it can also easily be transported to other places. This molecule is also authorised in products made for non-agricultural uses, such as private weeding and treatment of trees, so private gardens in towns can also emit diflufenican in the air.

Cyazofamid, fluroxypyr and isoproturon are found in four of the five sites. Cyazofamid is a fungicide used on vegetables and vineyards. Since vineyards are one of the most common cultures in Alsace, cyazofamid could be transported from these crops to others. This theory could be confirmed by the period at which the molecule was detected: the beginning of July and the beginning of August are when fungicide treatment in done in vineyards. Fluroxypyr and isoproturon are herbicides used mostly on cereals, including wheat and maize that are found in every part of the region. They could then easily be transported to several sites away from their source site. Fluroxypyr is also authorised in gardens, meaning it can be detected in towns without having been transported.
Three molecules that are prohibited in France were detected during the study: carbendazim, diuron and terbutryn, though only diuron and terbutryn were quantified. Phytosanitary products containing these molecules have been banned between 2005 and 2010. All three were only detected once, in quantities no greater than 1.4 ng sampler^{-1}. It is possible that what was detected were traces of past use, and that accumulated pesticides were resuspended due to ploughing or revolatilised due to the heat.

There were 20 detections including 12 quantifications in XAD®-2 resin, against 30 detections and 25 quantifications in SiC foam.

Since SiC foam is more suited than XAD®-2 resin to collecting particles, on which less volatile pollutants are found, these results were expected. LC is used to analyse heavier pollutants than GC, so more of them are in the particulate phase. LC pesticides are also more polar than GC pesticides, so they have a greater affinity with SiC foam that is less hydrophobic than XAD®-2 resin.

Another noticeable fact was that SiC chromatograms were cleaner than XAD®-2's, which may be due to interferences from the resin matrix. LC analysis is not preceded by concentration and purification through SPME, which means there is a higher risk of matrix interference that reduces the analysis' sensitivity.

Sampling rates

Sampling rates were calculated when the same pesticide was detected at the same time and the same place in a passive and active sampler, and quantified for both. Four pesticides were then eligible for comparison, and nine sampling rates were calculated for XAD®-2 resin and eight for SiC foam. They are summarised in Table 3-3 and Table 3-4 respectively. The date, place and pesticide used for the calculation are included.

Table 3-3 – XAD®-2 resin sampling rates in $m^3\ d^{-1}$

Pesticides	Village-Neuf 03/06-17/06	Sigolsheim 24/06-08/07	Niederau 01/07-15/07	Sigolsheim 15/07-29/07	Ohnenheim 22/07-29/07	Sigolsheim 05/08-12/08
Cyprodinil						0.43
Lindane			2.14			
s-Metolachlor	3.56	3.47	0.94	62.08	4.91	67.03
Tebuconazole		0.78				

Table 3-4 – SiC foam sampling rates in $m^3\ d^{-1}$

Pesticides	Niederau 23/05-09/06	Sigolsheim 24/06-08/07	Niderau 01/07-15/07	Sigolsheim 15/07-29/07	Ohnenheim 22/07-29/07	Sigolsheim 05/08-12/08
Lindane	0.08					
s-Metolachlor	0.14	1.15	1.45	16.28	2.27	5.43
Tebuconazole		5.82				

Some of these values were much higher than expected: 16.28 $m^3\ d^{-1}$ for SiC foam, and 62.08 and 67.03 $m^3\ d^{-1}$ for XAD®-2 resin. These sampling rates have been calculated for the same compound (s-metolachlor) on the same site (Sigolsheim), for some on the same period (15/07-29/07). Several explanations are possible, including the placement of the samplers on the site that could favour adsorption on the passive samplers rather than the active ones, or the rain which does not affect different matrices in the same way…

It is also worth noting that the active samplers use PUF as their adsorbent, while passive samplers are XAD®-2 resin and SiC foam. Both matrices have a higher specific surface area than PUF, and thus can adsorb greater quantities of pollutants. It is possible that, during treatment with s-metolachlor at these dates, PUF reached its adsorption limit while the passive samplers accumulated more of this pesticide.

Outside of these highest values, calculated sampling rates ranged between 0.43 and 4.91 $m^3\ d^{-1}$ for XAD®-2 resin and between 0.08 and 5.82 $m^3\ d^{-1}$ for SiC foam. These values are comparable to those found in the literature for XAD®-2 resin, which are between 0.60 and 3.70 $m^3\ d^{-1}$ (Wania et al., 2003 ; Gouin et al., 2008b ; Xiao-Ping et al., 2010).

A similar campaign had taken place in 2013, comparing the ASPA's results only to XAD®-2 resin. Nine sampling rates have been calculated for this campaign, ranging from 0.66 to 6.14 $m^3\ d^{-1}$. While higher than expected compared to the literature, these values are coherent with those calculated in 2014. They are summarised in Table 3-5 below.

Table 3-5 – SiC and XAD®-2's sampling rates compared to each other and to the literature

	SiC 2014	XAD®-2 2014	XAD®-2 2013	XAD®-2 literature*
Minimum	0.08	0.43	0.66	0.60
Maximum	5.82	4.91	6.14	3.70
Average	2.33	2.32	3.23	2.78
Median	1.45	2.14	3.76	2.75

* Wania et al., 2003 ; Gouin et al., 2008b ; Xiao-Ping et al., 2010

After this first comparison campaign, it seems that SiC foam's sampling rates are on the same order of magnitude as XAD®-2's.

III/ Sampling campaign in Strasbourg's botanical garden – introducing grafted SiC foam

1. Context of the study

A second sampling campaign was done in Strasbourg's botanical garden between September and October 2014 in order to further compare SiC foam and XAD®-2 resin.

The goal was to include PAH, PCB and OCP in the comparison, and if possible to try different kinds of SiC foams. Nitrogen-doped carbon or CNT can be grafted onto the foam's surface to increase its surface area, thus increasing its adsorption capacity without compromising its structural integrity. These foams are called N-C SiC and N-CNT SiC respectively. Due to the respective properties of carbon and CNT, N-C SiC are less hydrophobic than N-CNT SiC, but also present lower specific surface areas.

Like CNT foam, these grafted SiC foams can be heated to 900 °C in order to become more hydrophobic. Otherwise, the regular treatment is to heat them to 450 °C. One of each kind of grafted SiC foam was provided towards the end of this campaign: 450 °C N-C, 900 °C N-C, 450 °C N-CNT and 900 °C N-C.

2. Materials and methods

The campaign lasted five weeks, from September 8th 2014 to October 14th 2014. Each week, two SiC foams and two resin-filled cylinders were placed next to each other. During the fifth week, in addition to these samplers, the four grafted SiC foams were tested. They were placed next to the regular SiC foams and XAD®-2 cylinders.

The target pollutants were PAH, PCB, OCP and non chlorinated pesticides.

3. Results of the five-week comparison between XAD®-2 resin and SiC foam

While OCP were monitored during this study, their results are unusable for the comparison of the two matrices. Nineteen out of twenty-one were detected, in quantities up to hundreds and thousands of nanograms per sampler. Despite the persistence of these pollutants, they have been prohibited for decades and while some traces could be detected, these numbers are not realistic.

Since there are other pesticides that can be used to compare the different adsorbents, OCP results were omitted in this report. Only PAH, PCB and non-chlorinated pesticides will be discussed.

PAH results

Overall, SiC foam was more sensitive than XAD®-2 resin towards PAH, and especially the heaviest ones. Results were averaged for each pair of samplers and are shown in Figure 3-4. A table with detailed results can be found in Annex IV.

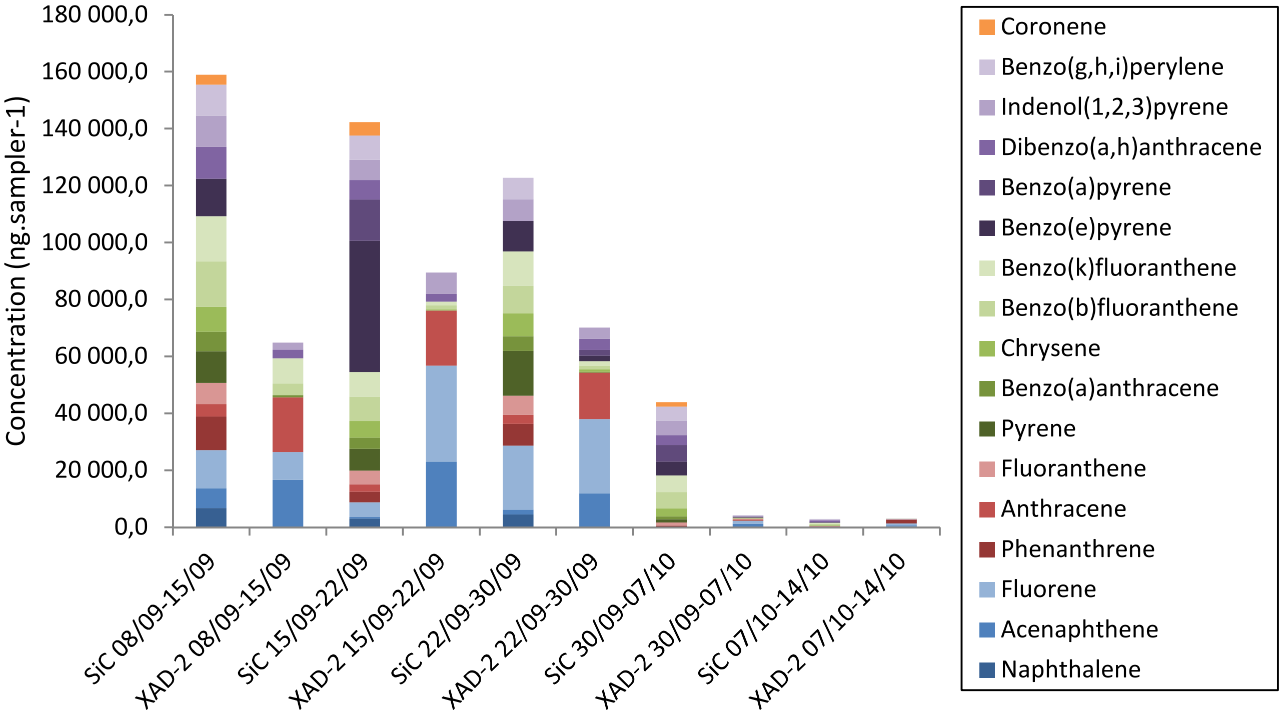


Figure 3-4 – PAH quantities detected in SiC and XAD®-2 each sampling week

The different colours used represent the number of aromatic cycles in the pollutants: blue for two, red for three, green for four, purple for five and orange for six.

There were more detections in SiC foam than in the resin: 150 detections against 96 over the five sampling weeks. Every PAH was detected at least once in SiC foam, while 15 out of 17 were detected at least once in XAD®-2 resin.
When the same PAH was detected at the same time in both samplers, the quantity was usually higher in SiC foam. Out of 53 such detections, SiC had the greater quantity 35 times (66 % of results). There is a clear divide between lighter and heavier PAH: from naphthalene to fluoranthene, the two- and three-ringed PAH, XAD®-2 has higher quantities 90 % of the time. From pyrene to coronene, the four-, five- and six-ringed PAH, SiC foam has greater quantities 100 % of the time.
Averaged quantities found in XAD®-2 resin varied between 0.6 and 33,717.3 ng sampler^{-1} with an average at 3,731.5 ng sampler^{-1}. In SiC foam, they varied between 12.7 and 46,114.6 ng sampler^{-1}, with an average at 5,864.4 ng sampler^{-1}.
All in all, despite the resin's efficiency for lighter PAH, SiC foam is the better sampler for these molecules.

PCB results

Depending on the compound, either SiC foam or XAD®-2 resin can be the more sensitive matrix. Results were averaged for each pair of samplers and are shown in Figure 3-5. A table with detailed results can be found in Annex IV.

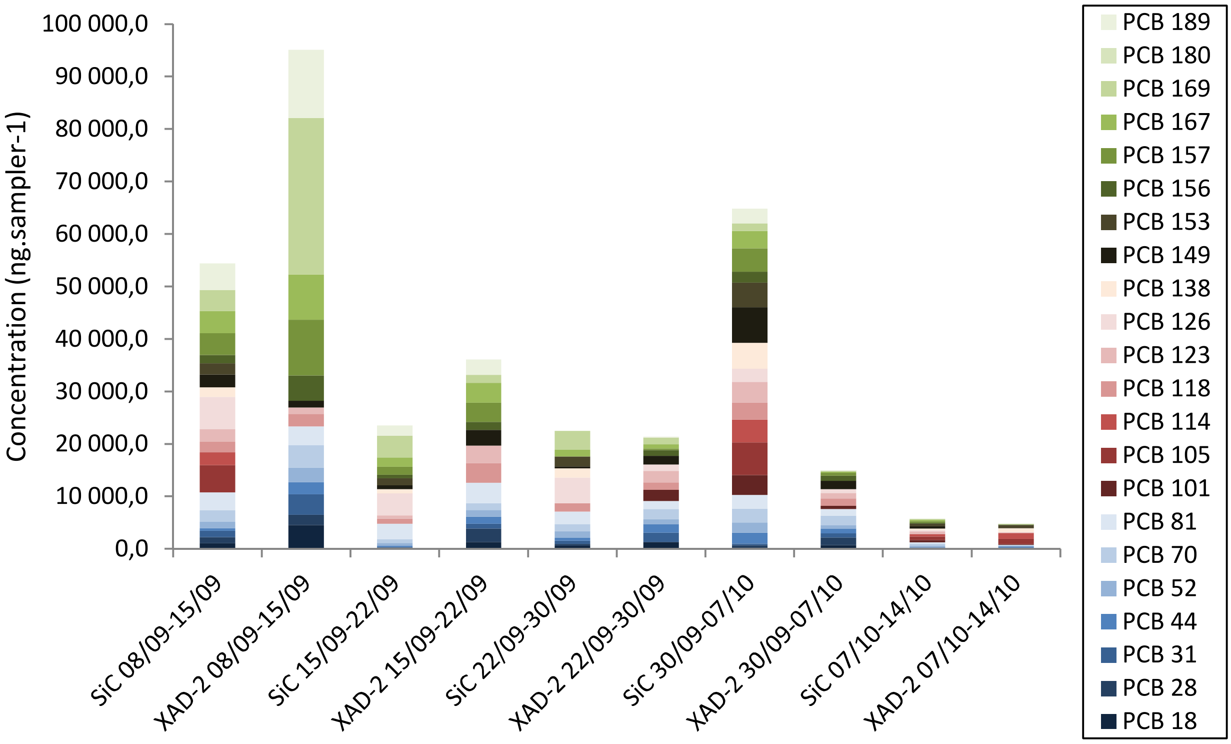


Figure 3-5 – PCB quantities detected in SiC and XAD®-2 each sampling week

Different colours were arbitrarily used to represent the heaviness of the pollutants: blue for PCB < 100, red for PCB between 100 and 140, and green for PCB > 140.

There were more detections in SiC foam than in the resin: 171 detections against 130 over the five sampling weeks. Every PCB was detected at least once in XAD®-2 resin, and all but PCB 180 were detected at least once in SiC foam.

No sampler consistently had higher PCB quantities when the same compound was detected at the same time by both matrices. Out of 79 such detections, SiC foam had the greater quantity 37 times (47 % of results) and XAD®-2 foam 42 times (53 % of results).

Quantities found in XAD®-2 resin varied between 7.0 and 29,793.0 ng sampler^{-1}, with an average at 2,026.0 ng sampler^{-1}. In SiC foam, they varied between 33.3 and 6,735.2 ng sampler^{-1} with an average at 1,818.8 ng sampler^{-1}.

In conclusion, while XAD®-2 allows greater PCB quantities to be sampled, SiC foam can adsorb more of them. Depending on what information is needed in a given study, one or the other can be used.

GC pesticides results

Fifteen GC pesticides were detected at least once over the five sampling weeks, and twelve quantified. Overall, the results of the two samplers were close to each other, though more pesticides were detected in SiC foam and higher quantities in XAD®-2 resin. Results were averaged for each pair of samplers and are shown in Figure 3-6. A table with detailed results can be found in Annex IV.

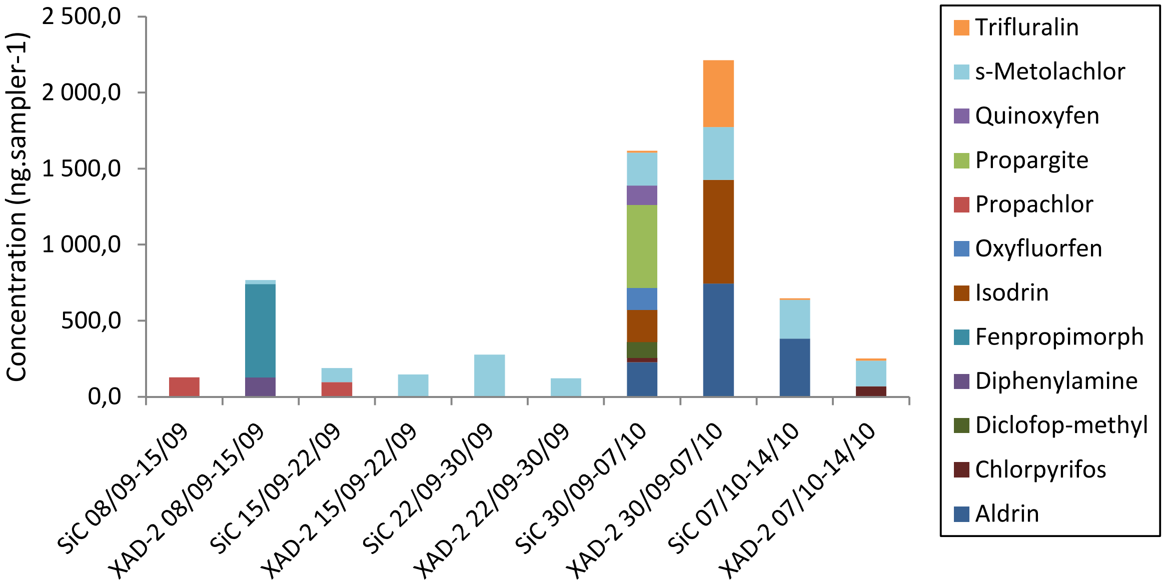


Figure 3-6 – Pesticides quantities detected by GC in SiC and XAD®-2 each sampling week

Nine pesticides were detected at least once in XAD®-2 resin and thirteen in SiC foam. Eight and eleven were quantified, respectively. In total, there were 29 detections and 24 quantifications in the resin against 39 detections and 27 quantifications in the foam.

Higher pesticides quantities were detected in XAD®-2 resin. Out of the eight times a given pesticide was detected in both matrices at the same time, the resin had a greater quantity seven times.

Averaged quantities found in XAD®-2 resin varied between 13.0 and 744.7 ng sampler^{-1}, with an average at 291.4 ng sampler^{-1}. In SiC foam, they were between 11.9 and 547.2 ng sampler^{-1} with an average at 178.6 ng sampler^{-1}.

Two of the pesticides should probably not be taken into account in the comparison: aldrin and trifluralin. Aldrin is an insecticide that has been prohibited in France since 1992. Finding such quantities (between 226.2 and 744.7 ng sampler^{-1}) several times in a botanical garden in the centre of a city is very improbable, even taking into account the persistence of aldrin. Trifluralin is a herbicide prohibited since 2008, and while quantities detected were majoritarily below the quantification limit, up to 438.8 ng sampler^{-1} have been found during this campaign. Trifluralin peaks on the chromatogram could be an artefact due to the use of trifluralin d14 as an internal standard.

Even when these pesticides are not considered, the trend stays the same: more pesticides are detected in SiC foam, and greater quantities in XAD®-2 resin.

LC pesticides results

Thirteen LC pesticides were detected during this study. SiC foam and XAD®-2 resin had a comparable number of detections over the five sampling weeks, but higher quantities were detected in SiC foam. Results were averaged for each pair of samplers and are shown in Figure 3-7. A table with detailed results can be found in Annex IV.

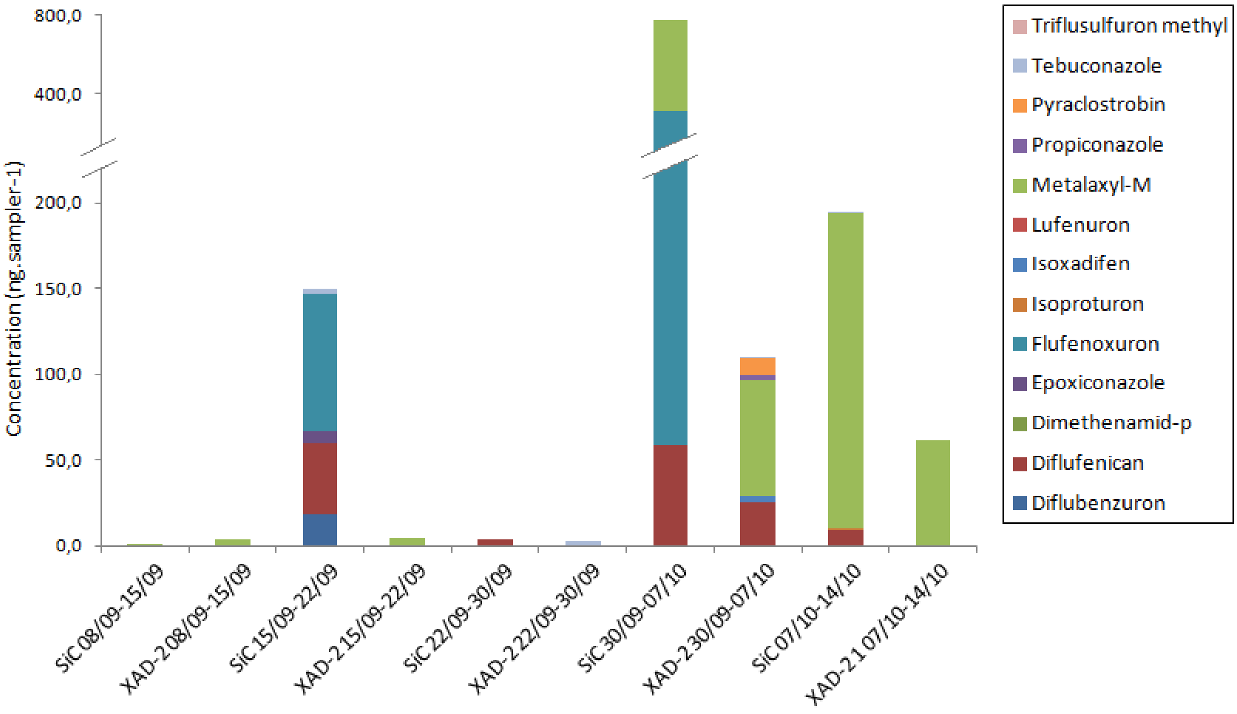


Figure 3-7 – Pesticides quantities detected by LC in SiC and XAD®-2 each sampling week

There were 18 detections and 14 quantifications in XAD®-2 resin against 21 detections in SiC foam, all quantified. Eight pesticides were detected at least once in the resin and nine in the foam.

Higher pesticides quantities were detected in SiC foam. Five times, the same pesticide was detected in both samplers at the same time; SiC foam had a greater quantity four times out of these.

Averaged concentrations found in XAD®-2 resin varied between 0.3 and 67.4 ng sampler^{-1}, with an average of 15.2 ng sampler^{-1}. In SiC foam, they varied between 0.3 and 419.6 ng sampler^{-1} with an average of 66.8 ng sampler^{-1}.

Discussion

PAH results clearly illustrate the differences between XAD®-2 resin and SiC foam. The more volatile PAH, from naphthalene to anthracene, were detected in higher quantities in XAD®-2 resin, but very few of the four- or five-ringed PAH were detected. SiC foam, while accumulating lesser quantities of lighter PAH, was able to detect all of them. This is due to their different physical characteristics: SiC foam, despite have a smaller specific surface area less suited to accumulate gaseous pollutants, has an open porosity that can easily trap particles. XAD®-2 resin, with its nanoporous network and meshed cylinder, provides many obstacles to particulate compounds.

Such a difference in results was not observed for PCB. This could mean that there is an equal amount of gaseous and particulate PCB, or that particles are fine enough to be trapped by XAD®-2 resin.

Comparing pesticides results confirmed the observations of the previous ASPA campaign and similar conclusions were drawn regarding the two samplers. SiC foam was able to detect more LC pesticides in greater quantities, probably due to the high particles/gas ratio of these compounds.

However, contrary to the ASPA campaign, more GC pesticides were detected on SiC foam, despite the highest quantities still being found in XAD®-2 resin. This was mostly the case during the fourth week, when most of the pesticides were detected. The explanation might be that, while XAD®-2 resin still has the advantage of a higher specific surface area to adsorb gaseous compounds, it is more hydrophobic than SiC foam and thus can detected a narrower range of pollutants. This may not be noticeable in rural areas where pesticides are regularly used, but it could make a difference in a city where there are less.

All in all, while SiC foam does not have the adsorption capacity of XAD®-2 resin for volatile compounds, it can still adsorb high quantities of pollutants and has the advantage of efficiently trapping particles.

4. Results of the one-week comparison between regular and grafted SiC foam

Out of the four grafted SiC foams, the 450 °C N-C and 900 °C N-CNT gave the best results for all target pollutants.

PAH results

There is a clear difference in efficiency between these foams for PAH: 900 °C N-CNT SiC is the most efficient sampler for the lightest compounds, from acenaphtene (2 rings) to pyrene (4 rings); but from chrysene (4 rings) to coronene (6 rings), the heavier PAH, 450 °C N-C SiC is the most efficient while nothing is detected on the 900 °C N-CNT SiC.

Results, averaged for the pair of regular SiC foams, are shown in Figure 3-8 and a table with detailed results can be found in Annex IV.

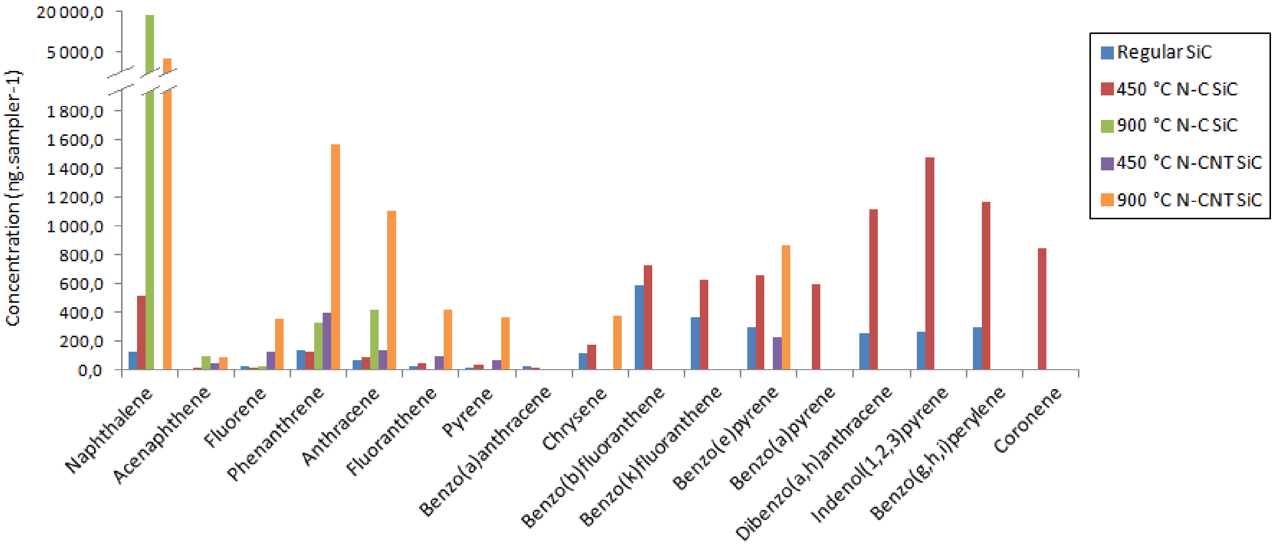


Figure 3-8 – PAH quantities detected in regular and grafted SiC foams over one week

These results are coherent with previous observations that hydrophobic pollutants, and especially PAH, are strongly adsorbed on CNT and very difficult to extract. N-C SiC does not have this problem, while still having a greater specific surface area than regular SiC.

From naphthalene (2 rings) to chrysene (4 rings), 900 °C N-CNT SiC has adsorbed quantities between 12.4 and 4,025.3 ng sampler^{-1}, while 450 °C N-C SiC is between 14.2 and 514.5 ng sampler^{-1} and regular SiC between 12.7 and 135.4 ng sampler^{-1}. However, from benzo(b)fluoranthene (4 rings) to coronene (6 rings), N-CNT SiC detected only one PAH while N-C SiC had quantities between 602.0 and 1,477.8 ng sampler^{-1} and regular SiC between 259.0 and 593.0 ng sampler^{-1}.

The difference in specific surface area means that grafted SiC can better adsorb gaseous pollutants, which is why the difference between grafted and regular SiC is more striking for lighter PAH.

PCB results

The same phenomenon is observed for PCB. Results, averaged for the pair of regular SiC foams, are shown in Figure 3-9 and a table with detailed results can be found in Annex IV.

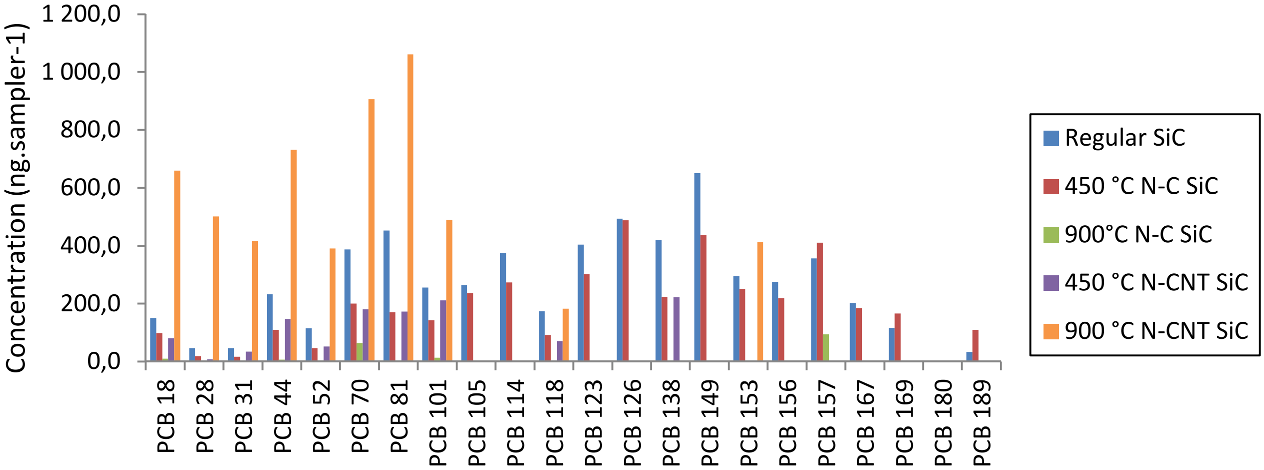


Figure 3-9 – PCB quantities detected in regular and grafted SiC foams over one week

For lighter PCB, from 18 to 101, 900 °C N-CNT SiC is the most efficient matrix. Quantities detected in this matrix varied between 390.2 and 1,060.6 ng sampler^{-1}, while 450 °C N-C SiC results were between 16.4 and 200.6 ng sampler^{-1} and regular SiC between 46.2 and 452.4 ng sampler^{-1}.

From PCB 105 onwards, results are tied between regular SiC foam and 450 °C N-C SiC. Quantities in the grafted SiC varied between 92.4 and 488.1 ng sampler^{-1} while they were between 33.3 and 654.7 ng sampler^{-1} for regular SiC. 900 °C N-CNT foam only allowed two PCB to be detected, 118 and 153.

One possible explanation for these observations is that heavier PCB are mostly particulate compounds, and since regular and grafted SiC have the same structure, their efficiency for trapping particles is similar. A difference only occurs when there are gaseous compounds to adsorb. Then the CNT's high specific surface area makes a difference.

GC pesticides results

Next to no pesticides were detected by GC during this week, making it impossible to reliably compare SiC foams for these compounds. Results, averaged for the pair of regular SiC foams, are shown in Figure 3-10 and a table with detailed results can be found in Annex IV.

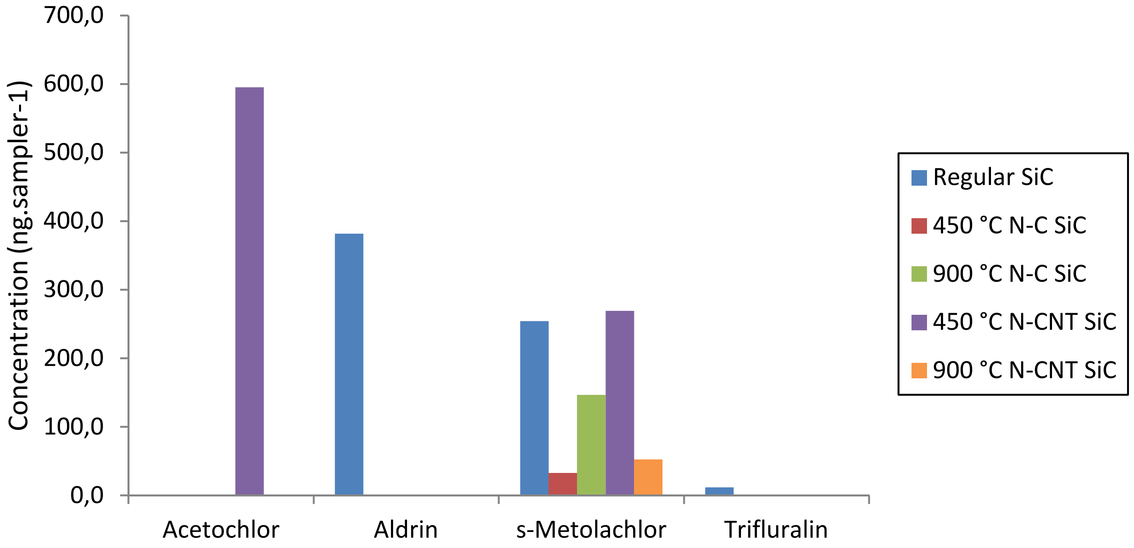


Figure 3-10 – Pesticides quantities detected by GC in regular and grafted SiC foams over one week

s-Metolachlor and trifluralin were both found in every sampler. However, as noted in the previous section, aldrin and trifluralin results may not be accurate representations of actual air concentrations. Acetochlor too is prohibited in France, and has been since 2011. Stocks could be used until 2013, but it is improbable to find such a concentration (595.0 ng sampler^{-1}) in a city as it was a herbicide used in field crops.

Contrary to other pollutants, for these compounds 900 °C N-C SiC and 450 °C N-CNT SiC seem to be more effective than the other grafted foams. But this conclusion cannot at present be extended to other GC pesticides.

LC pesticides results

Twelve pesticides were detected by LC. For the majority, the two N-C SiC were the most efficient samplers. Results, averaged for the pair of regular SiC foams, are shown in Figure 3-11 and a table with detailed results can be found in Annex IV.

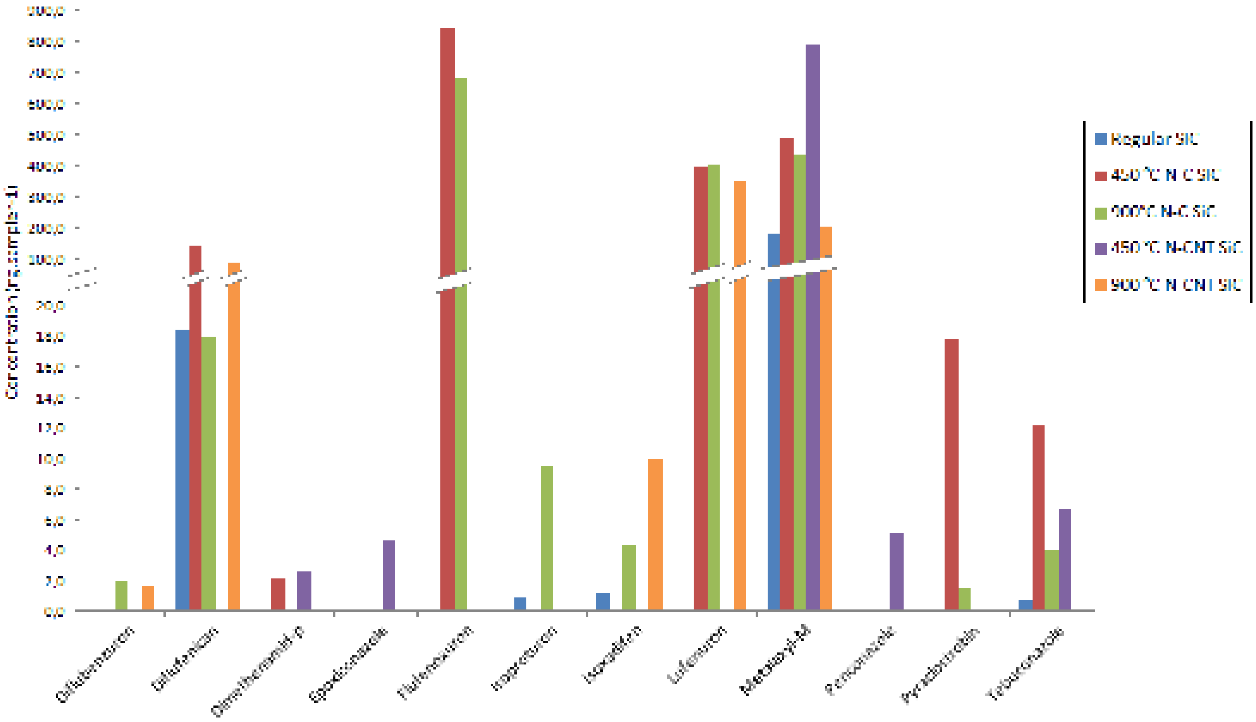


Figure 3-11 – Pesticides quantities detected by LC in regular and grafted SiC foams over one week

Only metalaxyl-M was detected in every foam, which limits comparison. However, results are generally on the same order of magnitude between samplers despite N-C SiC giving the highest concentrations for the heaviest pesticides.

Regular SiC and N-CNT SiC detected five pesticides, while 450 °C N-C SiC detected seven and 900 °C N-C SiC nine. Plain SiC had the lowest concentrations, ranging from 0.4 to 183.6 ng sampler^{-1}. Results from the two N-CNT SiC were between 1.8 and 791.5 ng sampler^{-1} while those from the two N-C SiC were between 1.6 and 834.3 ng sampler^{-1}.

Grafted SiC, especially N-C SiC, seemed to be more efficient than regular SiC. N-C SiC with either thermal treatment was probably more effective than N-CNT SiC due do its lower hydrophobicity that increases its affinity with these pesticides.

Comparison between grafted SiC and XAD®-2 resin

Since two of the grafted SiC foams appeared to be more efficient than SiC foam, they needed to be compared to XAD®-2 resin too. Results were averaged for the pair of XAD®-2 tubes during the last sampling week, and compared to those of 450 °C N-C SiC foam and 900 °C N-CNT SiC foam. They are summarised in Figures 3-12 to 3-15 and a table with detailed results can be found in Annex IV.

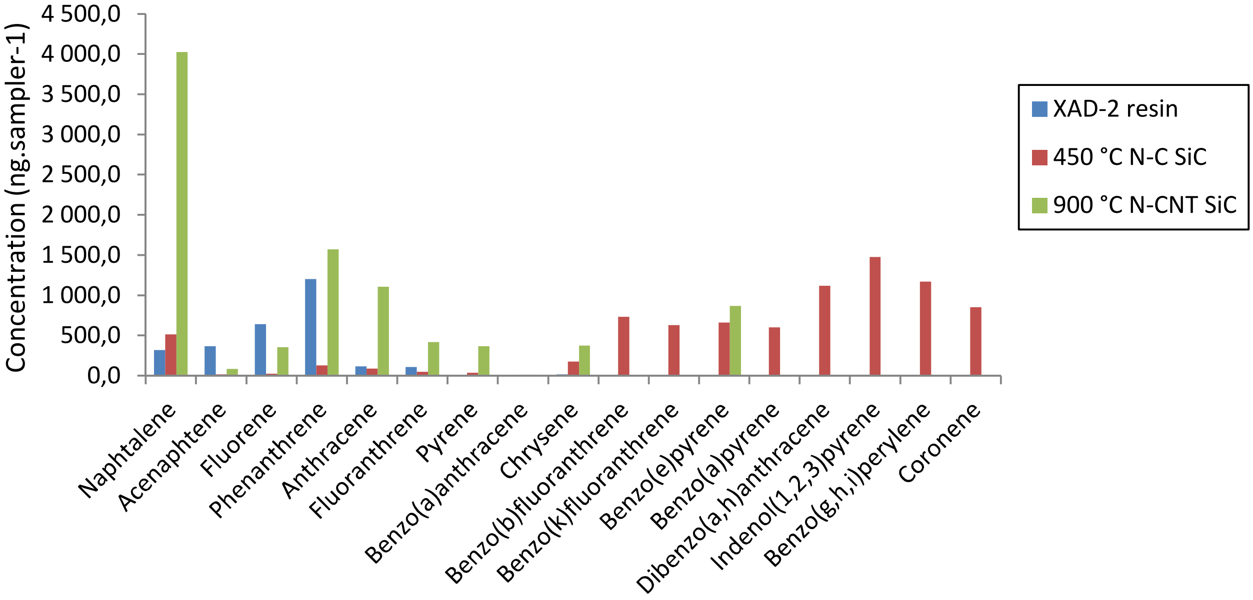


Figure 3-12 – PAH quantities detected in XAD®-2 resin and grafted SiC foams over one week

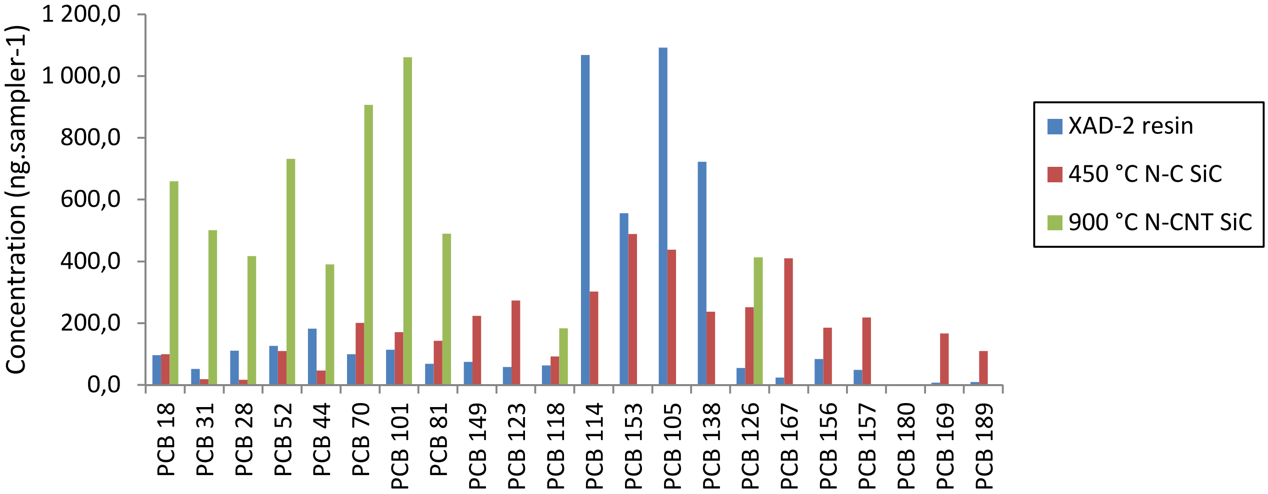


Figure 3-13 – PCB quantities detected in XAD®-2 resin and grafted SiC foams over one week

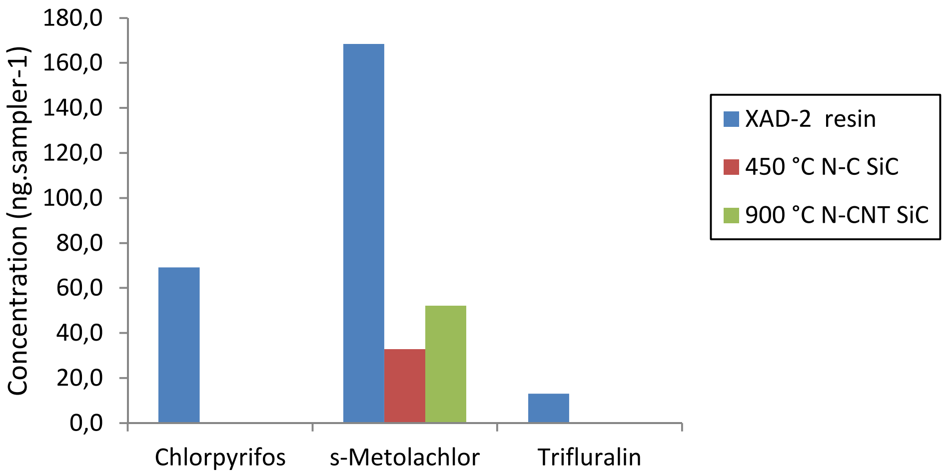


Figure 3-14 – GC pesticides quantities detected in XAD®-2 resin and grafted SiC foams over one week

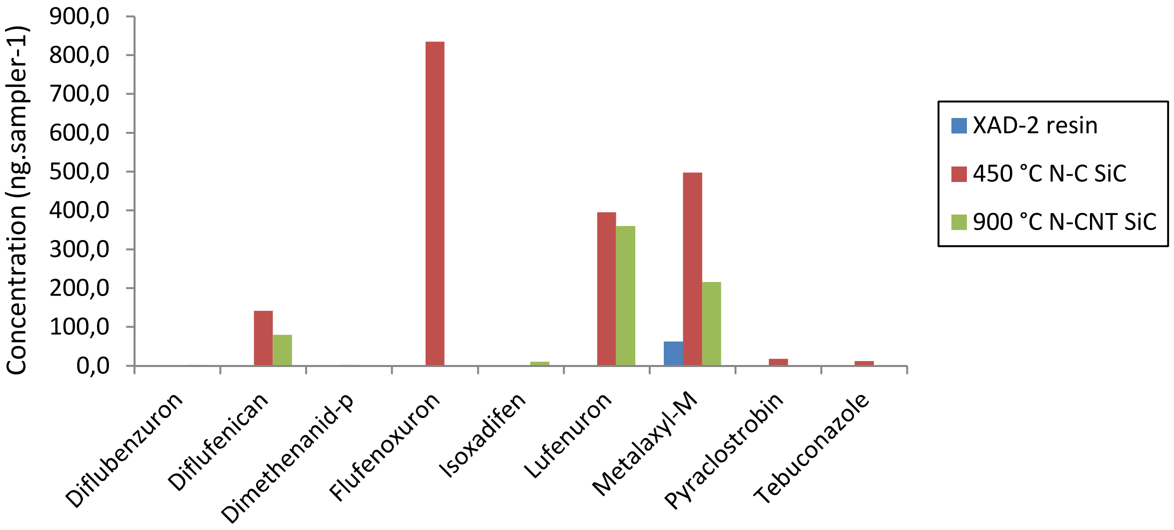


Figure 3-15 – LC pesticides quantities detected in XAD®-2 resin and grafted SiC foams over one week

As seen in the previous sampling weeks, XAD®-2 resin can adsorb the more volatile PAH and about every PCB. However, for both families of molecules, grafted SiC foams were more efficient. For volatile compounds, 900 °C N-CNT SiC foam adsorbed greater quantities than the resin (twice to six times more), and for heavier molecules 450 °C N-C SiC foam was the most efficient of the three. XAD®-2 resin may still be the best adsorbent for GC pesticides, though it is hard to conclude with so few detections. For LC pesticides, grafted SiC foams performed consistently better than XAD®-2 resin, with greater quantities detected for every pesticide.

It appears then that grafted SiC foam are more efficient adsorbents than both regular SiC foam and XAD®-2 resin. 450 °C N-C SiC foam seems to be the best overall, since there is no decrease in adsorption efficiency for heavier PAH and PCB like observed for 900 °C N-CNT SiC foam.

Discussion

Excellent results were obtained with 450 °C N-C SiC and 900 °C N-CNT SiC for every family of pollutant.

CNT are naturally hydrophobic, so N-CNT SiC is more hydrophobic than N-C SiC. This could explain the lack of detection of heavier PAH and PCB in N-CNT SiC: they have more affinity with this material and are more strongly retained on it, and so are difficult to extract. For lighter molecules, N-CNT SiC's high surface area allows it to adsorb important quantities of pollutants.

N-C SiC, being less hydrophobic than N-CNT SiC, is more suited to detecting LC pesticides, hence their good performance for adsorbing these compounds. 450 °C N-C SiC in particular was the most effective at detecting heavy PAH and LC pesticides. For other pollutants, its results were at least comparable to those of regular SiC foam, if not better.

The difference in results between 450 °C N-CNT SiC, which was very effective, and 900 °C N-CNT SiC, which detected next to no pollutants, can be explained by a difference in porosity. At 450 °C, only a part of the polymer used in the growth of CNT is burned, so the porosity is mostly closed. Air then flows around the foam rather than through it and only a few pollutants can be trapped. At 900 °C, the polymer is completely removed and the SiC foam regains an open porosity.

It is not known at the moment why 450 °C N-C SiC performed better than 900 °C SiC.

However, even in another context, when used as catalysts in the dehydrogenation of ethylbenzene to styrene, 450 °C N-C SiC and 900 °C N-CNT SiC performed better than 900 °C N-C SiC and 450 °C N-CNT SiC (source: Institute of Chemistry and Processes for Energy, Environment and Health). So these observations about 450 °C N-C SiC foam are not an isolated case.

In addition to performing as well as or better than regular SiC foam, grafted SiC foam proved to be more efficient adsorbents than XAD®-2 resin for all families of pollutants, with some uncertainty regarding volatile pesticides. For LC pesticides, grafted SiC foams are definitely the better adsorbents, as their results are up to ten times higher than the resin's. Regarding PAH and PCB, 450 °C N-C SiC in particular allows for a consistent detection over the whole range molecular masses. While it gives results comparable to XAD®-2 resin's for more volatile compounds, it is far more efficient than both XAD®-2 and 900 °C N-CNT SiC for heavier compounds.

In the end, 450 °C N-C SiC foam would be the preferred material, as there is no decrease in efficiency for higher molecular weight compounds. It gave some of the best results for every family of pollutants tested.

IV/ Second pesticides monitoring campaign – comparison between N-C SiC foam and N-CNT SiC foam

1. Context of the study

The second study made in collaboration with the ASPA was to test the best SiC foams, 450 °C N-C and 900 °C N-CNT, on a larger scale than the botanical garden.

For the ASPA, this campaign was still a part of the regional project on phytosanitary products, so for this campaign too the only pollutants analysed were pesticides. Like the results of the previous campaign, these results are confidential until approved by a regional council and will not be disclosed in this study.

Our goal was to compare the two grafted SiC foams, which will be referred to as simply N-C SiC and N-CNT SiC, and to determine their respective sampling rates by comparing said results with those of the active samplers.

2. Materials and methods

The campaign took place between April 8th 2015 and August 13th 2015, on four agricultural sites and an urban site. Four sites were the same as the previous campaign, but due to official demands, the market gardening site had to be put aside in favour of a second field crops site.

The sampling sites, placed on Figure 3-16 below, were as follows:

- Field crops site (1) – Ohnenheim, a village in the middle of Alsace, with wheat and maize crops
- Viticulture site (2) – Kintzheim, a village in the middle of Alsace
- Arboriculture site (3) – Sigolsheim, a village in the southern part of Alsace
- Field crops site (4) – Aspach-le-haut, a village in the south of Alsace
- Urban site (5) – Niederau, a school in the residential area Robertsau in Strasbourg

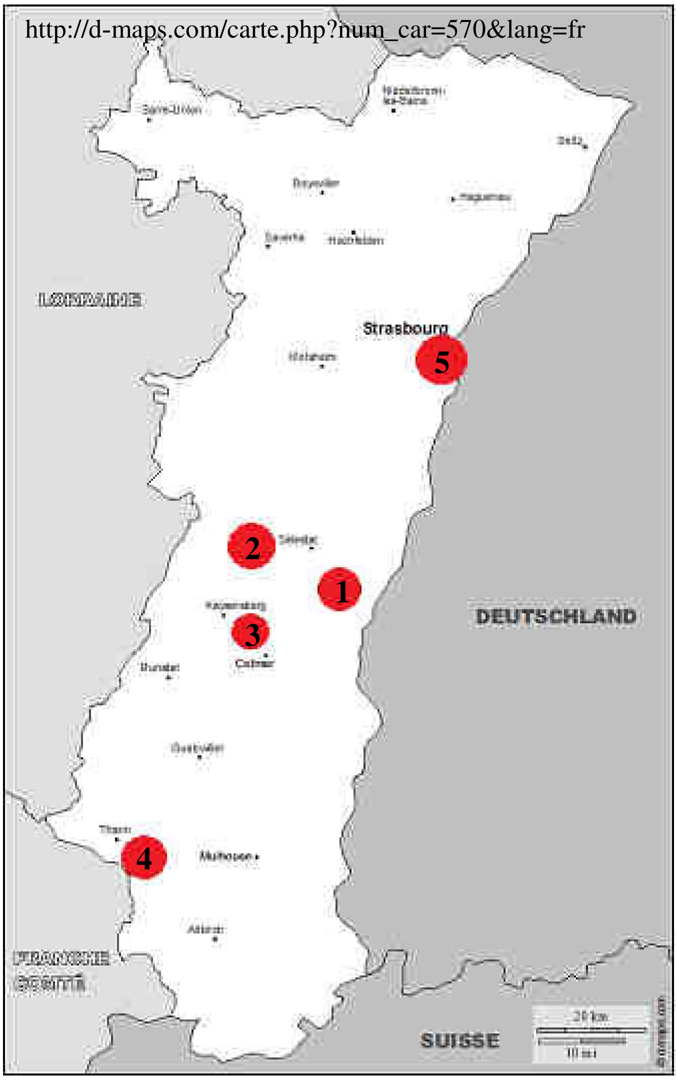

http://d-maps.com/carte.php?num_car=570&lang=fr

Figure 3-16 – Map situating the five sampling locations (2015)

Each site was sampled for five weeks, one week at a time. This totalled to 25 sampling periods. Each week, one N-C and one N-CNT SiC were placed close to the active sampler used by the ASPA. There were two kinds of active samplers this time, both low volume using PUF and GFF to collect pesticides. The two Partisol Plus samplers had a sampling rate of 1 m^3 h^{-1} while the two Leckel were pumping at 2.3 m^3 h^{-1}.

3. Results

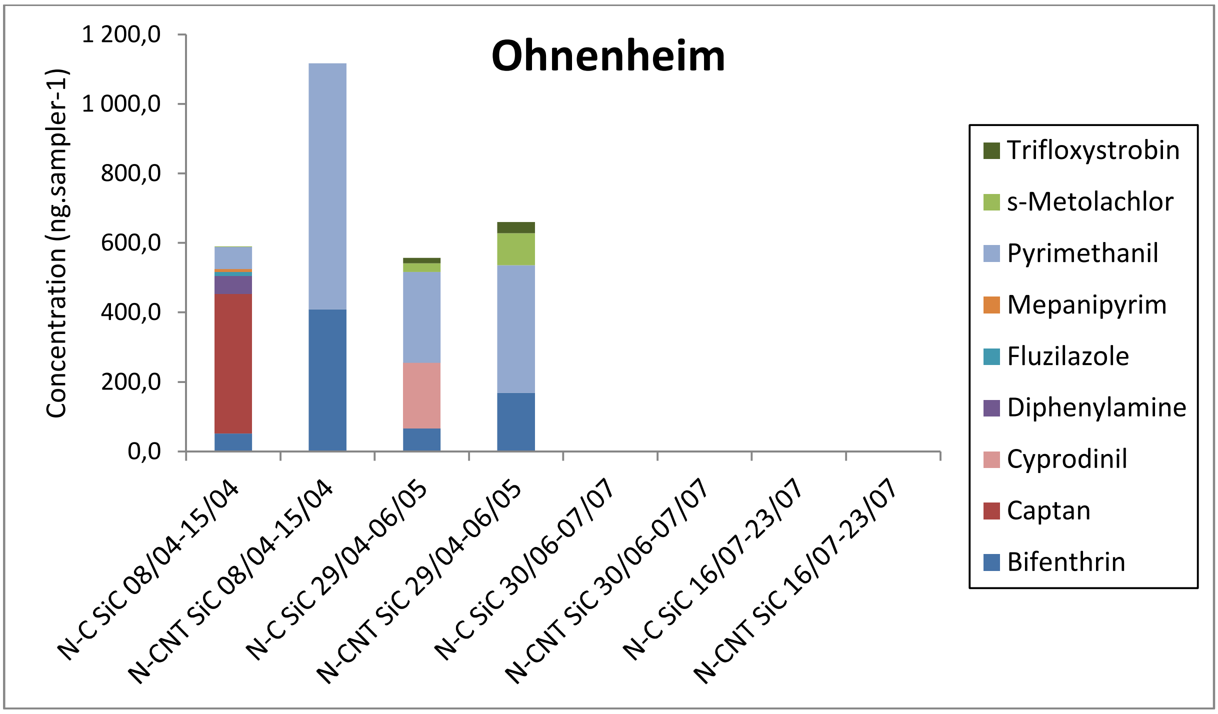
Due to scheduling changes, three sampling periods were missing passive samplers. One week is missing at Niederau between August 13th and August 20th, and two weeks at Sigolsheim: between June 16th and June 23th, and between July 16th and July 23th. This is why, instead of having 25 batches of results per matrix, there are only 22.

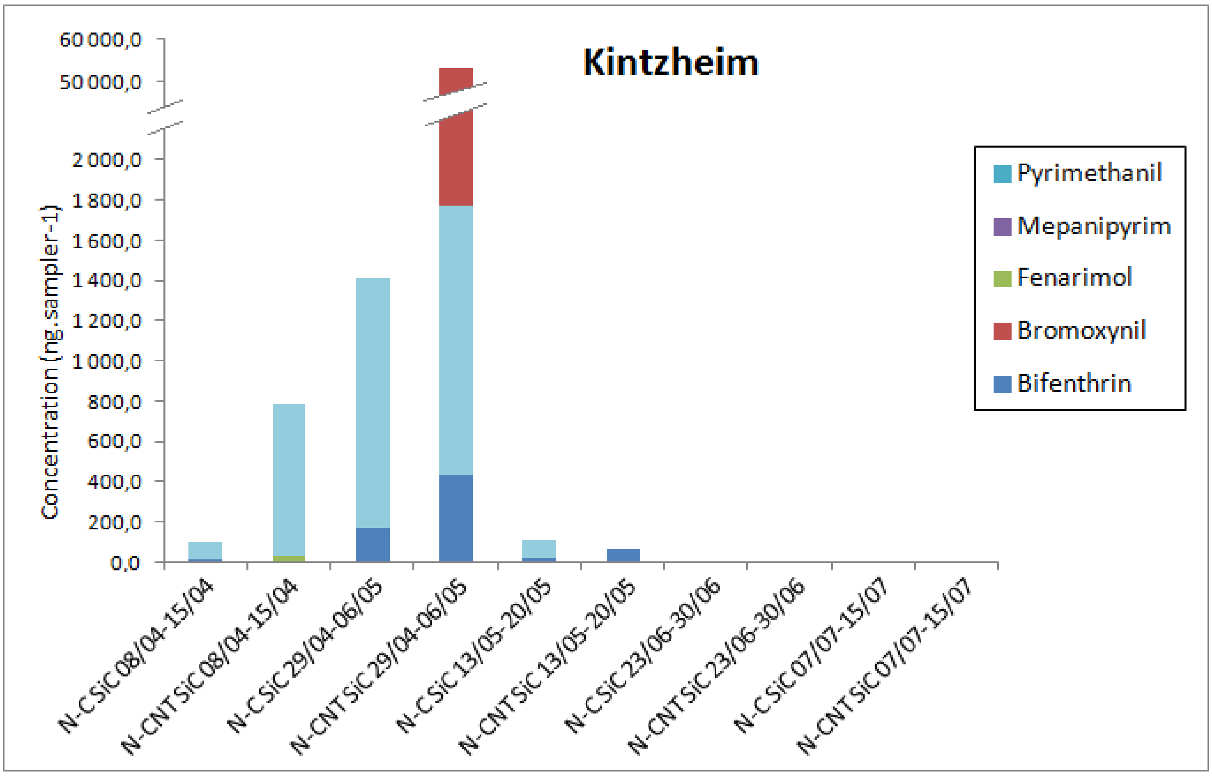
Moreover, due to technical problems, the N-C sample from Ohnenheim between May 13th and May 20th could not be analysed in GC. Therefore, only 21 GC batches can be compared.

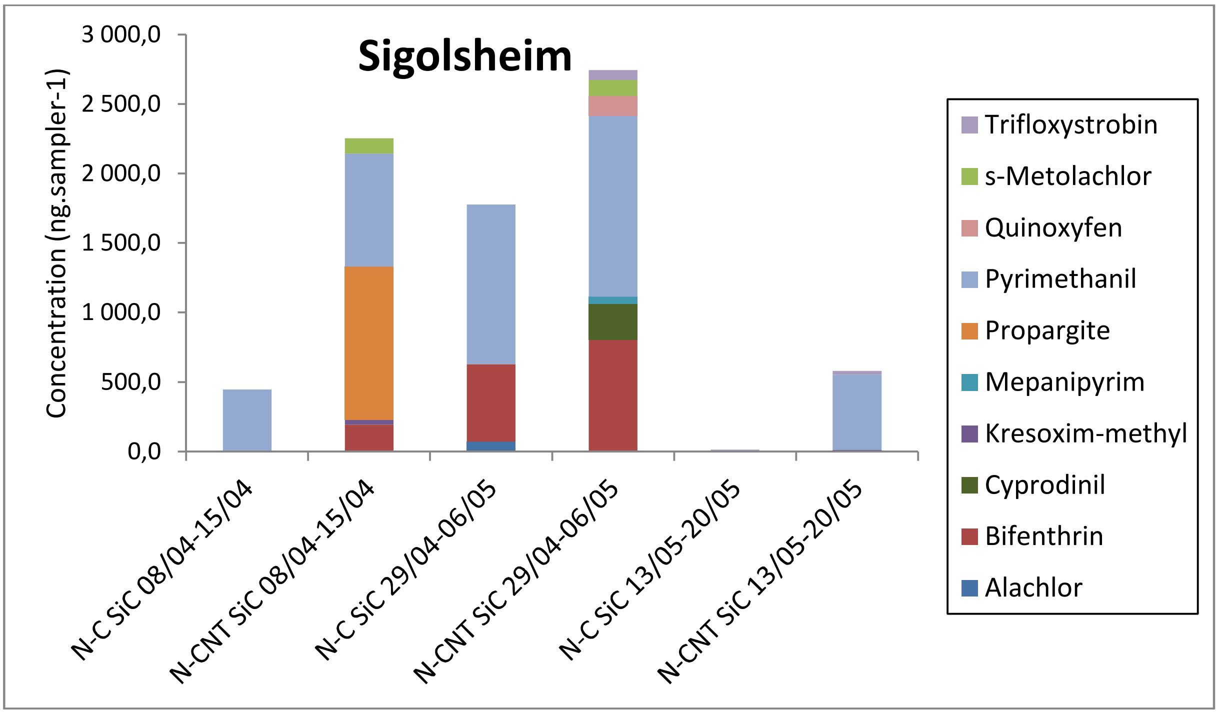
GC pesticides results

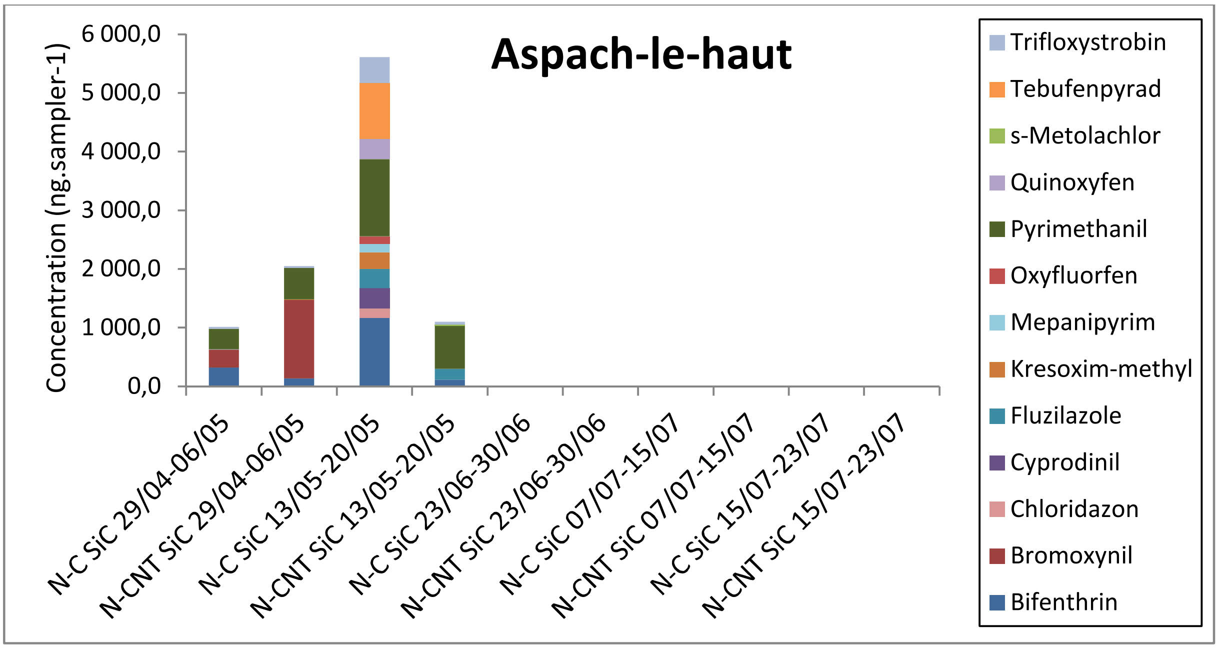
Thirty-one pesticides were detected and twenty-eight quantified over 16 of the 21 sampling week. All of them were detected at least once in N-C SiC while fourteen were in N-CNT SiC. But when a given pesticide was found in both foams, N-CNT had the highest quantity.

Results are summarized in the following graphs (Figure 3-17), site by site. A table with detailed results can be found in Annex V.






Sigolsheim
Concentration (ng.sampler-1)
3 000,0
2 500,0
2 000,0
1 500,0
1 000,0
500,0
0,0
N-C SiC 08/04-15/04
N-CNT SiC 08/04-15/04
N-C SiC 29/04-06/05
N-CNT SiC 29/04-06/05
N-C SiC 13/05-20/05
N-CNT SiC 13/05-20/05
Trifloxystrobin
s-Metolachlor
Quinoxyfen
Pyrimethanil
Propargite
Mepanipyrim
Kresoxim-methyl
Cyprodinil
Bifenthrin
Alachlor


Aspach-le-haut
Concentration (ng.sampler-1)
6 000,0
5 000,0
4 000,0
3 000,0
2 000,0
1 000,0
0,0
N-C SiC 29/04-06/05
N-CNT SiC 29/04-06/05
N-C SiC 13/05-20/05
N-CNT SiC 13/05-20/05
N-C SiC 23/06-30/06
N-CNT SiC 23/06-30/06
N-C SiC 07/07-15/07
N-CNT SiC 07/07-15/07
N-C SiC 15/07-23/07
N-CNT SiC 15/07-23/07
Trifloxystrobin
Tebufenpyrad
s-Metolachlor
Quinoxyfen
Pyrimethanil
Oxyfluorfen
Mepanipyrim
Kresoxim-methyl
Fluzilazole
Cyprodinil
Chloridazon
Bromoxynil
Bifenthrin

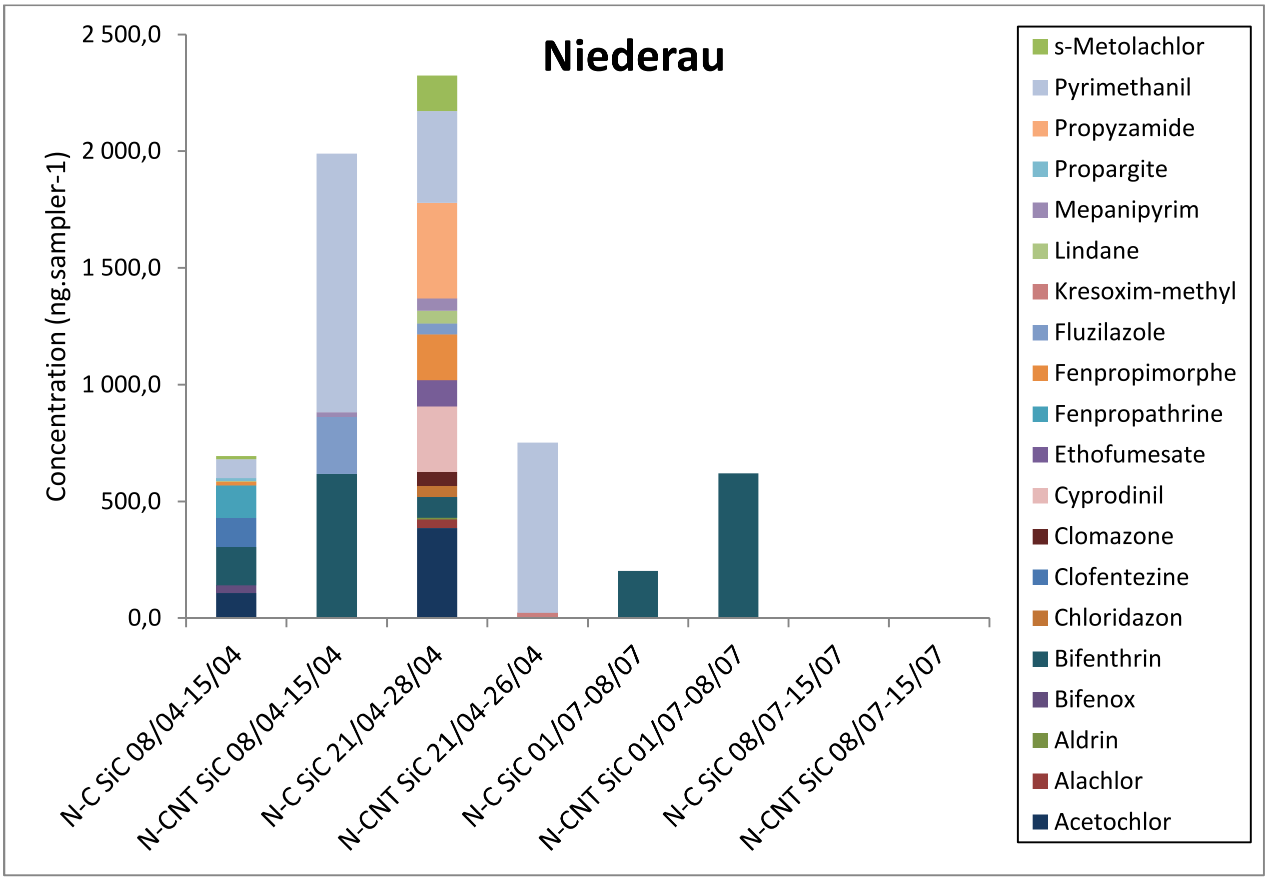


Figure 3-17 – Graphic results for GC pesticides site by site (2015)

Four pesticides were found on every site: bifenthrin, mepanipyrim, pyrimethanil and trifluralin.

Out of these, pyrimethanil is the most often detected pesticide with 22 detections, all quantified. It was also detected in the greatest quantities, between 63.7 and 1,333.8 ng sampler^{-1}. This can be explained by its numerous uses in market gardening, arboriculture and viticulture. Pyrimethanil is extensively used on vineyard, which is one of the dominant cultures in Alsace. It makes sense, then, that pyrimethanil could be transported to several different places. Mepanipyrim is a fungicide authorised on strawberry crops and vineyards, also making it an ubiquitous pesticide. However, mepanipyrim is used in lower quantities and on fewer cultures than pyrimethanil, explaining the fewer detections (12 detections and 6 quantifications).

Bifenthrin and trifluralin, however, are both prohibited in France. Trifluralin has been banned since 2008. However, it was extensively used for weeding colza crops, which are present throughout Alsace, so it is possible there are still persistent remnants in soil. In this study, trifluralin has been detected 11 times in quantities always inferior to its quantification limit of 5.4 ng sampler^{-1}, so these may be traces of past use. Bifenthrin is an insecticide whose prohibition is more recent. It was banned as a phytosanitary product in 2010, but its use as a biocide was authorised until the end of 2013. This double usage might explain why it was detected in considerable quantities, between 14.7 and 1,165.4 ng sampler^{-1}. Moreover, since private individuals had access to bifenthrin through insecticide bombs, it might have been used even past its interdiction.

s-Metolachlor was found in four out of five sites, which was expected due to its extensive use as a herbicide for wheat and maize. The same observation was made for kresoxim methyl, a fungicide used for field crops, arboriculture and viticulture.

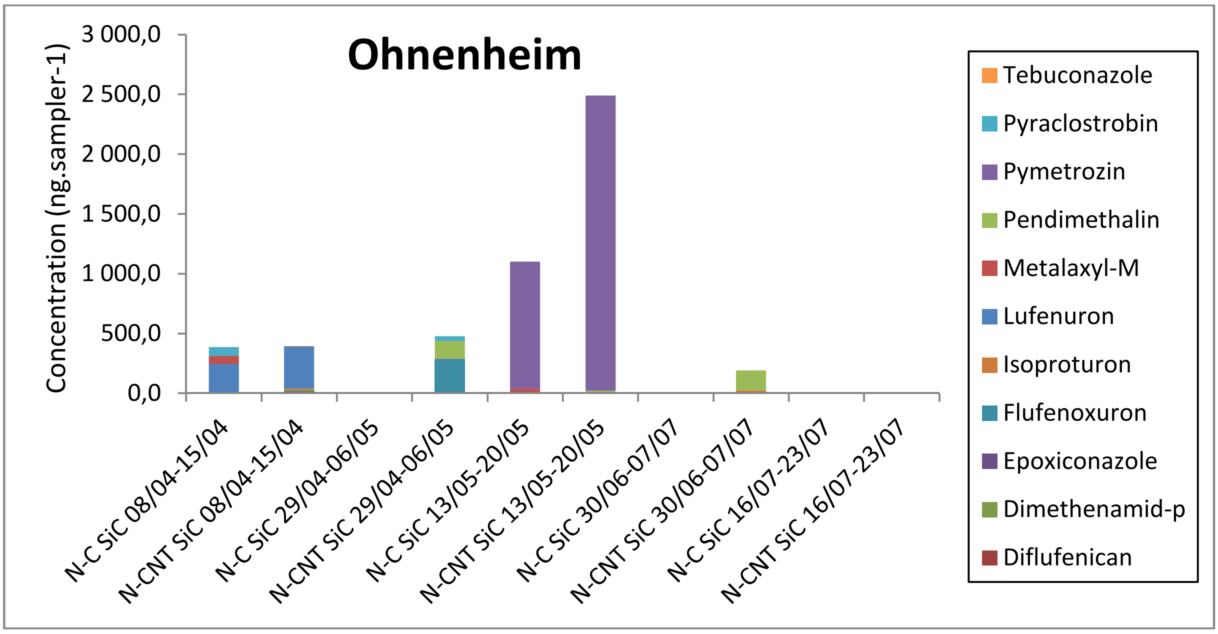
There is a noticeable lack of pesticides detection in July. This month was particularly rainy, which has two consequences on pesticides. First, farmers do not treat their fields during heavy rain, resulting in a lack of pesticides in the air. Second, rain washes down airborne pesticides, resulting in their adsorption in soil or their trickling to underground water. In both cases, pesticides have left the air compartment and cannot be detected.

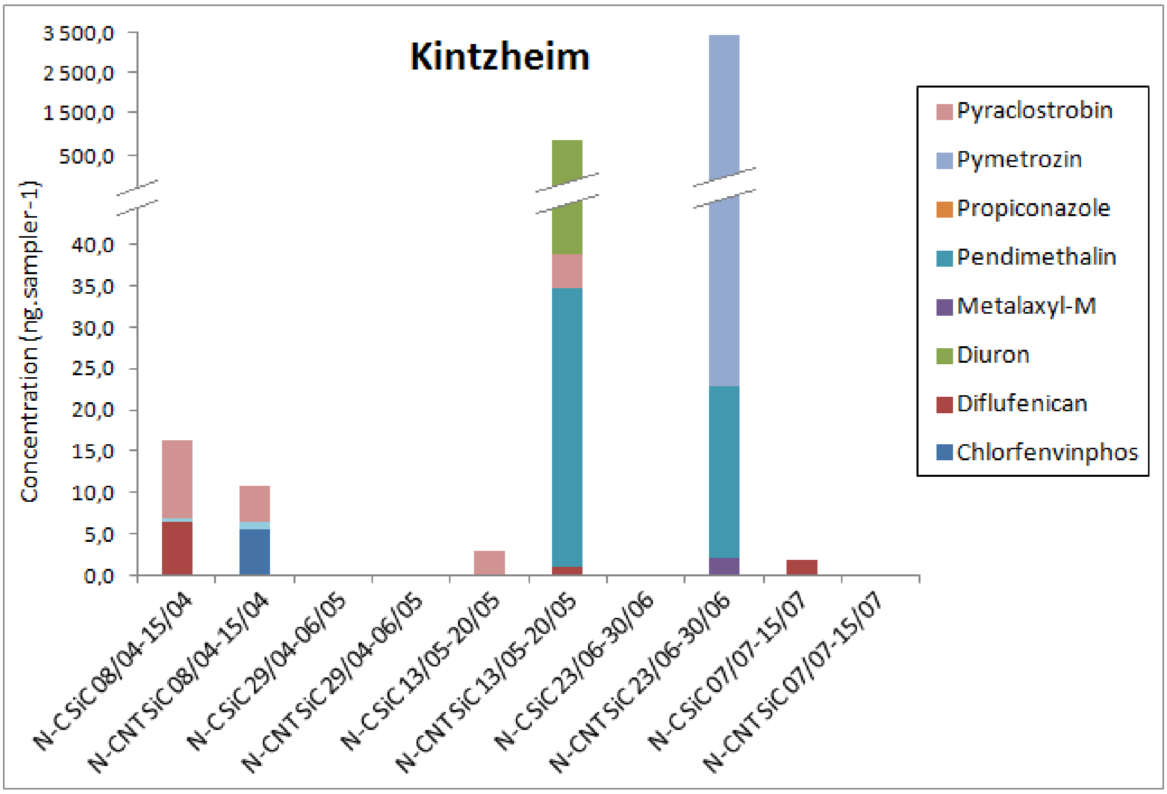
Over the sampling period, there were 90 detections and 65 quantifications in N-C SiC against 54 detections and 44 quantifications in N-CNT SiC. While this comparison favours N-C SiC, N-CNT SiC usually gave higher quantities. Out of 31 times when the same pesticide was detected at the same place and time in both samplers, N-CNT SiC had a higher quantity than N-C 24 times (77 % of results). This observation is coherent with previous results that showed N-CNT can adsorb greater quantities than N-C SiC due to the CNT's high specific surface area. It is however less effective for particulate or polar compounds and is more difficult to extract, so N-C SiC would be preferred as the most versatile material.

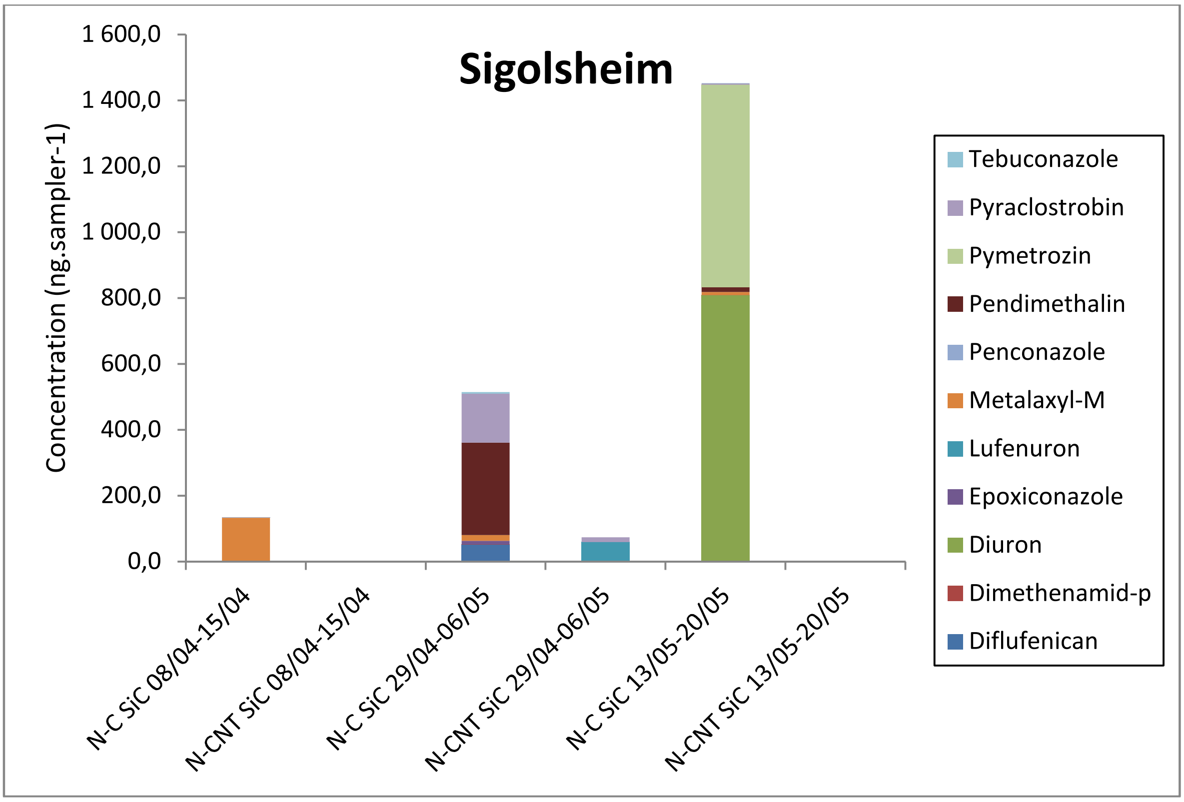
LC pesticides results

Twenty-one LC pesticides were detected over 20 of the 22 sampling weeks. Seventeen were detected at least once in N-C SiC and sixteen in N-CNT SiC. There was an equal amount of detections on both foams, and quantities adsorbed were close to each other, despite N-C SiC having higher quantities more often.

Results are summarized in the following graphs (Figure 3-18), site by site. A table with detailed results can be found in Annex V.




Kintzheim
Concentration (ng.sampler-1)
3 500,0
2 500,0
1 500,0
500,0
40,0
35,0
30,0
25,0
20,0
15,0
10,0
5,0
0,0
N-C SiC 08/04-15/04
N-CNT SiC 08/04-15/04
N-C SiC 29/04-06/05
N-CNT SiC 29/04-06/05
N-C SiC 13/05-20/05
N-CNT SiC 13/05-20/05
N-C SiC 23/06-30/06
N-CNT SiC 23/06-30/06
N-C SiC 07/07-15/07
N-CNT SiC 07/07-15/07
Pyraclostrobin
Pymetrozin
Propiconazole
Pendimethalin
Metalaxyl-M
Diuron
Diflufenican
Chlorfenvinphos


Sigolsheim
Concentration (ng.sampler-1)
1 600,0
1 400,0
1 200,0
1 000,0
800,0
600,0
400,0
200,0
0,0
N-C SiC 08/04-15/04
N-CNT SiC 08/04-15/04
N-C SiC 29/04-06/05
N-CNT SiC 29/04-06/05
N-C SiC 13/05-20/05
N-CNT SiC 13/05-20/05
Tebuconazole
Pyraclostrobin
Pymetrozin
Pendimethalin
Penconazole
Metalaxyl-M
Lufenuron
Epoxiconazole
Diuron
Dimethenamid-p
Diflufenican

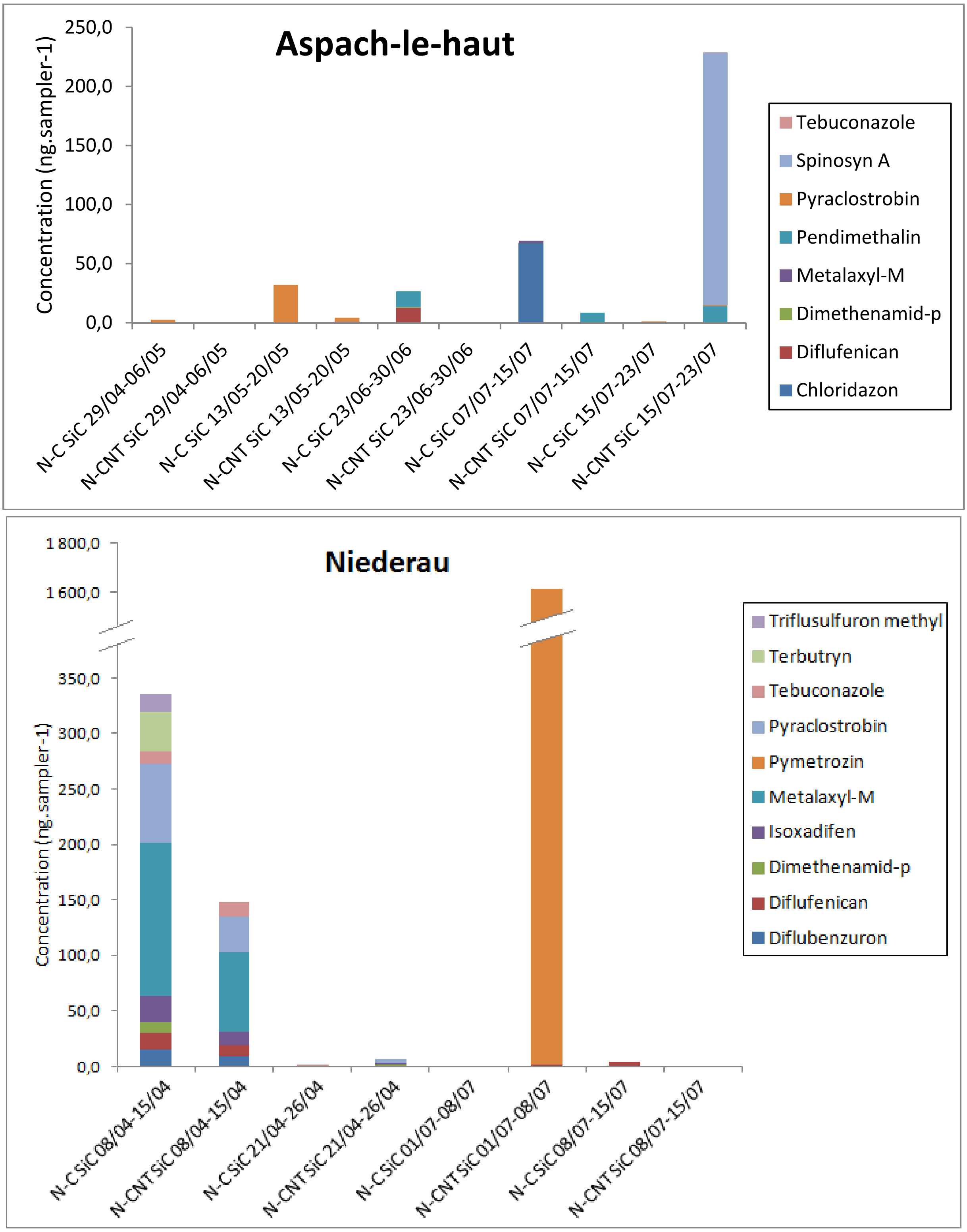


Figure 3-18 – Graphic results for LC pesticides site by site (2015)

Three pesticides were found on every site: diflufenican, metalaxyl-M and pyraclostrobin. Diflufenican is a herbicide used on wheat, ornamental trees, and is available to private individuals. It is a versatile pesticide that can understandably be found in very different places. The latter two are fungicides used for treating market gardens, field crops and vineyards, meaning they can be found in a wide variety of sampling sites.

The two pesticides detected in highest quantities are diuron (808.0 and 846.7 ng sampler^{-1}) and pymetrozin (between 614.6 and 3498.8 ng sampler^{-1}). Detected diuron quantities seem improbably high, given that this pesticide is prohibited in France. Since 2007 products containing diuron cannot be manufactured or sold in France, though stocks could be used until mid-2008. It is a herbicide that used to be used in viticulture, private garden and on roads to remove unwanted grasses, so it is possible to find traces of this pesticide in a wide range of sampling sites. In this study, diuron was detected the same week in Sigolsheim, the arboriculture site, and Kintzheim, the viticulture site. While it is possible that diuron was present at these sites, there may have been a bias during analysis that increased the calculated quantities. Pymetrozine is an insecticide used to protect fruits and vegetables, ornamental trees and flowers. Its presence in Ohnenheim, Kintzheim and Sigolsheim could be due to the treatment of the villages' greenery, though quantities are especially high. The Niederau school, however, is in Strasbourg, which is a "zero pesticides" area. It is unlikely that such an important quantity of was transported from neighbouring villages, but this factor may have contributed to the total.

Over the course of the campaign, pesticides were detected 49 times and quantified 48 times in N-C SiC against 50 detections and 47 quantifications in N-CNT SiC. The difference in quantities adsorbed was also minimal. Out of 17 detections of the same pesticide at the same place and time, N-C SiC had a higher quantity than N-CNT SiC 11 times (65 % of results).
These LC pesticides are heavier and less volatile than those analysed by GC, so there is a higher probability of them being particulate instead of gaseous. Since N-C SiC and N-CNT SiC have the same structure with large pores, they are equally able to collect these particles. The difference between the two samplers is probably N-CNT SiC's hydrophobicity, which reduces its affinity with the pesticides. So for these pesticides too N-C SiC foam would be the material of choice.

Sampling rates

Sampling rates were calculated when the same pesticide was detected at the same time and the same place in a passive and active sampler. Six pesticides were eligible for comparison; seven sampling rates were calculated for N-C SiC and eleven for N-CNT SiC. They are summarised in Tables 3-6 and 3-7, including the date, place and pesticide used for the calculations:

Table 3-6 – N-C SiC sampling rates in m^3 d^{-1}

Pesticides	Niederau 08/04-15/04	Ohnenheim 08/04-15/04	Sigolsheim 29/04-06/05	Ohnenheim 29/04-06/05	Sigolsheim 13/05-20/05	Aspach-le-haut 23/06-30/06
Lindane	0.84					
s-Metolachlor		0.39		0.28		
Dimethenamid-p			1.77			0.98
Pendimethalin			81.80		9.97	

Table 3-7 – N-CNT SiC sampling rates in m^3 d^{-1}

Pesticides	Sigolsheim 08/04-15/04	Ohnenheim 08/04-15/04	Sigolsheim 29/04-06/05	Ohnenheim 29/04-06/05	Aspach-le-haut 13/05-20/05
Cyprodinil			331.73		
Kresoxim-methyl					
s-Metolachlor	196.76		4.36	0.99	5.71
Dimethenamid-p		1.40			
Pendimethalin				5.49	
Pesticides	**Sigolsheim 13/05-20/05**	**Ohnenheim 13/05-20/05**	**Kintzheim 13/05-20/05**	**Ohnenheim 30/06-07/07**	
Cyprodinil					
Kresoxim-methyl	7.11				
s-Metolachlor					
Dimethenamid-p					
Pendimethalin		30.04	2.45	31.02	

Two values for N-CNT SiC were way higher than expected: 196.76 and 331.73 m^3 d^{-1} are higher sampling rates than even a low-volume active sampler. These may be due to the difference in surface are between PUF and N-CNT SiC, as discussed in I.3: N-CNT SiC can adsorb greater quantities than PUF, so it is possible that the PUF was saturated before the SiC foam. The comparison would then artificially boost calculated rates.
Some of the values calculated for pendimethalin on both samplers were also too high for passive samplers: 81.80, 30.04 and 31.02 ng sampler^{-1}. Since they all concern the same pesticide, the reason could be tied to the analytical process, leading to overestimation of the quantities on our side or underestimation on the other laboratory's side.

Outside of these high values, calculated sampling rates ranged from 0.28 to 9.97 m^3 d^{-1} for N-C SiC and from 0.99 to 7.11 m^3 d^{-1} for N-CNT SiC. These values can be compared to the sampling rates calculated in previous years, summarised in Table 3-8.

Table 3-8 – Grafted SiC's sampling rates compared to other adsorbents and the litterature

	N-C SiC 2015	N-CNT SiC 2015	Regular SiC 2014	XAD®-2 2014	XAD®-2 2013	XAD®-2 literature*
Minimum	0.28	0.99	0.08	0.43	0.66	0.60
Maximum	9.97	7.11	5.82	4.91	6.14	3.70
Average	2.37	3.93	2.33	2.32	3.23	2.78
Median	0.91	4.36	1.45	2.14	3.76	2.75

* Wania et al., 2003 ; Gouin et al., 2008b ; Xiao-Ping et al., 2010

N-C SiC, despite having the highest maximum sampling rate, had overall low results and is best compared to the regular SiC foam used in 2014. N-CNT SiC, on the contrary, consistently had the highest results. Since it has been shown that this material is a better adsorbent than other SiC foams and XAD®-2 resin, it would make sense that the difference between PUF and N-CNT SiC would be greater than between PUF and other material. This difference would then artificially increase N-CNT SiC's sampling rates. Despite this drawback, results were still in the same range as the other materials'.

V/ Conclusion

The first ASPA campaign allowed several observations to be made. XAD®-2 resin is more efficient than SiC foam for gaseous compounds. However, SiC foam can adsorb these too and has several other advantages. As seen with GC pesticides, SiC foam can better adsorb polar compounds due to its lower hydrophobicity. Its porosity also allows it to trap less volatile compounds, which was observed for both GC and LC pesticides.

Further comparing these two samplers by additionally monitoring PAH and PCB confirmed these observations. It was especially striking for PAH, the heavier of which were poorly detected by XAD®-2 resin. While the resin's hydrophobicity could mean that these PAH are not well extracted from it, the particulate nature of these compounds means that they probably were not trapped in the XAD®-2 sampler in the first place. No such problem was encountered with SiC foam. Surprisingly, both samplers gave comparable results for PCB.

All in all, while XAD®-2 resin can be useful in specific cases, SiC foam is usually an equal, if not a superior alternative for a wide range of atmospheric pollutants.

Introducing grafted SiC further improved the performances of SiC foam by negating its main weakness – its surface area.

When comparing these grafted SiC foams to regular SiC and XAD®-2 resin, they performed best for all families of pollutants. When monitoring PAH and PCB, 900 °C N-CNT SiC performed consistently better than any other adsorbent for volatile molecules, but quantities detected quickly decrease for heavier compounds. This is due to the CNT's hydrophobicity that makes it difficult to extract hydrophobic compounds. For this reason, 450 °C N-C SiC was the adsorbent of choice for PAH and PCB: while detecting lesser quantities than N-CNT SiC for the most volatile compounds, it quickly became the most efficient adsorbent, performing as well as or better than regular SiC foam.

For LC pesticides, no decrease was observed in the efficiency of 900 °C N-CNT SiC, which gave results comparable to 450 °C N-C SiC. These results are higher than those of regular SiC foam and XAD®-2 resin for all pesticides.

When 450 °C N-C SiC and 900 °C N-CNT SiC were compared during a longer sampling campaign, a trend was noticed where N-CNT SiC foam, with its higher surface area, could adsorb greater quantities of GC pesticides. Both foams gave similar results for LC pesticides due to them having the same physical structure suited to collecting particles. However, N-C SiC foam's lower hydrophobicity allowed it to adsorb a wider range of GC pesticides and to have a greater affinity with LC pesticides.

In the end, grafted SiC foams have proven to be more efficient than the common XAD®-2 resin and the regular SiC foam. 450 °C N-C SiC foam especially is the adsorbent of choice over 900 °C N-CNT foam due to its consistent detection of every family of pollutants over the whole range of molecular weights. Its lesser hydrophobicity is also an advantage when adsorbing pesticides, that have a wider range of polarity than PAH and PCB.

References

Armstrong J. L., Fanske R. A., Yost M. G., Tchong-French M., Yu J., **2013**, “Comparison of polyurethane foam and XAD®-2 sampling matrices to measure airborne organophosphorous pesticides and their oxygen analogs in an agricultural community”, *Chemosphere*, *92*, 451-457

Association française de normalisation (2007). *Air ambiant – Dosage des substances phytosanitaires (pesticides) dans l’air ambiant – Prélèvement actif.* Norme XP X 43-058. La Plaine Saint-Denis : Association française de normalisation.

Dobson R., Scheyer A., Rizet A-L., Mirabel P., Millet M., **2006**, “Comparison of the efficiencies of different types of adsorbents at trapping currently used pesticides in the gaseous phase using the technique of high-volume sampling”, *Analytical and Bioanalytical Chemistry*, *386*, 1781-1789

DREAL, **2012**, 2^{e} Plan régional 2011>2015 (Report)

Eng A., Harner T., Pozo K., *Environmental Science & Technology Letters*, **2014**, “A prototype passive air sampler for measuring dry deposition of polycyclic aromatic hydrocarbons”, *1*, 77-81

Gouin T., Harner T., Blanchard P., Mackay D., **2005**, “Passive and active air samplers as complementary methods for investigating persistent organic pollutants in the Great Lakes Basin”, *Environmental Science & Technology*, *39*, 9115-9122

(a) Gouin T., Shoeib M., Harner T., **2008**, “Atmospheric concentrations of current-use pesticides across south-central Ontario using monthly-resolved passive air samplers”, *Atmospheric Environment*, *42*, 8096-8104

(b) Gouin T., Wania F., Ruepert C., Castillo L. E., **2008**, “Field testing passive air samplers for current use pesticides in a tropical environment”, *Environmental Science & Technology*, *42*, 6625-6630

Guéguen F., Stille P., Millet M., **2013**, “Persistent organic pollutants in the atmosphere from urban and industrial environments in the Rhine Valley: PCB, PCDD/Fs”, *Environmental Science and Pollution Research*, *20*, 3852-3862

Harner T., Shoeib M., Diamond M., Stern G., Rosenberg B., **2004**, “Using passive air samplers to assess urban-rural trends for persistent organic pollutants.” 1. Polychlorinated biphenyls and organochlorine pesticides", *Environmental Science & Technology*, *38*, 4474-4483

Hayward S. J., Gouin T., Wania F., "Comparison of four active and passive sampling techniques for pesticides in air", *Environmental Science & Technology*, **2010**, *44*, 3410-3416

Jaward F. M., Farrar N. J., Harner T., Sweetman A. J., Jones K. C., **2004**, "Passive air sampling of PCB, PBDEs, and organochlorine pesticides across Europe", *Environmental Science & Technology*, *38*, 34-41

Persoon C., Hornbuckle K.C., **2009**, "Calculation of passive sampling rates from both native PCB and depuration compounds in indoor and outdoor environments", *Chemosphere*, *74*, 917-923

Pozo K., Harner T., Shoeib M., Urrutia R., Barra R., Parra O., Focardi S., **2004**, "Passive-sampler derived air concentrations of persistent organic pollutants on a North-South transect in Chile", *Environmental Science & Technology*, *38*, 6529-6537

Schummer C., Mothiron E., Appenzeller B. M. R., Rizet A-L., Wennig R., Millet M., **2010**, "Temporal variations of concentrations of currently used pesticides in the atmosphere of Strasbourg, France", *Environmental Pollution*, *158*, 576-584

Schummer C., Tuduri L., Briand O., Appenzeller B. M., Millet M., **2012**, "Application of XAD-2 resin-based passive samplers and SPME-GC-MS/MS analysis for the monitoring of spatial and temporal variations of atmospheric pesticides in Luxembourg", *Environmental Pollution*, *170*, 88-94

University of Hertfordshire, **2007**, *Pesticide Properties DataBase* [Online] Available at http://sitem.herts.ac.uk/aeru/ppdb/en/index.htm [Accessed September 2014]

Waite D. T., Droneck N. R., Tuduri L., Sproull J. F., Chau D. F., Quiring D.V., **2007**, "Comparison of active versus passive atmospheric samplers for some current-use pesticides", *Bulletin of Environmental Contamination and Toxicology*, *74*, 1011-1018

Wania F., Shen L., Duan Lei Y., Teixeira C., Muir D. C. G., **2003**, "Development and calibration of a resin-based passive sampling system for monitoring persistent organic pollutants in the atmosphere", *Environmental Science & Technology*, *37*, 1352-1359

Xiao-Ping W., Ping G., Tan-Dong Y., Jones K.C., **2010**, "Passive air sampling of organochlorine pesticides, polychlorinated biphenyls, and polybrominated diphenyl ethers across the Tibetan plateau", *Environmental Science & Technology*, *44*, 2988-2993

Chapter 4: Calculating sampling rates

I/ Introduction: Calculation methods

Passive air sampling is an efficient way of monitoring atmospheric pollutants, but its major drawback compared to active sampling is the lack of information regarding the volume of air sampled.

1. Comparing active and passive samplers

Active samplers use a pump to regulate the flow of air passing through the adsorbent. A fixed, known amount of air is sampled over a certain amount of time, which allows for direct calculation of pollutants concentration in air.

Passive samplers let air diffuse freely through the adsorbent, and in the end pollutants quantities cannot be expressed as air concentrations. Passive sampling results are often qualitative, being expressed in nanograms of pollutants, or nanograms of pollutants per gram of adsorbent. However, there are ways of determining a passive sampler's sampling rate, expressed in cubic metres of air per day. Using this number, air concentrations can be calculated as follows (Persoon & Hornbuckle, 2009):

$$\mathrm{C_{air}} = \frac{\mathrm{M_{PAS}}}{\mathrm{SR} \times \mathrm{t}} \qquad (\mathrm{Eq.\,1})$$

C_{air}: air concentration of a given pollutant, in ng m^{-3}
M_{PAS}: mass of said pollutant in the passive air sampler, in ng
SR: sampling rate, in m^3 d^{-1} or m^3 h^{-1}
t: sampling duration, in days (d) or hours (h)

The most direct method of determining a passive sampler's sampling rate is to compare its results with those of an active sampler (Hazrati & Harrad, 2007 ; Klánová et al., 2008).

If both samplers monitor the same pollutants at the same place and time, using the concentrations given by active sampling and the quantities found with passive sampling, the amount of air that must have passed through the passive sampler can be estimated. The following equation (Eq. 2) is used, obtained by rearranging Eq.1:

$$\mathrm{SR} = \frac{\mathrm{M_{PAS}}}{\mathrm{C_{air}} \times \mathrm{t}} \qquad (\mathrm{Eq.\,2})$$

SR: sampling rate, in m^3 d^{-1} or m^3 h^{-1}
M_{PAS}: mass of a given pollutant in the passive air sampler, in ng
C_{air}: air concentration of said pollutant, found by active sampling, in ng m^{-3}
t: sampling duration, in days (d) or hours (h)

However, there are concerns that the comparison is not always accurate when using high-volume active samplers (HVS), due to the difference in sampling duration and air volume sampled (Persoon & Hornbuckle, 2009). Indeed, the sampling rates of HVS range from 15 to 30 $m^3 h^{-1}$, meaning these samplers are most often used over the course of a day (Association française de normalisation, 2007). Such a short time is not enough for passive samplers to accumulate a detectable amount of pollutants.

This is why the present study always used low-volume active samplers (LVS), with sampling rates ranging from 1.0 to 2.3 $m^3 h^{-1}$. LVS are used for sampling over a week or two (Association française de normalisation, 2007), which is enough for passive samplers to accumulate pollutants. The two can then be safely compared.

2. Depuration compounds

Another method exists to calculate a passive sampler's sampling rate, one that does not rely on active samplers. It is based on the use of depuration compounds.

Depuration compounds (DC) are compounds that are not found in the atmosphere, often deuterated ones, that are spiked in the sampler before a sampling campaign. Over the course of the campaign, the rate at which DC quantity decreases is equal to the uptake rate of pollutants by the passive sampler.

They can be used as a kind of internal standard when comparing passive and active samplers, because while active samplers have a constant sampling rate, passive samplers are influenced by meteorological parameters, particularly wind (Tuduri et al., 2006). It has been showed by Meockel et al. (2009) that on windy days the passive samplers' uptake rate is higher than usual. This phenomenon is explained by the laminar air layer between the adsorbent and ambient air, which grows thinner when winds are strong, meaning faster adsorption kinetics. While protection housings dampen the effect of wind (Tuduri et al., 2006), using DC allows these variations to be accounted for when estimating air concentrations of pollutants.

It has been noted that when using DC, only those with losses between 20 and 80 % should be taken into account so the loss cannot be attributed to analytical uncertainty (Moeckel et al., 2009).

One drawback of DC is that they do not accurately represent the behaviour of particulate compounds (Tuduri et al., 2012). Equations based on DC loss were developed with volatile compounds in mind, so caution has to be taken when applying them to heavier pollutants (Shoeib & Harner, 2002). It has been showed by Klánová et al. (2008) that particles have lower sampling rates than gaseous compounds, but this may be in part due to the sampler's housing that acts as a barrier between particulate compounds and the adsorbent.

While the commonly-used tube housing is used for SiC foam, this material is made to be able to collect particles, so differences in sampling rates with the literature are expected.

The equation linking DC loss and sampling rate is as follows (Moeckel et al., 2009, Tuduri et al., 2012):

$$\mathrm{SR} = \frac{-\ln\frac{\mathrm{C_{DC}}}{\mathrm{C_{DC,0}}} \times \mathrm{K_{PAS-A}} \times \rho_{\mathrm{PAS}} \times \mathrm{V_{PAS}}}{\mathrm{t}} \qquad (\mathrm{Eq.}\,3)$$

SR: sampling rate in $m^3\ d^{-1}$ or $m^3\ h^{-1}$
C_{DC}: concentration of a depuration compound in the passive sampler at the end of the sampling period in ng $sampler^{-1}$
$C_{DC,0}$: concentration of a depuration compound in the passive sampler at the beginning of the sampling period in ng $sampler^{-1}$
$K_{PAS\text{-}A}$: a given pollutant's passive sampler/air partition coefficient in $m^3\ g^{-1}$
ρ_{PAS}: bulk density of the passive sampler in $g\ m^{-3}$
V_{PAS}: volume of the passive sampler in m^3
t: sampling period in days (d) or hours (h)

This equation is a valid estimation of SR when the adsorption on the sampler is still in the linear phase (Shoeib & Harner, 2002 ; Persoon & Hornbuckle, 2009).
According to passive air sampling theory (Bartkow et al., 2005), there are three stages of adsorption on the samplers: linear, curvilinear and equilibrium (Figure 4-1). Only during the linear phase is the loss rate of DC equal to the uptake rate of atmospheric pollutants; this has been verified by Persoon & Hornbuckle (2009).

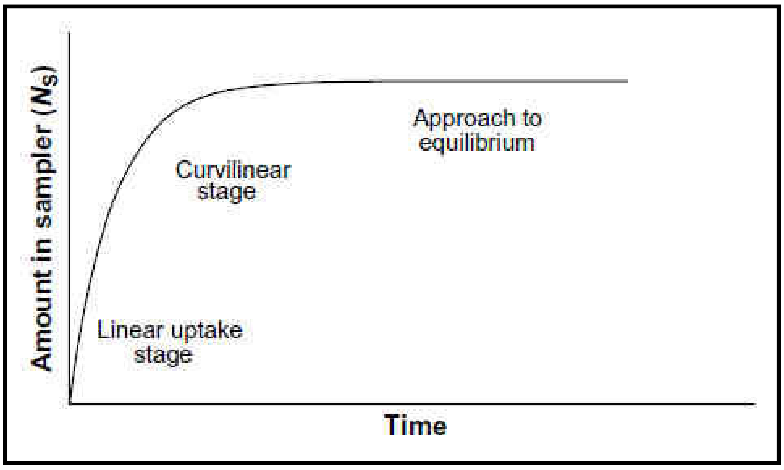


Figure 4-1 – The three stages of adsorption in a passive air sampler, from Bartkow et al. (2005)

For passive samplers, attaining equilibrium can take months (Tuduri et al., 2012). The actual time can vary between samplers depending on their adsorption capacity.
It has been reported that PUF can still be in the linear phase after 28 days when monitoring PAH, PCB and OCP (Klánová et al., 2008). SiC foams used in this study have a greater adsorption capacity than PUF, and when spiked with DC they were placed outside for no longer than 35 days, so they should be in the linear adsorption phase.

Time to reach equilibrium also depends on the characteristics of the pollutants considered. For instance, the smaller their K_{OA}, the faster they reach equilibrium. This is shown on Figure 4-2, though these particular curves were drawn for polymer-coated glass samplers. The time to reach equilibrium might differ on other matrices.

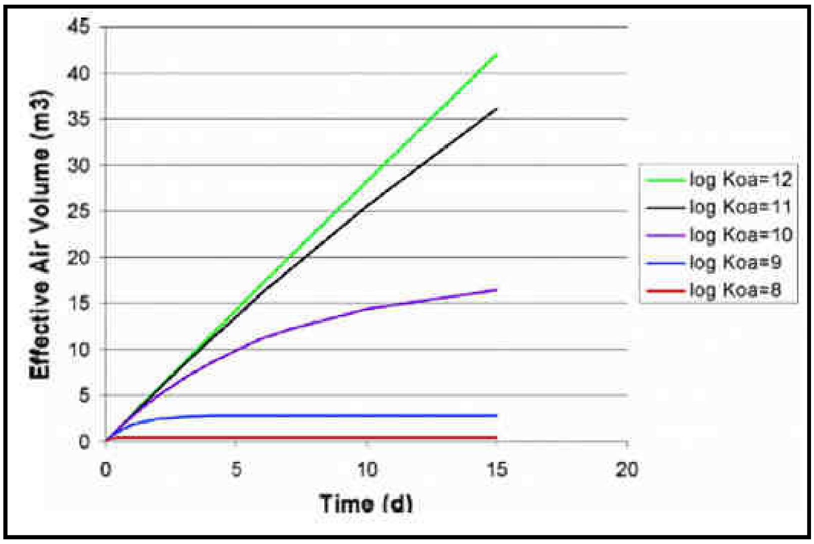


Figure 4-2 – Time to reach equilibrium depending on a compound's log K_{OA}, from Farrar et al. (2005)

This means that calculated sampling rates will differ based on both target compound and sampler material.

Values from Eq. 3 are either experimental (C_{DC}, t) or known characteristics of the sampler (ρ_{PAS}, V_{PAS}). Only $K_{PAS\text{-}A}$ has to be calculated, and must be determined for each DC.
It can be calculated from a molecule's K_{OA}, and in certain cases K_{OA} can be used instead (Shoeib & Harner, 2002).

In the present study, both methods were used to determine SiC foam's sampling rates. First, comparison between active and passive sampling was tested, but did not give coherent results. Thus, the longer but more precise method using depuration compounds was used.

II/ Comparison between active and passive samplers using SiC foam

1. Context of the study

Previous attempts at calculating SiC foam's sampling rates gave results coherent with the literature. However, passive and active samplers did not use the same matrices. Comparisons had been done using SiC foam or XAD®-2 resin as passive samplers, while the active samplers used PUF. None of these materials have comparable specific surface area, porosity or hydrophobicity.
In order to compare comparable samplers, a new sampling campaign was held in Strasbourg's botanical garden. The goal was to use N-C and N-CNT SiC as passive samplers and in active samplers, and compare results in order to determine these foams' sampling rates.

2. Materials and methods

The campaign lasted ten weeks, from June 24th 2015 to September 2nd 2015.

Each week, two SiC foams were placed as passive samplers next to an active sampler fitted with a SiC foam with the same grafting. The first week N-C SiC foams were used, then N-CNT SiC, alternating until the end of the campaign. The active samplers used were low-volume Leckel machines pumping at 2.3 m^3 h^{-1}.

During the first four weeks, the active sampler was used with one SiC foam followed by a GFF, as is usually done for active sampling. For the last six weeks, an additional active sampler was used with one SiC foam only, since SiC foam proved to be able to collect particles. This second sampler was used to compare whether a filter was needed when using SiC.

The target pollutants were PAH, PCB, OCP and non chlorinated pesticides (GC and LC).

3. Results

PAH, PCB and OCP results

All 17 PAH were detected at least once during the ten-week sampling campaign. The lightest nine, from naphthalene to chrysene, were detected every week. Between zero and 6 PCB were detected the first six weeks, while nearly all 22 were detected the last four weeks. Few OCP were detected, except in the last four weeks when up to 19 were detected in both SiC foams. Otherwise, between zero and 8 OCP were detected.

Contrary to what was expected, calculated sampling rates were much higher than those calculated from the ASPA's results. They are summarised in Table 4-1.

Table 4-1 – Calculated sampling rates of PAH, PCB and OCP on grafted SiC foams (m^3 d^{-1})

	PAH		PCB		OCP	
	N-C SiC	N-CNT SiC	N-C SiC	N-CNT SiC	N-C SiC	N-CNT SiC
Minimum	0.7	0.4	0.4	0.8	2.6	0.5
Maximum	545.8	1,371.8	735.3	665.1	492.8	357.8
Average	57.4	102.5	128.6	58.6	76.0	36.1
Median	25.2	26.3	43.2	34.5	23.5	16.3

Out of 534 calculated rates, only 127 (24 %) were inferior to 10 m^3 d^{-1} while 407 (76 %) were over this limit, sometimes going as high as several hundreds of cubic metres per day. This is true for both N-C SiC and N-CNT SiC.

Such numbers are not only higher than what is expected for passive samplers, they are also higher than some active HVS' sampling rates.

GC pesticides results

Twelve pesticides were detected at least once, among which only three were detected more than once during the sampling campaign. For the last five weeks, there were not enough detections to calculate sampling rates, so all calculations come from data from the first five weeks. For these compounds too sampling rates were higher than expected. They are summarised in Table 4-2.

Table 4-2 – Calculated sampling rates of GC pesticides on grafted SiC foams ($m^3\ d^{-1}$)

	N-C SiC	N-CNT SiC
Minimum	1.8	0.3
Maximum	85.9	79.5
Average	20.7	26.2
Median	13.4	24.7

Out of 27 calculated sampling rates, only 14 (52 %) were below 10 $m^3\ d^{-1}$. Out of these, 13 were below 5 $m^3\ d^{-1}$, which are numbers comparable to those obtained during the ASPA campaigns.

However, this means that half of the calculated sampling rates were too high. While not as high as those of PAH, PCB or OCP, they were still comparable to active LVS.

These observations were the same for both N-C SiC and N-CNT SiC.

LC pesticides results

Due to technical problems, the samples from the July 29th to August 5th week could not be analysed by LC. Sampling rates were thus only calculated for nine weeks. This should not have a significant impact on results, as few pesticides were detected in high enough quantities for sampling rates to be calculated. Twenty-five pesticides were detected at least once but only twenty-one sampling rates were calculated.

Table 4-3 – Calculated sampling rates of LC pesticides on grafted SiC foams ($m^3\ d^{-1}$)

	N-C SiC	N-CNT SiC
Minimum	10.0	7.4
Maximum	514.2	597.9
Average	137.5	138.5
Median	67.3	81.6

Out of 21 calculated sampling rates, only 2 (10 %) were below 10 $m^3\ d^{-1}$. Others are much higher than expected and higher than calculated from ASPA results, rising to hundreds of cubic metres per day. This is observed for both N-C SiC and N-CNT SiC.

Discussion

With such high sampling rates calculated, it was at first thought that either passive and active samplers had been mixed up, or that SiC foams had been contaminated.

The first hypothesis was abandoned for several reasons: when bringing back SiC foams to the laboratory, they were explicitly labelled and active and passive foams were put in different bags. Passive SiC samplers were also consistently a pair of foams, while active samplers were first one foam and one filter, then two foams and one filter. Mixing the bags would not be possible.

Contamination could be a factor, especially since there were more detections at the end of the campaign than at the beginning. But in order for sampling rates to be consistently this high, it would mean that each week passive SiC foams exclusively would be contaminated, while active SiC foams remained untouched. Since they were handled and stored in the same conditions, this did not seem realistic.

Another possible explanation for these results is that the SiC foams that were used are not suited for active sampling due to their porosity. Their wide, open pores make it easy for air to pass through the material. While it is a desirable property for a passive sampler, it is a liability in an active sampler that pumps air through the adsorbent. Forcing air to pass through such a porous material greatly reduces the contact duration between air and SiC foam, meaning pollutants cannot be adsorbed. This results in low concentrations detected by active sampling, that artificially increase sampling rates of passive samplers when the two are compared.

This possibility hadn't been considered earlier, so it was not possible at the time to make a new sampling campaign to test this theory further. For instance, SiC foam with smaller pores could be used in active samplers, or one with a less open porosity. This could slow the flow of air passing through the foam.

III/ Using depuration compounds

1. Context of the study

Since direct comparison between passive and active samplers did not produce exploitable results, another method was used to calculate sampling rates.

This method uses depuration compounds (Moeckel et al., 2009), as presented in the introduction. DC are molecules not found in the atmosphere that are spiked on the sampler at the beginning of the sampling period. Their desorption rate over time is proportional to the adsorption of pollutants, which means they can be used to calculate sampling rates.

In order for the calculated sampling rate to be as close as possible to reality, DC should have characteristics close to the monitored pollutants, or even be their deuterated counterpart – for instance naphthalene d8 for naphthalene. Since this study follows hundreds of compounds, choices had to be made. Among PAH, PCB and OCP, only deuterated PAH were chosen due to cost and availability. Regarding non chlorinated pesticides, deuterated counterparts were found mostly for GC pesticides, though there is also one LC pesticide.

The relation between sampling rate and DC loss as presented by Moeckel et al. (2009) and Tuduri et al. (2012) has been written in Eq. 3. This equation was used as is to calculate SiC foam's sampling rates.

The physical characteristics of SiC foam were known, and most of the other values needed for this calculation were experimental data that could be acquired. In order to obtain such data, a short sampling campaign was held over one month in Strasbourg's botanical garden.

Afterwards, only $K_{PAS\text{-}A}$ needed to be calculated.

At first, sampling rates were calculated only for the fourteen deuterated compounds rather than the 163 hydrogenated ones, in order to keep the number of calculations manageable. Once all the parameters of Eq.3 were optimised, sampling rates were calculated for hydrogenated pesticides whose SR had already been determined during ASPA campaigns: cyprodinil, dimethenamid-p, kresoxim-methyl, lindane, s-metolachlor, pendimethalin and tebuconazole.

2. Materials and methods

The experiment took place between March 24th and April 28th 2015.

Eight regular SiC foams were spiked with 100 µL of a 10 mg L^{-1} solution of the selected depuration compounds. There were 14 deuterated molecules, all PAH and pesticides: alachlor d13, 2-chlorophenol d4, chrysene d12, 2,4-D d3, diphenylamine d6, mecoprop d3, metolachlor d6, naphthalene d8, nitrophenol d4, pendimethalin d5, phenanthrene d10, propachlor d5, pyrene d10 and trifluralin d14.

All SiC foams were placed in Strasbourg's botanical garden on the same day. One SiC foam was picked up after a week, another after two weeks, and the remaining SiC were collected every three or four days.

After sampling, SiC foams were extracted by ASE, using the same method as when extracting non deuterated compounds: two 10 min cycles at 150 °C and 1500 psi with 100 % acetonitrile. The extract was evaporated to a drop by rotary evaporation, then resolubilised in 1 mL acetonitrile. In order to derivate pesticides with an –OH function, 50 µL of MtBSTFA were added to the solution, which was heated to 80 °C and stirred for one hour. Atrazine was added as an internal standard, and then the solution was injected in the TRACE™ GC Ultra via the syringe of the CombiPal Autosampler. The GC was equipped with an Optima® 5MS capillary column (30 m × 0.25 mm, DF = 0.25 µm, dimethylpolysiloxane phase). It was coupled to the ITQ™ 700 ion trap mass spectrometer, which was used to perform MSMS in electron EI mode. The transfer line was heated to 300 °C and the ion source at 200 °C. The oven ramp was programmed as follows: start at 50 °C (hold 1 min), increase to 300 °C at a rate of 10 °C min^{-1}, then hold 2 min. High purity (≥ 99.999 %) helium was used as the carrier gas flowing at 1 mL min^{-1}.

3. Results

Since no quantification method was in place to determine deuterated compounds' concentrations, results are given as relative peak areas: the ratio of the compound's peak area over the internal standard's peak area.

Four curves are given in Figure 4-3 as examples of DC loss rates: two PAH and two pesticides.

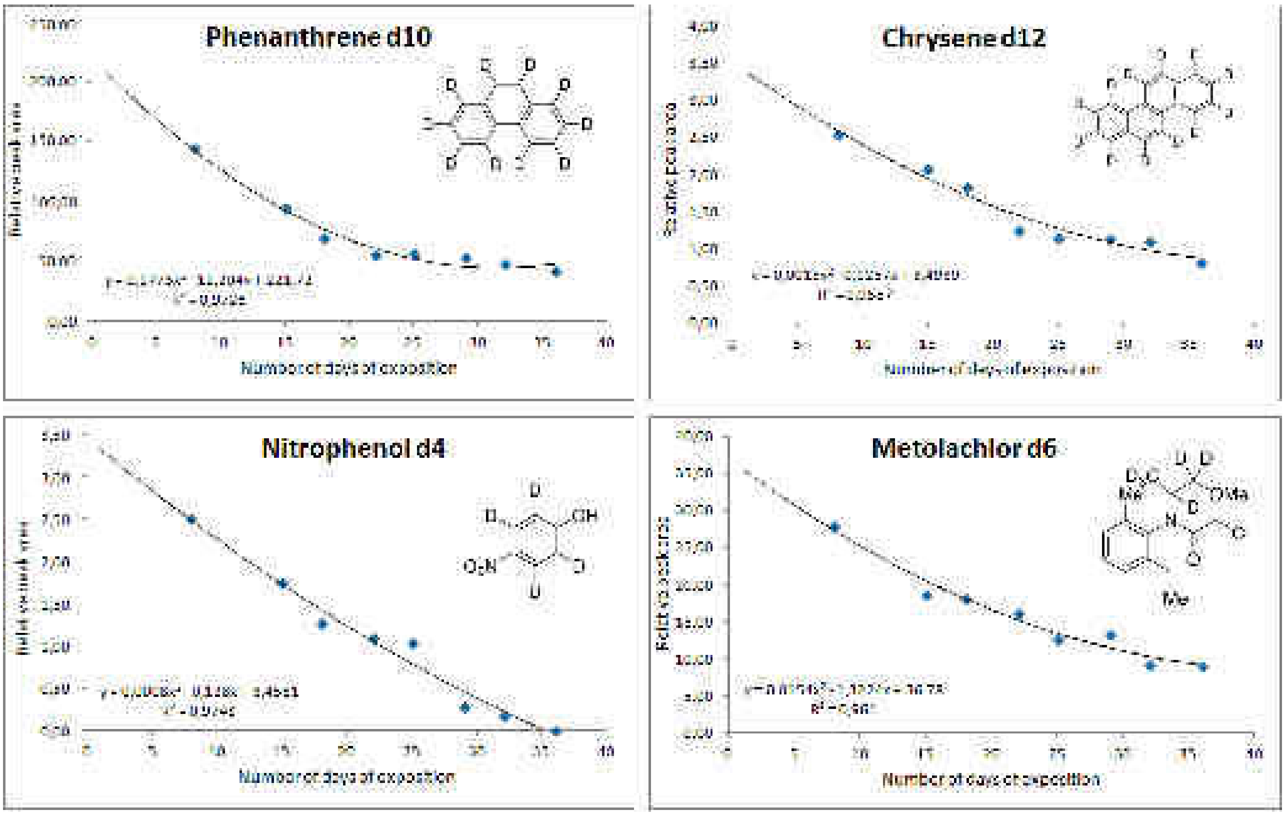


Figure 4-3 – Curves of DC loss rate over one month

For every compound, a quadratic decrease was observed. Some, like nitrophenol d4, were close to a linear decrease.

Naphthalene d8, which is particularly volatile, was completely desorbed from the foam by the 29th day, which means that the last 3 foams had no naphthalene d8 on them by the time they were analysed. This also happened to nitrophenol d4, albeit only on the last foam.

When calculating Eq. 3 with these two compounds, the chosen C_{DC} was the last value superior to zero. The value of t was adjusted to fit the time at which this C_{DC} was obtained.

Heavier molecules like phenanthrene d10 were still present in important quantities on the foam at the end of the testing period (Figure 4-3).

$C_{DC,0}$ and C_{DC} could not be expressed in ng sampler^{-1} due to the lack of a quantification method, but since they are used as a ratio in Eq. 3, expressing them as relative peak areas is not a problem.

All spiked SiC foams were placed in the botanical garden, which means the $C_{DC,0}$ used is not the peak area at Day 0, but rather at Day 7, after a week outside.
The values obtained for all DC are listed in Table 4-4:

Table 4-4 – Initial and final concentrations of DC as relative peak areas and sampling duration

Depuration compound	$C_{DC,0}$ (dimensionless)	C_{DC} (dimensionless)	t (days)
Alachlor d13	9.06	2.88	28
2-Chlorophenol d4	0.60	0.01	28
Chrysene d12	2.52	0.80	28
2,4-D d3	1.17	0.01	28
Diphenylamine d6	0.83	0.06	28
Mecoprop d3	16.34	0.16	28
Metolachlor d6	27.92	8.98	28
Naphthalene d8	3.01	0.02	17
Nitrophenol d4	2.50	0.18	24
Pendimethalin d5	12.05	3.40	28
Phenanthrene d10	146.16	41.78	28
Propachlor d5	0.06	0.02	28
Pyrene d10	84.93	31.13	28
Trifluralin d14	12.91	0.85	28

The ratio $-\ln\frac{C_{DC}}{C_{DC,0}}$ was not calculated as an intermediate value. $C_{DC,0}$ and C_{DC} were used directly in the final equation.

4. Calculating $K_{PAS\text{-}A}$ using the $K_{PUF\text{-}A}$ formula

After gathering data on DC loss, the last part of the equation had to be determined: each compound's $K_{PAS\text{-}A}$. This is not a readily available coefficient; it has to be calculated.
The mathematical relation between a compound's $K_{PAS\text{-}A}$ and its octanol/air partition coefficient K_{OA} has been determined by Shoeib & Harner (2002).
In this publication, the relation is calculated using data from a year-long sampling campaign. The passive samplers that were used were PUF, SPMD and soil, and the pollutants monitored were exclusively PCB. So the $K_{PAS\text{-}A}$ calculated were actually $K_{PUF\text{-}A}$, $K_{SPMD\text{-}A}$ and $K_{soil\text{-}A}$, and they were determined through data from a single family of pollutants.

Despite these differences, it was supposed that the results for PUF could be applied to SiC foam, since comparison between these two matrices during ASPA campaigns (Chapter 3) had given coherent results. Therefore, the relation that was used to calculate Eq. 3's $K_{PAS\text{-}A}$ was the following Eq. 4:

$$K_{PUF-A} = 10^{0.6366 \log K_{OA} - 3.1774} \qquad (Eq. 4)$$

K_{PUF-A}: PUF/air partition coefficient in $m^3\ g^{-1}$
K_{OA}: octanol/air partition coefficient, dimensionless

Currently, K_{OA} is not a value commonly available for a wide variety of compounds. It can, however, be accurately estimated based on a compound's octanol/water partition K_{OW} and its Henry's law constant H (Meylan & Howard, 2005). The following relation has been validated in this publication:

$$K_{OA} = K_{OW} \times \frac{RT}{H} \qquad (Eq. 5)$$

K_{OA}: octanol/air partition coefficient, dimensionless
K_{OW}: octanol/water partition coefficient, dimensionless
R: ideal gas constant, here in m^3 atm K^{-1} mol^{-1}
T: absolute temperature at which K_{OW} and H are calculated, in K
H: Henry's law constant, here in atm m^3 mol^{-1}

This publication used the PHYSPROP database (Syracuse Research Corporation, 2013) to get values for K_{OW} and H, so the same was done in the present study. As the values for deuterated compounds are not known, K_{OW} and H values were those of the hydrogenated compounds. Using these values as well as Eq.5 and Eq.4, K_{OA} and then K_{PAS-A} were calculated for all DC used in this study. Results are summarised in Table 4-5:

Table 4-5 – K_{OA} and K_{PAS-A} calculated for each DC using the K_{OA}-to-K_{PUF-A} relation

Depuration compound	K_{OA} (dimensionless)	K_{PAS-A} ($m^3\ g^{-1}$)
Alachlor d13	9.67E+09	1.51E+03
2-Chlorophenol d4	3.09E+05	2.08E+00
Chrysene d12	3.02E+09	7.20E+02
2,4-D d3	4.46E+08	2.13E+02
Diphenylamine d6	2.88E+07	3.72E+01
Mecoprop d3	4.33E+10	3.92E+03
Metolachlor d6	2.18E+10	2.53E+03
Naphthalene d8	1.11E+05	1.08E+00
Nitrophenol d4	4.79E+09	9.67E+02
Pendimethalin d5	2.36E+08	1.42E+02
Phenanthrene d10	1.67E+07	2.63E+01
Propachlor d5	1.03E+07	1.93E+01
Pyrene d10	1.56E+08	1.09E+02
Trifluralin d14	5.20E+07	5.43E+01

With these values, the sampling rate of each DC could be calculated using Eq. 3. ρ_{PAS} and V_{PAS} were averaged for all SiC foams used, with ρ_{PAS} = 2.42E+05 g m^{-3} and V_{PAS} = 3.3E-05 m^3. Calculated sampling rates are gathered in Table 4-6:

Table 4-6 – SiC sampling rates for each compound calculated using K_{PUF-A}

Depuration compound	Sampling rate (m^3 d^{-1})
Alachlor d13	493.97
2-Chlorophenol d4	2.50
Chrysene d12	235.02
2,4-D d3	288.42
Diphenylamine d6	27.04
Mecoprop d3	5,177.84
Metolachlor d6	818.93
Naphthalene d8	2.66
Nitrophenol d4	842.16
Pendimethalin d5	51.36
Phenanthrene d10	9.39
Propachlor d5	5.36
Pyrene d10	31.22
Trifluralin d14	41.98

Sampling rates were once again too high, sometimes as high as several hundreds of cubic metres per day. Mecoprop d3 was an especially absurd case with several thousands of cubic metres per day. Naphthalene d8 and 2-chlorophenol d4 were the only compounds to have expected sampling rates. Propachlor d5 and phenanthrene d10, while having sampling rates below the 10 m^3 d^{-1} limit, were slightly higher than expected. Overall, out of 14 molecules, only 4 had believable sampling rates (29 %).

The first hypothesis made to explain these results was that values used in the various equations were incorrect. Indeed, K_{OW} and especially H values can vary from source to source. However, results were still in the same range when using different references for K_{OW} and H: the Pesticides Properties DataBase (University of Hertforshire, 2007) or the Illustrated Handbook of physical-chemical properties and environmental fate of organic chemicals.

Sampling rates were also calculated from one sampling week to another instead of from beginning to end of the study in order to minimise variations, but this did not change the order of magnitude of the results.

In order to eliminate a potential bias introduced by the internal standard, calculations were made using the DC's peak areas instead of their relative peak areas. However, no significant change was observed. Quantities in ng were even estimated from the loss rate curves, but results stayed the same.

Another hypothesis was that some DC should not have been used to calculate sampling rates. Moeckel et al. (2009) advised to only use DC whose losses were between 20 and 80 %. These values were calculated for all DC and are summarised in Table 4-7:

Table 4-7 – Percentile loss of each DC at the end of the study

Depuration compound	DC loss (%)
Alachlor d13	68.2
2-Chlorophenol d4	98.5
Chrysene d12	68.2
2,4-D d3	99.1
Diphenylamine d6	92.2
Mecoprop d3	99.0
Metolachlor d6	67.8
Naphthalene d8	99.5
Nitrophenol d4	92.7
Pendimethalin d5	71.8
Phenanthrene d10	71.4
Propachlor d5	62.2
Pyrene d10	63.3
Trifluralin d14	93.4

Discarding DC whose losses are superior to 80 % does not change the main issue. While it would invalidate the improbably high sampling rates of mecoprop d3 and nitrophenol d4, it also takes away naphthalene d8 and 2-chlorophenol d4 whose sampling rates are the lowest.

In the end, the hypothesis was that using the $K_{PUF\text{-}A}$ was the problem. SiC foam cannot be likened to PUF as a passive sampler, and the data used to calculate $K_{PUF\text{-}A}$ was based on PCB when the present study uses only PAH and pesticides.
Consequently, an actual $K_{SiC\text{-}A}$ had to be calculated, using PAH and pesticides in addition to PCB.

5. Determining a formula for $K_{SiC\text{-}A}$

In order to calculate actual $K_{SiC\text{-}A}$ from scratch, one needs to understand how this coefficient can been correlated to a compound's K_{OA}.

According to Shoeib & Harner (2002), $K_{PAS\text{-}A}$ can be expressed as the ratio of pollutants concentration in the passive sampler over pollutants concentration in air. This ratio can be calculated after a sampling campaign, but is only valid for pollutants that attain equilibrium between air and passive sampler. This relation is summarised by Eq. 6:

$$K_{PAS-A} = \frac{C_{PAS}}{C_A} \qquad (\text{Eq. }6)$$

$K_{PAS\text{-}A}$: a given pollutant's passive sampler/air partition coefficient in $m^3\ g^{-1}$
C_{PAS}: a given pollutant's concentration in the passive sampler in $ng\ g^{-1}$
C_A: a given pollutant's concentration in air, determined by active sampling, in $ng\ m^{-3}$

After a sampling campaign, one can plot log K_{PAS-A} against log K_{OA} for every detected compound. Then, using a linear regression model, a correlation can be found between log K_{PAS-A} and log K_{OA} and thus between K_{PAS-A} and K_{OA}.

In order to plot log K_{PAS-A} against log K_{OA}, results from the previous sampling campaign (detailed at the beginning of this chapter) were used. Despite its mixed results and the fact that it used grafted SiC foams while DC were deposited on regular SiC foams, it was the only long duration campaign that monitored all pollutants considered in this thesis. However, several limits were defined regarding which results could be exploited.

First, only results considered coherent were used for the linear regression. Those that gave sampling rates superior to 10 m^3 d^{-1} were discarded. For this reason, LC results were not used. Second, since only compounds that were at equilibrium at the time of analysis should be used for these calculations (Shoeib & Harner, 2002), they had to be identified. A sampling campaign to determine equilibrium time of every compound could not be held, but Figure 4-2 gives an idea of which pollutants reach equilibrium first depending on K_{OA}. Despite this reference describing another matrix than SiC foam, it was used as a guideline and molecules with $K_{OA} \leq 9$ were used preferentially.

Given these restrictions and the few results obtained for GC pesticides, only one regression curve (Figure 4-4) could be drawn for these compounds (n°1 in Table 4-8).

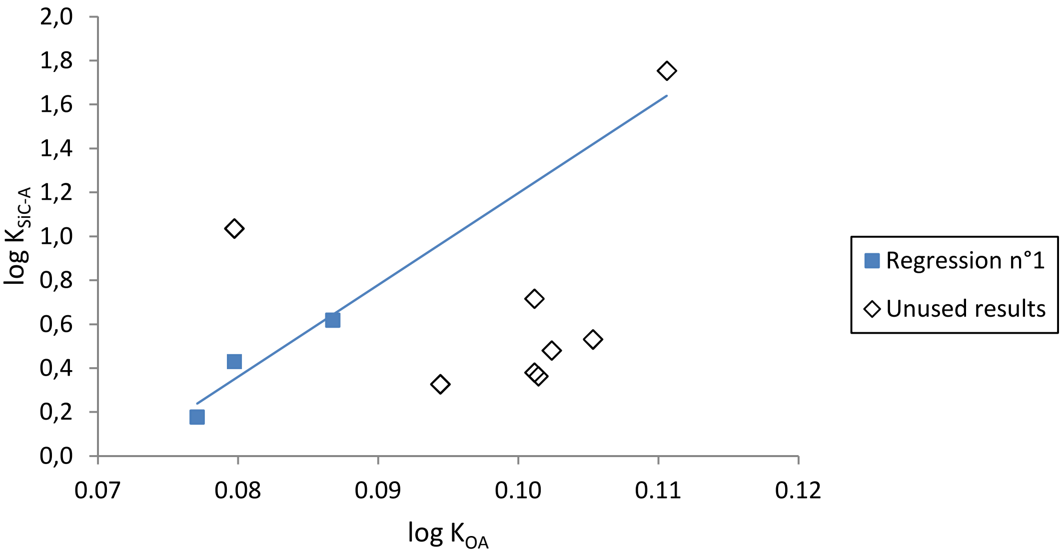


Figure 4-4 – Linear regression curve using all GC pesticides results

From the PAH, PCB and OCP analysis, only PAH were taken into account since there were no deuterated PCB or OCP. A lot of results were exploitable, meaning that several curves could be considered. In the end, eleven were drawn:

- three from Week 7 results (Figure 4-5 ; n°2 to 4 in Table 4-8)

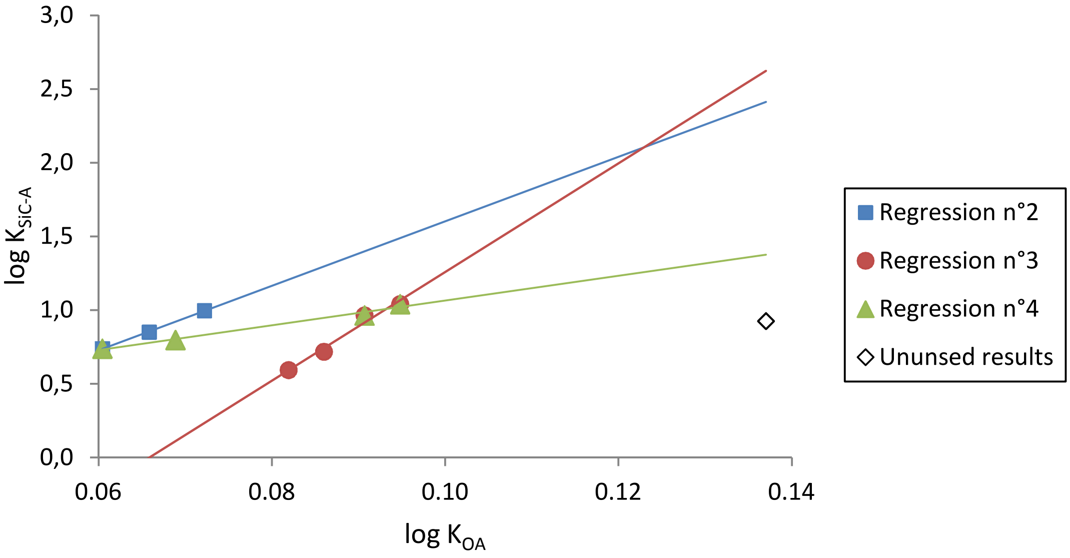


Figure 4-5 – Linear regression curve using PAH results from Week 7

- one from Week 8 results (Figure 4-6 ; n°5 in Table 4-8)

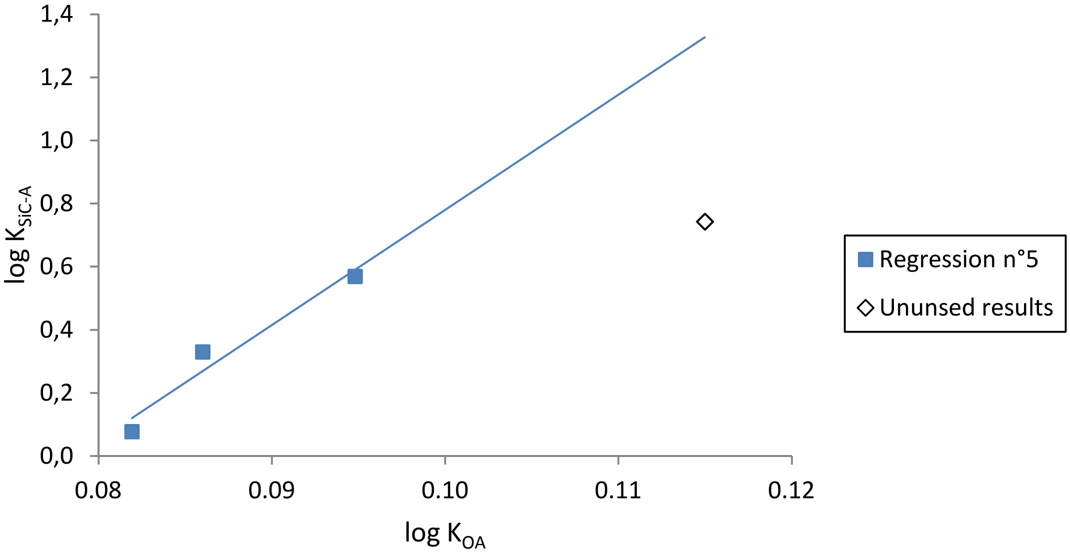


Figure 4-6 – Linear regression curve using PAH results from Week 8

- two from Week 9 results (Figure 4-7 ; n°6 and 7 in Table 4-8)

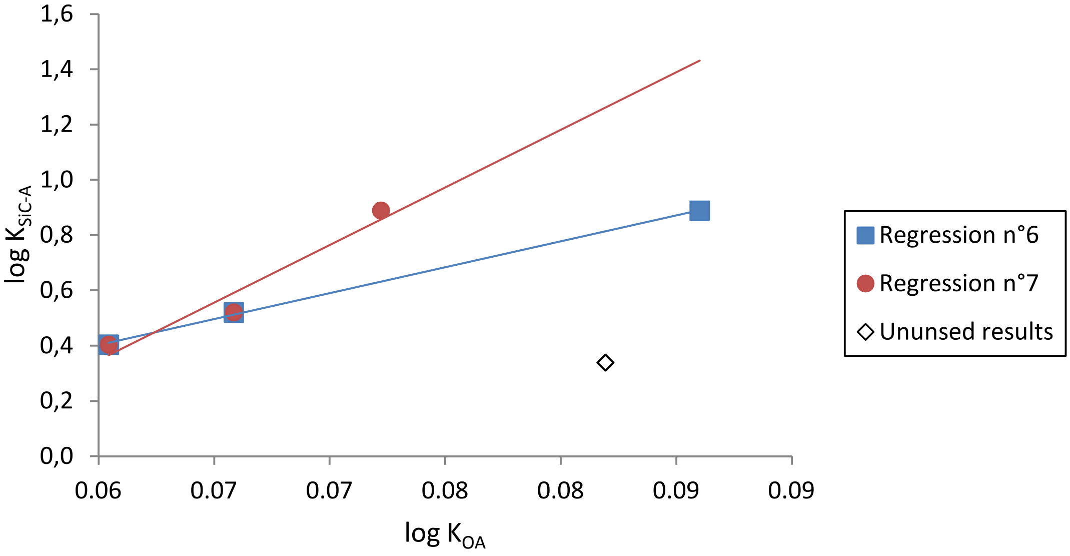


Figure 4-7 – Linear regression curve using PAH results from Week 9

- and five from all campaign results (Figure 4-8 ; n°8 to 12 in Table 4-8)

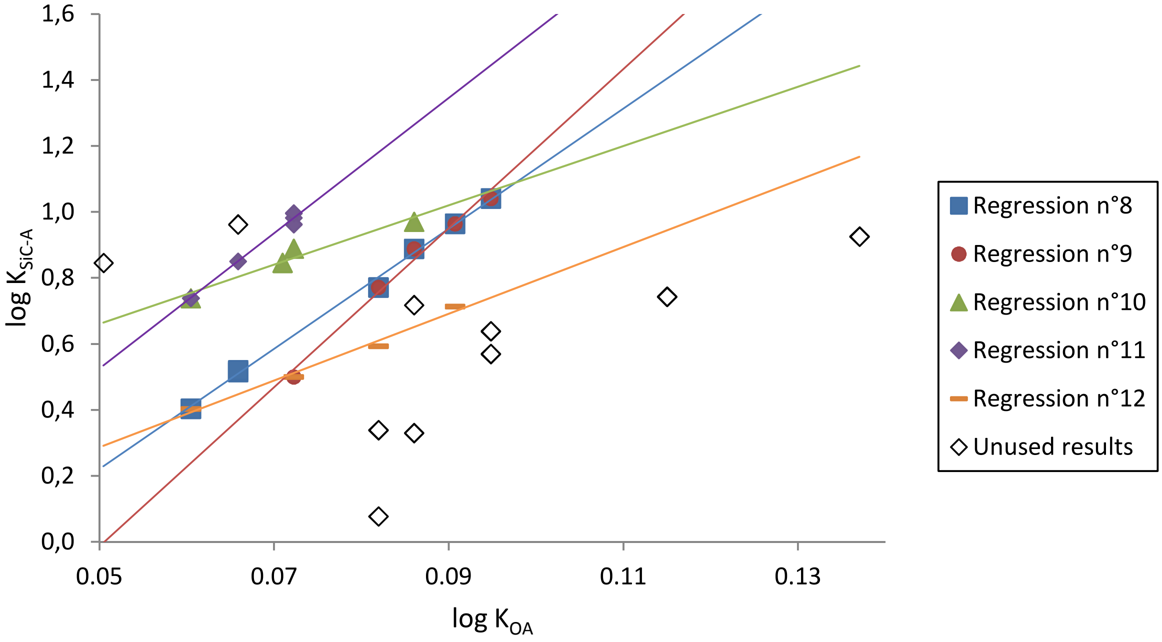


Figure 4-8 – Linear regression curve using all PAH results

Some of these linear regression models (n°3, 4, 5, 8 and 9) were drawn using results from compounds with a $K_{OA} > 9$ in addition to compounds with smaller K_{OA}. This was done due to the obvious linearity of the results: compounds with higher K_{OA} aligned well with those below 9.

The equations of all twelve curves are summarised in Table 4-8, along with their R².

Despite having one curve made from GC pesticides and several from PAH, each equation was used to calculate the sampling rate of every DC. The number of sampling rates that were above 10 m^3 d^{-1} when calculated with the corresponding $K_{SiC\text{-}A}$ are also reported in Table 4-8:

Table 4-8 – Possible mathematical relations between K_{OA} and $K_{SIC\text{-}A}$

N°	Equation	R²	Number of SR > 10 m^3 d^{-1}
1	$\log K_{SiC\text{-}A} = 0.4183 \log K_{OA} - 2.9865$	0.8899	2
2	$\log K_{SiC\text{-}A} = 0.2189 \log K_{OA} - 0.5862$	0.9990	4
3	$\log K_{SiC\text{-}A} = 0.3686 \log K_{OA} - 2.4274$	0.9720	2
4	$\log K_{SiC\text{-}A} = 0.0839 \log K_{OA} + 0.2249$	0.9837	3
5	$\log K_{SiC\text{-}A} = 0.3650 \log K_{OA} - 2.8702$	0.9509	1
6	$\log K_{SiC\text{-}A} = 0.1876 \log K_{OA} - 0.7233$	0.9991	3
7	$\log K_{SiC\text{-}A} = 0.4167 \log K_{OA} - 2.1529$	0.9415	6
8	$\log K_{SiC\text{-}A} = 0.1821 \log K_{OA} - 0.6900$	0.9965	3
9	$\log K_{SiC\text{-}A} = 0.2411 \log K_{OA} - 1.2193$	0.9859	2
10	$\log K_{SiC\text{-}A} = 0.0899 \log K_{OA} + 0.2108$	0.9548	4
11	$\log K_{SiC\text{-}A} = 0.2050 \log K_{OA} - 0.5001$	0.9881	5
12	$\log K_{SiC\text{-}A} = 0.1011 \log K_{OA} - 0.2187$	0.9855	0

While the sampling rates calculated using $K_{SiC\text{-}A}$ from these equations were much smaller than those calculated from $K_{PUF\text{-}A}$, some equations gave better results than others. For instance, the five highlighted equations (n°1, 3, 5, 9 and 12) are those who gave the least sampling rates above 10 m^3 d^{-1}. They are therefore considered to be the best approximation of $K_{SiC\text{-}A}$.

It should be noted that the compounds that are systematically above 10 m^3 d^{-1} are pesticides. There are only three instances of PAH being above this limit: naphthalene d8 two times and chrysene d12 one time.

When using the five highlighted equations, only mecroprop d3 and nitrophenol d4 are above 10 m^3 d^{-1}.

Detailed sampling rates calculated with these five equations' $K_{SiC\text{-}A}$ are summarised in Table 4-9.

Table 4-9 – Sampling rates for each DC calculated using K_{SIC-A} from equations n° 1, 2, 5 and 6

Depuration compound	SR n°1 ($m^3 d^{-1}$)	SR n°3 ($m^3 d^{-1}$)	SR n°5 ($m^3 d^{-1}$)	SR n°9 ($m^3 d^{-1}$)	SR n°12 ($m^3 d^{-1}$)
Alachlor d13	5.07	5.86	1.94	5.04	2.02
2-Chlorophenol d4	0.25	0.48	0.16	1.53	2.62
Chrysene d12	3.11	3.81	1.27	3.80	1.79
2,4-D d3	5.79	7.80	2.62	9.94	6.12
Diphenylamine d6	0.99	1.52	0.52	2.76	2.49
Mecoprop d3	38.30	41.08	13.57	29.22	9.49
Metolachlor d6	7.04	7.81	2.59	6.06	2.17
Naphthalene d8	0.33	0.66	0.23	2.44	4.81
Nitrophenol d4	10.07	12.05	4.01	11.35	5.01
Pendimethalin d5	1.18	1.65	0.55	2.27	1.53
Phenanthrene d10	0.39	0.61	0.21	1.19	1.16
Propachlor d5	0.25	0.40	0.14	0.82	0.86
Pyrene d10	0.79	1.12	0.38	1.63	1.16
Trifluralin d14	1.35	2.02	0.68	3.39	2.82

It should be noted that the three compounds that have consistently higher sampling rates than the others are three polar pesticides: mecoprop d3, nitrophenol d4 and 2,4-D d3. Polar compounds have not been specifically mentioned in the bibliography regarding this calculation method, so there is a possibility that their behaviour is not accurately described by these equation systems. Their affinity with SiC foam is also different than with more traditional samplers, which could induce a bias.

During the sample preparation method, polar compounds have to be derivatized through reaction with M*t*BSTFA. Their detection in GC-MSMS is dependent upon the success of the derivatization, so there is a higher incertitude for their results than for those of non polar compounds.

Metolachlor d6 gave the highest SR after these compounds. Such behaviour has also been observed during the ASPA campaigns with s-metolachlor, when its sampling rate could be as high as tens or hundreds of cubic metres per day. These values had been attributed to the difference in adsorption efficiency between samplers, but s-metolachlor may also have a naturally high adsorption rate on SiC foam.

In general, these sampling rates were comparable to those that were found when comparing passive and active samplers during the ASPA campaigns (Table 4-10). Excluding sampling rates above 10 $m^3 d^{-1}$, they range from 0.14 to 9.94 $m^3 d^{-1}$, averaging at 2.55 $m^3 d^{-1}$.

Table 4-10 – Comparing SR calculated with the DC method to those calculated from ASPA results ($m^3\ d^{-1}$)

	DC method	ASPA campaigns					
	All SiC 2015	N-C SiC 2015	N-CNT SiC 2015	Regular SiC 2014	XAD®-2 2014	XAD®-2 2013	XAD®-2 literature*
Minimum	0.14	0.28	0.99	0.08	0.43	0.66	0.60
Maximum	9.94	9.97	7.11	5.82	4.91	6.14	3.70
Average	2.55	2.37	3.93	2.33	2.32	3.23	2.78
Median	1.65	0.91	4.36	1.45	2.14	3.76	2.75

* Wania et al., 2003 ; Gouin et al., 2008b ; Xiao-Ping et al., 2010

However, in order to be able to directly compare these results to the ASPA's, additional calculations had to be made.

6. Applying the formula to hydrogenated compounds

Depuration compounds are normally used during an actual sampling campaign to be directly compared with the pollutants detected.
Since we studied DC on their own, sampling rates calculated for actual pollutants would be hypothetical predictions. This is why several adjustments needed to be made in order to compare with ASPA results.

First, sampling rates calculated from ASPA results were averaged over one week. In order to mimic this timeframe, $C_{DC,0}$ and C_{DC} were chosen a week apart, and t was fixed at 7 days.

Then, one DC had to be attributed to each molecule of interest.
Over the course of the two ASPA campaigns, sampling rates were calculated for seven different pesticides on SiC foam: the GC pesticides cyprodinil, kresoxim-methyl, lindane and s-metolachlor, and the LC pesticides dimethenamid-p, pendimethalin and tebuconazole.
For GC pesticides, s-metolachlor was matched with metolachlor d6. Cyprodinil, kresoxim-methyl and lindane were matched to trifluralin d14, as it is their assigned internal standard during analysis.
Dimethenamid-p, pendimethalin and tebuconazole were all matched to the only LC pesticide DC, pendimethalin d5.

All five possible linear regressions were used, and the resulting sampling rates are summarised in Table 4-11.

Table 4-11 – Hypothetical sampling rates for seven selected pesticides

Depuration compound	SR n°1 (m^3 d^{-1})	SR n°3 (m^3 d^{-1})	SR n°5 (m^3 d^{-1})	SR n°9 (m^3 d^{-1})	SR n°12 (m^3 d^{-1})
Cyprodinil	8.39	10.29	3.43	10.32	4.89
Kresoxim-methyl	17.66	19.83	6.57	15.85	5.85
Lindane	1.15	1.78	0.60	3.27	3.02
S-metolachlor	8.82	9.79	3.24	7.60	2.72
Dimethenamid-p	0.36	0.54	0.18	0.94	0.80
Pendimethalin	0.74	1.03	0.35	1.42	0.95
Tebuconazole	22.63	20.94	6.84	10.20	2.18

Most of these values were below the arbitrary 10 m^3 d^{-1}, and four of the seven pesticides consistently had sampling rates below this value.

As was expected, s-metolachlor had some of the highest values each time, though it was surpassed by cyprodinil, kresoxim-methyl and tebuconazole. Kresoxim-methyl is a difficult pesticide to detect, which might lead to uncertainties regarding its results, but there is no explanation for cyprodinil and tebuconazole.

Comparison with previously calculated sampling is summarised in Table 4-12. “ASPA” indicates SR calculated with ASPA results, and “DC” are SR predicted by the depuration compounds method. Sampling rates above 10 m^3 d^{-1} have been removed.

Table 4-12 – Sampling rates calculated from the ASPA and DC method for seven selected pesticides

	Minimum (m^3 d^{-1})		Maximum (m^3 d^{-1})		Average (m^3 d^{-1})		Median (m^3 d^{-1})	
Pesticides	**ASPA**	**DC**	**ASPA**	**DC**	**ASPA**	**DC**	**ASPA**	**DC**
Cyprodinil*	-	3.43	-	8.39	-	5.57	-	4.89
Kresoxim-methyl**	7.11	5.85	7.11	6.57	7.11	6.21	7.11	6.21
Lindane	0.08	0.60	0.84	3.27	0.46	1.96	0.46	1.78
S-metolachlor	0.14	2.72	5.71	9.79	2.22	6.43	1.30	7.60
Dimethenamid-p	0.98	0.18	1.77	0.94	1.38	0.56	1.40	0.54
Pendimethalin	2.45	0.35	9.97	1.42	5.97	0.90	5.49	0.95
Tebuconazole**	5.82	2.18	5.82	6.84	5.82	4.51	5.82	4.51

*Cyprodinil’s sampling rate was calculated only once on SiC foam and its value was 331.73, so it was not taken into account here.

**Only one sampling rate was calculated for kresoxim-methyl and tebuconazole.

Overall, results rarely match. This could be expected due to the predictive nature of sampling rates calculated with the DC method, as the DC’s own experimental sampling rates were in good agreement with ASPA results. Moreover, the hypothetical sampling rates were taken from different linear regression equations, none of which have yet been confirmed as being a good approximation of reality.

One remark that can be made is that sampling rates from the DC method are consistently higher than those from the ASPA campaigns for GC pesticides, while they are lower for LC pesticides. Since this observation is systematic, it could also show that sampling rates from ASPA campaigns were over- or underestimated. And despite the differences and some rates being deemed too high, sampling rates were in the same order of magnitude.

Despite this issue, the DC method has proven to be a good way of determining a compound's sampling rate when using the appropriate $K_{PAS\text{-}A}$.

As of now, it is difficult to decide which regression model is the closest to reality.

Equation n°12 is a good candidate due to no sampling rate going over 10 m^3 d^{-1} when using it.

Equations n°1 and 5, in addition to having some of the lowest R^2, were given by curves drawn with only 3 points, which might not be reliable enough.

What is needed now is a long-term campaign to obtain information on equilibrium time for the pollutants of interest, whose results could then be used when tracing the linear regression linking K_{OA} and $K_{SiC\text{-}A}$.

Other sampling campaigns should be done to monitor both pollutants uptake and DC loss to have simultaneous experimental data on both.

Since $K_{SiC\text{-}A}$ can also be expressed as a function of air concentration (Eq. 6), accurate pollutants concentration in air is also needed. Active sampling with SiC foam could be optimised to minimise breakthrough volume by modifying its 3D structure. Using a SiC cylinder with smaller surface windows is a possibility, as is using SiC foam beads.

IV/ Conclusion

Two methods were tested to calculate the sampling rates of SiC foam as a passive sampler without resorting to comparison with another adsorbent.

Directly comparing SiC foam as passive and active samplers gave unrealistically high results. Sampling rates were up to the hundreds of cubic metres of air per day, for every sampled compound and for both N-C and N-CNT SiC foam.

This problem was attributed to SiC foam's porosity. It is a material with open porosity, and its surface pores are about a millimetre wide. Even when using a low volume pump, air can flow too easily through the foam, and passes quickly enough that pollutants cannot be reliably adsorbed. With such small quantities available on the active SiC foams, air concentrations of pollutants are underestimated, which leads to overestimating the passive samplers' sampling rates.

Further study is needed to see whether this drawback can be avoided. SiC foam with smaller pores could be used, or one with closed porosity, like 450 °C N-CNT SiC. For the moment, direct comparison between passive and active SiC foam is not a method that can give sampling rates of passive SiC.

Another method that does not involve active sampling had to be tested. This method uses depuration compounds, molecules not naturally found in the atmosphere that are spiked on the passive sampler and whose loss rate is proportional to the sampler's sampling rate for similar compounds. The equation including DC concentrations also requires knowing the target compound's passive sampler/air partition coefficient $K_{PAS\text{-}A}$.
At first, a $K_{PUF\text{-}A}$ value found in the literature was used, but calculated sampling rates were also in the hundreds of cubic metres per day. An actual $K_{SiC\text{-}A}$ had to be calculated, and using this value, sampling rates were found to be within the same order of magnitude as what was found in previous studies.

Based on the depuration compounds' sampling rates, it appears that like the currently-used XAD®-2 resin, SiC foam has an average sampling rate of 2.5 m^3 d^{-1}. Its rates can vary on a wider scale than XAD®-2, though, ranging from 0.14 to 9.94 m^3 d^{-1}. These values are close to those found for non deuterated compounds on SiC foam, and especially 450 °C N-C SiC.
The wider gap between highest and lowest sampling rates for SiC foam may be due to its capacity to trap polar and particulate compounds that are poorly retained on XAD®-2 resin. Since sampling rates vary from compound to compound, a wider variety of pollutants adsorbed mean a wider range of calculated sampling rates.

Now that the accuracy of the DC method has been tested, it would be interesting to use it in its intended conditions: spiking DC on SiC foams that are monitoring ambient pollutants, and use the depuration compounds to find the sampling rates of non deuterated pollutants.
Before that, adjustments will be needed. Determining $K_{SiC\text{-}A}$ as accurately as possible will require long sampling campaigns to find equilibrium times and have enough data to produce a reliable linear regression linking $K_{SiC\text{-}A}$ and K_{OA}.

References

Association française de normalisation (2007). *Air ambiant – Dosage des substances phytosanitaires (pesticides) dans l'air ambiant – Prélèvement actif.* Norme XP X 43-058. La Plaine Saint-Denis : Association française de normalisation.

Bartkow M. E., Booij K., Kennedy K. E., Müller J. F., Hawker D. W., **2005**, "Passive sampling theory for semivolatile organic compounds", *Chemosphere*, *60*, 170-176

Farrar N. J., Harner T., Shoeib M., Sweetman A, Jones K. C., **2005**, "Field deployment of thin film passive air samplers for persistent organic pollutants: A study in the urban atmospheric boundary layer", *Environmental Science & Technology*, *39*, 42-48

Gouin T., Wania F., Ruepert C., Castillo L. E., **2008**, "Field testing passive air samplers for current use pesticides in a tropical environment", *Environmental Science & Technology*, *42*, 6625-6630

Hazrati S., Harrad S., **2007**, “Calibration of polyurethane foam (PUF) disk passive air samplers for quantitative measurement of polychlorinated biphenyls (PCB) and polybrominated diphenyl ethers (PBDEs): Factors influencing sampling rates”, *Chemosphere*, *67*, 448-455

Klánová J., Èupr P., Kohoutek J., Harner T., **2008**, “Assessing the influence of meteorological parameters on the performance of polyurethane foam-based passive air samplers”, *Environmental Science & Technology*, *42*, 550-555

Meylan W. M., Howard P. H., **2005**, “Estimating octanol-air partition coefficients with octanol-water partition coefficients and Henry’s law constants”, *Chemosphere*, *61*, 640-644

Moeckel C., Harner T., Nizzetto L., Strandberg B., Lindroth A., Jones K. C., **2009**, “Use of depuration compounds in passive air samplers: results from active sampling-supported field deployment, potential uses, and recommendations”, *Environmental Science & Technology*, *43*, 3227-3232

Persoon C., Hornbuckle K. C., **2009**, “Calculation of passive sampling rates from both native PCB and depuration compounds in indoor and outdoor environments”, *Chemosphere*, *74*, 917-923

Shoeib M., Harner T., **2002**, “Characterization and comparison of three passive air samplers for persistent organic pollutants”, *Environmental Science & Technology*, *36*, 4142-4151

Syracuse Research Corporation, **2013**, *FatePointers Search Module* [Online] Available at http://esc.syrres.com/fatepointer/search.asp [Accessed March 2016]

Tuduri L., Harner T., Hung H., **2006**, “Polyurethane foam (PUF) disks passive air samplers: Wind effect on sampling rates”, *Environmental Pollution*, *144*, 377-383

Tuduri L., Millet M., Briand O., Montury M., **2012**, “Passive air sampling of semi-volatile organic compounds”, *Trends in Analytical Chemistry*, *31*, 38-49

University of Hertfordshire, **2007**, *Pesticide Properties DataBase* [Online] Available at http://sitem.herts.ac.uk/aeru/ppdb/en/index.htm [Accessed September 2014]

Wania F., Shen L., Duan Lei Y., Teixeira C., Muir D. C. G., **2003**, “Development and calibration of a resin-based passive sampling system for monitoring persistent organic pollutants in the atmosphere”, *Environmental Science & Technology*, *37*, 1352-1359

Xiao-Ping W., Ping G., Tan-Dong Y., Jones K.C., **2010**, “Passive air sampling of organochlorine pesticides, polychlorinated biphenyls, and polybrominated diphenyl ethers across the Tibetan plateau”, *Environmental Science & Technology*, *44*, 2988-2993

Conclusion and perspectives

In this exploratory study, an alternative to the currently used PUF and XAD®-2 resin was found to be used as a passive sampler for semi-volatile organic pollutants in air.
SiC foam was chosen among other carbon-based materials as it is a resistant, highly reusable material that can trap both gaseous and particulate compounds. Its medium surface area of 30 m^2 g^{-1} can be increased by grafting nitrogen-doped carbon or carbon nanotubes on its surface. This allows SiC foam to adsorb gaseous pollutants in higher quantities than even XAD®-2 resin. Its numerous macro- and mesopores are particularly suited to trap particles, making SiC foam the best material for monitoring heavier compounds. Its lower hydrophobicity compared to other adsorbents also allows it to trap polar compounds, something that cannot be reliably done with PUF or XAD®-2 resin.

An analytical method was developed to quantify PAH, PCB, OCP and other pesticides on SiC foam, coupling ASE, SPE and SPME. Some of these techniques had been used together to prepare environmental samples, but it is the first time the three are used in a single method. ASE was optimised to take as little solvent and time as possible. SPE as a following step allowed samples to be concentrated without using an aggressive evaporation method that would have resulted in a loss of the more volatile compounds. As SPE is also a cleaning process, cleanup and concentration were done at the same time. Finally, using SPME for injection in GC further cleaned the sample, and low limits of detection and quantification were reached. This final step had to be optimised by family of pollutants in order to reduce the number of injections needed. In the end, two SPME injections in GC and one liquid injection in LC are performed per sample.

Several sampling campaigns were done to compare SiC foam to XAD®-2 resin, confirming preliminary observations. SiC foam consistently was the best adsorbent to trap particulate and polar compounds, as could be seen with PAH and LC pesticides especially. Once grafted, SiC foam also became more efficient at trapping volatile compounds. Out of the two grafted materials tested in this study, 450 °C N-C SiC is the recommended adsorbent as it keeps the advantages of regular SiC foam – open porosity, lesser hydrophobicity – while having a greater specific surface area. These characteristics make this SiC foam an efficient sampler for a wide range of compounds.
It should be noted that the foams used in this study were one third of the size of the XAD®-2 tubes to which they were compared. Since SiC foam already performed better at these dimensions, it would be interesting to compare the two at equal size and see how SiC foam's efficiency scales with size.

Finally, SiC foam's sampling rates were determined through different methods. There are currently no reference values for SiC foam, so its results were compared to those published for XAD®-2 resin.

Comparing passive SiC foams to active PUF generally gave sampling rates comparable to the published values for XAD®-2. SiC foam usually had higher maximum sampling rates than XAD®-2 resin, which might be due to its greater adsorption capacity for specific compounds. Two sampling campaigns used this method to determine sampling rates, and results agree with each other.

Comparing passive and active SiC foam did not work as the foams used were not suited to active sampling. Wide surface windows and an open porosity allow pumped air to pass through too easily, which prevents efficient adsorption.

This observation was an opportunity to determine sampling rates using the depuration compounds method. When using this method, it was found that different samplers and pollutants families cannot be likened to each other and the parameters of the equation have to be determined for a specific adsorbent for specific compounds. This is why results were more coherent using K_{SiC-A} than K_{PUF-A}. Sampling rates calculated for the depuration compounds were very close to the rates calculated when comparing SiC foam and PUF. However, the DC method should not be used to predict sampling rates of other compounds. It is more precise when based on experimental data.

These first conclusions describing the behaviour of SiC foam as a passive sampler for semi-volatile organic compounds are a base from which other works can be developed.

Other tests remain to be done before SiC foams can become widespread samplers. For instance, their adsorption capacity should be tested for periods longer than two weeks. A maximum storage duration before extraction should be estimated, as well as the number of times they can be used without losing their efficiency.

The current sample preparation method could also be optimised in order to become standardised. Improving SPME in order to fix repeatability issues should be the next analytical goal, as well as testing how far detection limits can be decreased.

Alternatively, different extraction and cleaning methods could be investigated. Such a porous material could be well suited to ultrasonic extraction, for instance, which would also remove the need for a specific shape to fit ASE wells. When used as a catalyst, SiC foam is calcinated after a reaction in order to be re-used. Calcination would allow even the PAH that were not extracted to be removed from the foam, possibly preventing contamination.

Sampling rates will also need to be determined more precisely. The most precise method would be comparison between active and passive samplers, but active sampling will need to be optimised for use with SiC foam. Current suggestions are using SiC foam with smaller pores and/or using two successive foams before the GFF. This optimisation would also allow further tests to find the relation between K_{PAS-A} and sampling rate for passive samplers. When a precise K_{PAS-A} equation is determined, DC will be able to be used regularly on sampling campaigns.

In the long term, one could imagine using SiC foam for a wide range of sampling campaigns, changing the grafting depending on target pollutants in order to optimise adsorption. Like the currently used PUF-XAD-PUF ‘sandwiches’, hybrid samplers with different SiC foams could be used to maximise both gaseous and particulate pollutants uptake.

Annexes

Annex I: Pollutants monitored during the study
Annex II: Limits of detection and quantification
Annex III: Results of the 2014 ASPA sampling campaign
Annex IV: Results of the 2014 botanical garden sampling campaign
Annex V: Results of the 2015 ASPA sampling campaign

Annex I: Pollutants monitored during the study

Polycylic aromatic compounds
Acenaphtene
Anthracene
Benzo(a)anthracene
Benzo(a)pyrene
Benzo(b)fluoranthene
Benzo(e)pyrene
Benzo(g,h,i)perylene
Benzo(k)fluoranthene
Chrysene
Coronene
Dibenzo(a,h)anthracene
Fluoranthene
Fluorene
Indenol(1,2,3)pyrene
Naphtalene
Phenanthrene
Pyrene

Polychlorinated biphenyls
PCB 18
PCB 28
PCB 31
PCB 44
PCB 52
PCB 70
PCB 81
PCB 101
PCB 105
PCB 114
PCB 118
PCB 123
PCB 126
PCB 138
PCB 149
PCB 153
PCB 156
PCB 157
PCB 167
PCB 169
PCB 180
PCB 189

Organochlorine pesticides
Aldrin
α-endosulfan
α-HCH
β-endosulfan
β-HCH
Cischlordane
δ-HCH
Dieldrin
γ-HCH (Lindane)
Heptachlor epoxide A
Heptachlor epoxide B
Heptachlore
Hexachlorobenzene
Methoxychlor
o,p'-DDD
o,p'-DDE
o,p'-DDT
p,p'-DDD
p,p'-DDE
p,p'-DDT
Transchlordane

GC pesticides	
2,4-D*	Fludioxonil
2,4-MCPA*	Flusilazole
Acetochlor	Folpet
Aclonifen	Ioxynil*
Alachlor	Irgarol
Aldrin	Isodrin
Azoxystrobin	Kresoxim-methyl
Benoxacor	λ-cyhalothrin
Bifenox	Lenacil
Bifenthrin	Lindane
Boscalid	Mecoprop-p*
Bromoxynil*	Mepanipyrim
Bupirimate	Metamitron
Buprofezin	Metazachlor
Captan	Myclobutanil
Chloridazon	Oxadiazon
Chlorothalonil	Oxyfluorfen
Chlorpyrifos	Procymidone
Clofentezine	Propachlor
Clomazone	Propargite
Cyproconazole*	Propiconazole
Cyprodinil	Propyzamide
Deltamethrin	Prosulfocarb
Dicamba*	Pymetrozine
Dichlorvos	Pyrimethanil
Diclofop-methyl	Quinoxyfen
Difenoconazole	s-Metolachlor
Dimethomorph	Spiroxamine
Diphenylamine	Tebufenpyrad
Ethofumesate	Tebutam
Fenarimol	Thiamethoxam
Fenpropathrin	Tolylfluanid
Fenpropidin	Triclopyr*
Fenpropimorph	Trifloxystrobin
Florasulam	Trifluralin

*polar pesticides that need derivatization

LC pesticides
Acetamiprid
Carbendazim
Carbetamide
Chlorfenvinphos
Chloridazon
Chlortoluron
Cyazofamid
Diflubenzuron
Diflufenican
Dimethenamid-p
Diuron
Epoxiconazole
Flufenoxuron
Fluroxypyr
Foramsulfuron
Isoproturon
Isoxadifen
Lufenuron
Metalaxyl-M
Nicosulfuron
Penconazole
Pendimethalin
Propiconazole
Prothioconazole
Pymetrozin
Pyraclostrobin
Spinosyn A
Spinosyn D
Sulcotrione
Tebuconazole
Terbutryn
Thiacloprid
Triflusulfuron methyl

Annex II: Limits of detection and quantification

	SiC foam		XAD-2 resin	
PAH	**LOD (ng.sampler^{-1})**	**LOQ (ng.sampler^{-1})**	**LOD (ng.sampler^{-1})**	**LOQ (ng.sampler^{-1})**
Acenaphtene	0.6	1.8	0.6	1.8
Anthracene	0.4	1.2	0.1	0.3
Benzo(a)anthracene	2.3	6.9	0.1	0.3
Benzo(a)pyrene	6.3	18.9	0.4	1.2
Benzo(b)fluoranthene	3.5	10.5	0.1	0.3
Benzo(e)pyrene	1.0	3.0	0.3	0.9
Benzo(g,h,i)perylene	9.0	27.0	0.1	0.3
Benzo(k)fluoranthene	0.9	2.7	0.4	1.2
Chrysene	0.3	0.9	0.1	0.3
Coronene	1.2	3.6	40.0	120.0
Dibenzo(a,h)anthracene	0.6	1.8	0.2	0.6
Fluoranthene	0.3	0.9	0.1	0.3
Fluorene	0.2	0.6	0.7	2.1
Indenol(1,2,3)pyrene	0.9	2.7	0.2	0.6
Naphtalene	4.4	13.2	5.5	16.5
Phenanthrene	0.6	1.8	0.1	0.3
Pyrene	0.6	1.8	0.1	0.3

	SiC foam		XAD-2 resin	
PCB	**LOD (ng.sampler^{-1})**	**LOQ (ng.sampler^{-1})**	**LOD (ng.sampler^{-1})**	**LOQ (ng.sampler^{-1})**
PCB 18	0.1	0.3	0.1	0.3
PCB 28	0.1	0.3	0.1	0.3
PCB 31	0.1	0.3	0.1	0.3
PCB 44	0.2	0.6	0.1	0.3
PCB 52	0.3	0.9	0.1	0.3
PCB 70	1.7	5.1	0.1	0.3
PCB 81	0.6	1.8	0.1	0.3
PCB 101	1.5	4.5	0.1	0.3
PCB 105	0.1	0.3	3.0	9.0
PCB 114	4.8	14.4	1.7	5.1
PCB 118	2.6	7.8	0.1	0.3
PCB 123	2.6	7.8	0.1	0.3
PCB 126	1.0	3.0	0.4	1.2
PCB 138	0.7	2.1	1.0	3.0
PCB 149	1.0	3.0	0.1	0.3
PCB 153	1.0	3.0	1.1	3.3
PCB 156	3.5	10.5	0.1	0.3
PCB 157	0.2	0.6	0.4	1.2
PCB 167	2.0	6.0	0.1	0.3
PCB 169	1.9	5.7	0.1	0.3
PCB 180	14.5	43.5	0.6	1.8
PCB 189	0.6	1.8	0.1	0.3

	SiC foam		XAD-2 resin	
OCP	**LOD (ng.sampler^{-1})**	**LOQ (ng.sampler^{-1})**	**LOD (ng.sampler^{-1})**	**LOQ (ng.sampler^{-1})**
Aldrin	0.2	0.6	0.1	0.3
α-HCH	0.2	0.6	0.6	1.8
α-endosulfan	1.3	3.9	0.2	0.6
β-endosulfan	0.3	0.9	1.0	3.0
β-HCH	0.1	0.3	0.2	0.6
Cischlordane	0.1	0.3	0.1	0.3
δ-HCH	1.5	4.5	0.1	0.3
Dieldrin	1.8	5.4	1.5	4.5
γ-HCH	0.1	0.3	0.1	0.3
Heptachlor epoxide A	0.9	2.7	1.2	3.6
Heptachlor epoxide B	0.8	2.4	0.1	0.3
Heptachlore	0.7	2.1	0.1	0.3
Hexachlorobenzene	0.1	0.3	0.1	0.3
Methoxychlor	0.2	0.6	0.7	2.1
o,p’-DDD	5.8	17.4	0.1	0.3
o,p’-DDE	0.1	0.3	0.1	0.3
o,p’-DDT	0.8	2.4	0.1	0.3
p,p’-DDD	0.3	0.9	0.5	1.5
p,p’-DDE	0.1	0.3	0.2	0.6
p,p’-DDT	1.6	4.8	8.5	25.5
Transchlordane	0.8	2.4	0.1	0.3

	SiC foam		**XAD-2 resin**	
GC pesticides	**LOD (ng.sampler^{-1})**	**LOQ (ng.sampler^{-1})**	**LOD (ng.sampler^{-1})**	**LOQ (ng.sampler^{-1})**
2,4-D*	-	-	1.6	4.8
2,4-MCPA*	2.5	7.5	2.6	7.8
Acetochlor	7.0	21.0	-	-
Aclonifen	2.5	7.5	0.6	1.8
Alachlor	0.4	1.2	0.5	1.5
Aldrine	0.9	2.7	0.9	2.7
Azoxystrobin	9.1	27.3	29.0	87.0
Benoxacor	8.7	26.1	4.8	14.4
Bifenox	4.3	12.9	0.3	0.9
Bifenthrin	4.2	12.6	0.2	0.6
Boscalid	63.2	189.6	5.5	16.5
Bromoxynil*	3.1	9.3	1.0	3.0
Bupirimate	7.4	22.2	0.2	0.6
Buprofezin	1.6	4.8	3.6	10.8
Captan	13.3	39.9	2.4	7.2
Chloridazon	4.0	12.0	1.5	4.5
Chlorothalonil	7.3	21.9	4.8	14.4
Chlorpyrifos	3.3	9.9	1.0	3.0
Clofentezine	4.3	12.9	16.8	50.4
Clomazone	3.7	11.1	3.7	11.1
Cyproconazole*	36.6	109.8	-	-
Cyprodinil	1.8	5.4	0.1	0.3
Deltamethrin	-	-	-	-
Dicamba*	-	-	-	-
Dichlorvos	0.1	0.3	-	-
Diclofop-methyl	1.4	4.2	0.3	0.9
Difenoconazole	1 530.4	4 591.2	-	-
Dimethomorph	47.7	143.1	1.4	4.2
Diphenylamine	5.9	17.7	0.3	0.9
Ethofumesate	3.8	11.4	2.1	6.4
Fenarimol	8.2	24.6	0.2	0.6
Fenpropathrin	12.8	38.4	0.7	2.1
Fenpropidin	1.4	4.2	0.1	0.3
Fenpropimorph	2.0	6.0	0.6	1.8
Florasulam	-	-	-	-
Fludioxonil	1.4	4.2	2.4	7.2
Flusilazole	0.6	1.8	0.4	1.2
Folpet	-	-	6.6	19.8
Ioxynil*	19.5	58.5	2.3	6.9
Irgarol	5.7	17.1	0.6	1.8
Isodrin	7.6	22.8	1.9	5.7
Kresoxim-methyl	3.7	11.1	0.7	2.1
λ-cyhalothrin	21.0	63.0	1.8	5.4

	SiC foam		XAD-2 resin	
GC pesticides	**LOD (ng.sampler^{-1})**	**LOQ (ng.sampler^{-1})**	**LOD (ng.sampler^{-1})**	**LOQ (ng.sampler^{-1})**
Lenacil	-	-	-	-
Lindane	0.3	0.9	0.2	0.6
Mecoprop-p*	1.2	3.6	4.4	13.2
Mepanipyrim	0.6	1.8	1.4	4.2
Metamitron	-	-	-	-
Metazachlor	40.1	120.3	8.6	25.8
Myclobutanil	5.1	15.3	12.4	37.2
Oxadiazon	0.9	2.7	0.4	1.2
Oxyfluorfen	2.9	8.7	0.2	0.6
Procymidone	3.7	11.1	2.3	6.9
Propachlor	4.5	13.5	2.0	6.0
Propargite	1.8	5.4	0.7	2.1
Propiconazole	4.8	14.4	5.9	17.7
Propyzamide	0.3	0.9	0.5	1.5
Prosulfocarb	-	-	10.5	31.5
Pymetrozine	-	-	0.6	1.8
Pyrimethanil	6.0	18.0	1.0	3.0
Quinoxyfen	1.4	4.2	0.1	0.3
s-Metolachlor	0.3	0.9	0.3	0.9
Spiroxamine	5.2	15.6	-	-
Tebufenpyrad	1.2	3.6	4.4	13.2
Tebutam	2.3	6.9	1.3	3.9
Thiamethoxam	37.2	111.6	1.0	3.0
Tolylfluanid	36.4	109.2	3.1	9.3
Triclopyr*	4.2	12.6	1.9	5.7
Trifloxystrobin	0.4	1.2	0.1	0.3
Trifluralin	1.8	5.4	4.8	14.4

* polar pesticides that need derivatization

\- pesticides not detected often enough to have their LOD/LOQ calculated

	SiC foam		XAD-2 resin	
LC pesticides	**LOD (ng.sampler^{-1})**	**LOQ (ng.sampler^{-1})**	**LOD (ng.sampler^{-1})**	**LOQ (ng.sampler^{-1})**
Acetamiprid	0.9	2.7	30.1	90.3
Carbendazim	2.4	7.2	281.6	844.8
Carbetamide	0.1	0.3	0.4	1.2
Chlorfenvinphos	0.5	1.5	0.1	0.3
Chloridazon	1.3	3.9	1.6	4.8
Chlortoluron	0.1	0.3	0.2	0.6
Cyazofamid	0.1	0.3	0.1	0.3
Diflubenzuron	0.1	0.3	0.1	0.3
Diflufenican	0.1	0.3	0.1	0.3
Dimethenamid-p	0.1	0.3	0.1	0.3
Diuron	0.1	0.3	0.3	0.9
Epoxiconazole	0.2	0.6	0.1	0.3
Flufenoxuron	0.1	0.3	0.1	0.3
Fluroxypyr	1.0	3.0	30.0	90.0
Foramsulfuron	0.3	0.9	0.1	0.3
Isoproturon	0.1	0.3	0.1	0.3
Isoxadifen	0.2	0.6	0.7	2.1
Lufenuron	0.1	0.3	0.1	0.3
Metalaxyl-M	0.1	0.3	0.3	0.9
Nicosulfuron	0.1	0.3	0.1	0.3
Penconazole	0.1	0.3	0.2	0.6
Pendimethalin	0.2	0.6	0.4	1.2
Propiconazole	0.1	0.3	0.1	0.3
Prothioconazole	5.6	16.8	0.2	0.6
Pymetrozin	0.1	0.3	4.2	12.6
Pyraclostrobin	0.1	0.3	0.1	0.3
Spinosyn A	0.2	0.6	0.1	0.3
Spinosyn D	0.1	0.3	0.1	0.3
Sulcotrione	1.6	4.8	0.1	0.3
Tebuconazole	0.1	0.3	0.1	0.3
Terbutryn	0.1	0.3	0.1	0.3
Thiacloprid	0.1	0.3	2.0	6.0
Triflusulfuron methyl	0.6	1.8	0.1	0.3

Annex III: Results of the 2014 ASPA sampling campaign

XAD-2 resin (ng.sampler^{-1})													
GC pesticides	**Ohnenheim 28/04-12/05**	**Ohnenheim 22/07-29/07**	**Kintzheim 14/04-28/04**	**Kintzheim 29/07-05/08**	**Sigolsheim 24/06-08/07**	**Sigolsheim 15/07-29/07**	**Sigolsheim 05/08-12/08**	**Village-Neuf 03/06-17/06**	**Village-Neuf 08/07-22/07**	**Village-Neuf 29/07-05/08**	**Niederau 23/05-09/06**	**Niederau 01/07-15/07**	**Niederau 05/08-12/08**
2,4-MCPA			12.4										
Acetochlor				< LOQ			< LOQ						< LOQ
Alachlor										< LOQ			
Aldrin			< LOQ										
Buprofezin		< LOQ			< LOQ	33.6		< LOQ				< LOQ	
Captan							< LOQ						
Cyprodinil							0.6			< LOQ			
Diclofop-methyl												< LOQ	
Diphenylamine						39.0						13.5	
Fenpropidin			276.7										
Lindane				17.6	22.7	22.4			< LOQ	24.0		4.0	
Quinoxyfen												< LOQ	
s-Metolachlor	2.5	11.0		288.7	30.4	134.7	150.1	24.9	25.7	3.8		5.3	1.4
Trifloxystrobin				< LOQ									

SiC foam (ng.sampler^{-1})													
GC pesticides	**Ohnenheim 28/04-12/05**	**Ohnenheim 22/07-29/07**	**Kintzheim 14/04-28/04**	**Kintzheim 29/07-05/08**	**Sigolsheim 24/06-08/07**	**Sigolsheim 15/07-29/07**	**Sigolsheim 05/08-12/08**	**Village-Neuf 03/06-17/06**	**Village-Neuf 08/07-22/07**	**Village-Neuf 29/07-05/08**	**Niederau 23/05-09/06**	**Niederau 01/07-15/07**	**Niederau 05/08-12/08**
2,4-MCPA							149.3					< LOQ	8.8
Acetochlor				< LOQ						< LOQ			
Bromoxynil							22.6						
Cyprodinil				< LOQ									
Diphenylamine										25.2			
Lindane				4.8						8.5	2.6		
Mecoprop-p							59.6			< LOQ			5.6
Propargite								< LOQ					
Quinoxyfen					< LOQ			< LOQ					
s-Metolachlor	13.0	5.1		< LOQ	10.1	35.3	12.2		4.6	< LOQ	4.5	8.2	6.8
Triclopyr							< LOQ			< LOQ			< LOQ

XAD-2 resin (ng.sampler^{-1})

LC pesticides	Ohnenheim 28/04-12/05	Ohnenheim 22/07-29/07	Kintzheim 29/07-05/08	Sigolsheim 24/06-08/07	Sigolsheim 15/07-29/07	Sigolsheim 05/08-12/08	Village-Neuf 03/06-17/06	Village-Neuf 08/07-22/07	Village-Neuf 29/07-05/08	Niederau 23/05-09/06	Niederau 01/07-15/07	Niederau 05/08-12/08
Chloridazon	16.2											
Cyazofamid			1.8			2.7		3.1	3.4		8.3	
Diflufenican									12.4		5.7	
Isoproturon					< LOQ							
Isoxadifen								< LOQ				
Lufenuron			< LOQ		< LOQ						< LOQ	
Metalaxyl-M		2.3						9.2			1.1	
Pyraclostrobin						< LOQ						
Tebuconazole				1.0								
Triflusulfuron methyl								< LOQ				< LOQ

SiC foam (ng.sampler^{-1})

LC pesticides	Ohnenheim 28/04-12/05	Ohnenheim 22/07-29/07	Kintzheim 29/07-05/08	Sigolsheim 24/06-08/07	Sigolsheim 15/07-29/07	Sigolsheim 05/08-12/08	Village-Neuf 03/06-17/06	Village-Neuf 08/07-22/07	Village-Neuf 29/07-05/08	Niederau 23/05-09/06	Niederau 01/07-15/07	Niederau 05/08-12/08
Carbendazim												< LOQ
Diflubenzuron						25.7						27.1
Diflufenican	10.6	31.3	183.7	23.0	85.9							
Diuron											1.4	
Fluroxypyr		615.0				76.5			501.3			121.0
Isoproturon		6.6			7.1				2.2		0.5	
Metalaxyl-M								3.6	36.5			
Nicosulfuron								124.3				
Pendimethalin							7.2					
Pymetrozin						< LOQ			< LOQ			
Pyraclostrobin						< LOQ						
Spinosyn A							23.1					
Sulcotrione								< LOQ				
Tebuconazole				7.7		11.3						
Terbutryn							1.0					
Triflusulfuron methyl				16.0								

Annex IV: Results of the 2014 botanical garden sampling campaign

(ng.sampler^{-1})	08/09-15/09		15/09-22/09		22/09-30/09		30/09-07/10		07/10-14/10					
PAH	SiC foam	XAD-2 resin	SiC foam	XAD-2 resin	SiC foam	XAD-2 resin	SiC foam	XAD-2 resin	SiC foam	XAD-2 resin	450 °C N-C SiC	900 °C N-C SiC	450 °C N-CNT SiC	900 °C N-CNT SiC
Naphthalene	6,759.057		3,006.297		4,480.775		222.261	237.190	124.252	160.180	514.507	19,623.172		4,025.328
Acenaphthene	6,902.415	8,329.250	605.498	22,986.620	1,724.298	11,847.000		471.980	12.731	367.270	16.047	101.481	48.692	85.545
Fluorene	13,440.327	9,766.180	5,171.928	33,717.290	22,454.202	26,112.240	25.688	516.410	31.362	640.830	22.983	25.577	126.154	354.887
Phenanthrene	11,742.218		3,626.386		7,635.766		245.933	289.540	135.308	1,203.260	125.936	325.386	395.839	1,570.734
Anthracene	4,373.836	19,245.590	2,644.833	19,351.010	3,190.994	16,270.190	137.531	161.270	67.334	116.300	86.394	418.660	138.375	1,107.615
Fluoranthene	7,510.660		4,841.345		6,663.314		983.071	386.960	33.346	106.660	49.149	7.310	102.874	416.894
Pyrene	11,056.052		7,618.446		15,753.769		1,169.586		22.519		36.483	3.993	70.039	367.190
Benzo(a)anthracene	6,865.945	780.100	3,960.382	121.780	5,227.066	392.480	1,054.431	8.530	32.824	0.550	14.186			12.350
Chrysene	8,805.161	,	5,868.689	405.930	7,968.740	823.680	2,726.311	69.360	117.792	18.320	174.579			374.043
Benzo(b)fluoranthene	15,894.599	3,980.810	8,514.040	730.950	9,692.919	1,215.320	5,750.732	132.500	593.001	4.140	732.936			
Benzo(k)fluoranthene	15,892.865	8,949.520	8,668.989	619.560	12,102.924	1,658.000	5,852.562	126.710	365.907	1.440	629.892			
Benzo(e)pyrene	13,172.872		46,114.586		10,614.646	939.600	4,819.303	159.210	298.906	7.490	660.909		232.217	867.457
Benzo(a)pyrene			7,215.029			1,050.930	5,849.806	104.650			602.009			
Dibenzo(a,h)anthracene	11,181.181	1,509.550	3,416.884	1,335.040		3,932.710	3,536.559	112.930	258.996		1,118.899			
Indenol(1,2,3)pyrene	10,969.178	1,244.960	7,108.418	3,741.580	7,700.368	1,961.790	4,986.903	306.250	266.328	5.560	1,477.766			
Benzo(g,h,i)perylene	10,875.195		8,532.765		7,518.842		5,001.780	221.370	303.434	7.300	1,168.890			
Coronene	3,447.817		2,344.632				1,519.151				853.180			

(ng.sampler^{-1})	08/09-15/09		15/09-22/09		22/09-30/09		30/09-07/10		07/10-14/10					
PCB	SiC foam	XAD-2 resin	SiC foam	XAD-2 resin	SiC foam	XAD-2 resin	SiC foam	XAD-2 resin	SiC foam	XAD-2 resin	450 °C N-C SiC	900 °C N-C SiC	450 °C N-CNT SiC	900 °C N-CNT SiC
PCB 18	1,048.034	4,529.270	151.909	1,288.030	586.443	1,330.320	282.194	687.120	150.480	96.410	98.966	9.616	80.810	659.591
PCB 28	1,184.197	1,983.780	89.624	2,554.550	380.484		396.669	1,444.050	46.353	110.570	16.385	1.450	34.626	416.735
PCB 31	1,235.027	3,897.170	106.624	916.520	569.237	1,728.180	304.235	843.160	46.271	51.830	18.450	0.652	7.868	501.017
PCB 44	458.814	2,276.140	250.575	1,388.100	543.641	1,683.130	2,093.193	893.860	114.876	181.970	47.057	2.353	51.574	390.230
PCB 52	1,226.910	2,787.680	549.025	1,268.250	1,272.665	864.440	1,926.135	684.640	232.686	126.070	109.826	7.190	147.035	731.514
PCB 70	2,216.050	4,269.760	709.329	1,286.030	1,382.328	2,005.780	2,618.143	1,781.860	387.519	99.630	200.559	64.435	180.464	906.454
PCB 81	3,388.562	3,603.620	2,952.887	3,867.800	2,343.088	1,530.240	2,668.408	1,257.270	255.800	68.520	142.503	13.645	210.903	489.529
PCB 101						2,132.740	3,763.109	622.840	452.416	114.050	170.687		172.828	1,060.640
PCB 105	5,198.504						6,198.824		650.662	1,091.600	437.395			
PCB 114	2,442.962						4,376.352		404.423	1,068.040	302.680			
PCB 118	2,000.082	2,345.380	952.609	3,772.120	1,585.931	1,368.500	3,212.293	1,372.680	173.539	62.850	92.413		70.747	182.846
PCB 123	2,384.030	1,268.400	626.552	3,357.120		2,203.680	3,980.667	1,054.140	375.696	58.260	273.176			
PCB 126	6,186.677		4,189.525		4,901.055	1,204.280	2,489.222	701.790	294.958	54.700	251.351			412.911
PCB 138	1,783.140		783.732		1,770.913		4,963.771		264.973	722.440	236.865			
PCB 149	2,472.982	1,228.700	769.524	2,957.860	378.120	1,645.160	6,735.145	1,606.250	420.399	74.090	223.673		222.101	
PCB 153	2,115.996		1,339.115		1,852.691		4,714.227		493.694	555.580	488.123			
PCB 156	1,605.501	4,852.690	666.294	1,517.460		1,108.680	2,071.822	1,003.700	202.929	83.760	184.933			
PCB 157	4,119.405	10,598.310	1,521.525	3,694.020		286.100	4,456.231	536.060	275.548	48.910	218.672			
PCB 167	4,222.088	8,628.310	1,773.293	3,747.960	1,325.546	795.340	3,297.103	222.120	356.507	23.460	410.380	93.919		
PCB 169	4,043.157	29,792.950	4,104.920	1,536.520	3,601.044	1,335.000	1,443.076	111.480	115.929	7.000	166.418			
PCB 180								25.490						
PCB 189	5,072.509	13,056.260	1,953.114	2,915.080		147.960	2,843.966	99.680	33.268	9.640	109.255			

(ng.sampler^{-1})	08/09-15/09		15/09-22/09		22/09-30/09		30/09-07/10		07/10-14/10					
GC pesticides	**SiC foam**	**XAD-2 resin**	**SiC foam**	**XAD-2 resin**	**SiC foam**	**XAD-2 resin**	**SiC foam**	**XAD-2 resin**	**SiC foam**	**XAD-2 resin**	**450 °C N-C SiC**	**900 °C N-C SiC**	**450 °C N-CNT SiC**	**900 °C N-CNT SiC**
Acetochlor													595.0	
Aldrin							226.2	744.7	381.7					
Captan		< LOQ												
Chlorpyrifos							29.3			69.1				
Diclofop-methyl							102.6							
Diphenylamine		125.9												
Fenpropathrin							< LOQ							
Fenpropimorph		613.3												
Isodrin							212.3	681.2						
Mecoprop-p			< LOQ		< LOQ									
Oxyfluorfen							144.0							
Propachlor	127.9		96.6											
Propargite							547.2							
Quinoxyfen							125.9							
s-Metolachlor		27.6	92.8	146.5	276.1	120.2	216.6	347.5	254.3	168.4	32.8	146.3	269.2	52.0
Trifluralin	< LOQ	< LOQ	< LOQ	< LOQ		< LOQ	13.0	438.8	11.9	13.0	< LOQ	< LOQ	< LOQ	< LOQ

(ng.sampler^{-1})	08/09-15/09		15/09-22/09		22/09-30/09		30/09-07/10		07/10-14/10					
LC pesticides	**SiC foam**	**XAD-2 resin**	**SiC foam**	**XAD-2 resin**	**SiC foam**	**XAD-2 resin**	**SiC foam**	**XAD-2 resin**	**SiC foam**	**XAD-2 resin**	**450 °C N-C SiC**	**900 °C N-C SiC**	**450 °C N-CNT SiC**	**900 °C N-CNT SiC**
Diflubenzuron			18.2									2.0		1.8
Diflufenican	0.3	< LOQ	41.5	< LOQ	3.7		58.7	25.3	9.2		141.6	18.0		79.5
Dimethenanid-p								< LOQ			2.1		2.6	
Epoxiconazole			7.2										4.6	
Flufenoxuron			80.5				309.4				834.3	672.3		
Isoproturon									0.4			9.6		
Isoxadifen								3.8	0.6			4.3		10.0
Lufenuron			< LOQ								395.6	404.7		360.0
Metalaxyl-M	0.4	4.1		4.3			419.6	67.4	183.6	61.4	497.0	445.0	791.5	215.9
Penconazole													5.1	
Propiconazole								2.4						
Pyraclostrobin								10.2			17.9	1.6		
Tebuconazole		< LOQ	2.4			2.6		0.4	0.4		12.2	4.0	6.6	
Triflusulfuron methyl		< LOQ												

Annex V: Results of the 2015 ASPA sampling campaign

N-C SiC foam (ng.sampler^{-1})

GC pesticides	Ohnenheim 08/04-15/04	Ohnenheim 29/04-06/05	Ohnenheim 30/06-07/07	Ohnenheim 16/07-23/07	Kintzheim 08/04-15/04	Kintzheim 29/04-06/05	Kintzheim 13/05-20/05	Kintzheim 23/06-30/06	Kintzheim 07/07-15/07
Acetochlor									
Alachlor									
Aldrin									
Bifenox									
Bifenthrin	51.6	66.1			14.7	167.6	22.4		
Bromoxynil									
Captan	402.4								
Chloridazon	< LOQ								
Clofentezine									
Clomazone									
Cyprodinil		189.2							
Diclofop-methyl									
Diphenylamine	50.7	< LOQ							
Ethofumesate									
Fenarimol									
Fenpropathrine									
Fenpropimorphe									
Fluzilazole	13.0								
Kresoxim-methyl		< LOQ							
Lindane									
Mepanipyrim	6.9	< LOQ					< LOQ		
Oxadiazon									
Oxyfluorfen									
Propargite									
Propyzamide									
Pyrimethanil	63.7	260.8			86.2	1 243.3	83.8		
Quinoxyfen									
s-Metolachlor	2.2	25.5	< LOQ						
Tebufenpyrad									
Trifloxystrobin		15.5							
Trifluralin	< LOQ		< LOQ						

N-CNT SiC foam (ng.sampler^{-1})

GC pesticides	Ohnenheim 08/04-15/04	Ohnenheim 29/04-06/05	Ohnenheim 30/06-07/07	Ohnenheim 16/07-23/07	Kintzheim 08/04-15/04	Kintzheim 29/04-06/05	Kintzheim 13/05-20/05	Kintzheim 23/06-30/06	Kintzheim 07/07-15/07
Bifenthrin	409.1	168.4				434.7	64.7		
Bromoxynil						52 547.2			
Cyprodinil									
Diphenylamine									
Fenarimol					34.1				
Fluzilazole									
Kresoxim-methyl		< LOQ							
Mepanipyrim		< LOQ							
Propargite									
Pyrimethanil	707.9	367.7			749.7	1 333.8			
Quinoxyfen									
s-Metolachlor		91.3							
Trifloxystrobin		32.9							
Trifluralin	< LOQ							< LOQ	

N-C SiC foam (ng.sampler^{-1})

GC pesticides	Sigolsheim 08/04-15/04	Sigolsheim 29/04-06/05	Sigolsheim 13/05-20/05	Aspach-le-haut 29/04-06/05	Aspach-le-haut 13/05-20/05	Aspach-le-haut 23/06-30/06	Aspach-le-haut 07/07-15/07	Aspach-le-haut 15/07-23/07	Niederau 08/04-15/04	Niederau 21/04-28/04	Niederau 01/07-08/07	Niederau 08/07-15/07
Acetochlor									107.4	385.7		
Alachlor		70.1		< LOQ					< LOQ	36.9		
Aldrin										7.0		
Bifenox									32.7			
Bifenthrin		559.2		319.8	1 165.4				164.0	89.6	201.9	
Bromoxynil				308.2								
Captan												
Chloridazon					161.2					48.0		
Clofentezine									125.8			
Clomazone										59.8		
Cyprodinil					347.2					279.5		
Diclofop-methyl									< LOQ			
Diphenylamine									< LOQ			
Ethofumesate									< LOQ	112.9		
Fenarimol			< LOQ							< LOQ		
Fenpropathrine									137.5			
Fenpropimorphe									17.2	195.8		
Fluzilazole					328.2					46.1		
Kresoxim-methyl				< LOQ	279.7				< LOQ	< LOQ		
Lindane									2.1	55.7		
Mepanipyrim	< LOQ			2.6	150.2				< LOQ	52.7		
Oxadiazon									< LOQ			
Oxyfluorfen					126.2							
Propargite									12.6			
Propyzamide										408.4		
Pyrimethanil	446.6	1 147.5		348.9	1 311.1				81.0	394.1		
Quinoxyfen					351.8							
s-Metolachlor									13.5	151.5		
Tebufenpyrad					946.5							
Trifloxystrobin			13.4	31.4	440.4							
Trifluralin		< LOQ							< LOQ	< LOQ	< LOQ	

N-CNT SiC foam (ng.sampler^{-1})

GC pesticides	Sigolsheim 08/04-15/04	Sigolsheim 29/04-06/05	Sigolsheim 13/05-20/05	Aspach-le-haut 29/04-06/05	Aspach-le-haut 13/05-20/05	Aspach-le-haut 23/06-30/06	Aspach-le-haut 07/07-15/07	Aspach-le-haut 15/07-23/07	Niederau 08/04-15/04	Niederau 21/04-26/04	Niederau 01/07-08/07	Niederau 08/07-15/07
Bifenthrin	192.3	804.4		133.0	113.7				617.4		619.6	
Bromoxynil				1 336.2								
Cyprodinil		255.4										
Diphenylamine		< LOQ										
Fenarimol												
Fluzilazole					182.7				243.3			
Kresoxim-methyl	35.6		11.5	14.5	< LOQ					22.3		
Mepanipyrim		53.1		< LOQ					21.5			
Propargite	1 102.0											
Pyrimethanil	813.1	1 303.8	539.9	532.5	731.3				1 106.6	728.7		
Quinoxyfen		141.0										
s-Metolachlor	110.2	113.1			23.6							
Trifloxystrobin		73.2	27.6	32.0	47.5							
Trifluralin	< LOQ					< LOQ			< LOQ			

N-C SiC foam (ng.sampler^{-1})

LC pesticides	Ohnenheim 08/04-15/04	Ohnenheim 29/04-06/05	Ohnenheim 13/05-20/05	Ohnenheim 30/06-07/07	Ohnenheim 16/07-23/07	Kintzheim 08/04-15/04	Kintzheim 29/04-06/05	Kintzheim 13/05-20/05	Kintzheim 23/06-30/06	Kintzheim 07/07-15/07
Chloridazon										
Diflubenzuron										
Diflufenican				2.5		6.4				1.8
Dimethenanid-p										
Diuron										
Epoxiconazole				9.7						
Isoxadifen										
Lufenuron	244.3									
Metalaxyl-M	66.3		38.6							
Penconazole										
Pendimethalin										
Propiconazole						0.4				
Pymetrozin			1,061.4							
Pyraclostrobin	76.6					9.5		3.0		
Tebuconazole										
Terbutryn										
Triflusulfuron methyl										

N-CNT SiC foam (ng.sampler^{-1})

LC pesticides	Ohnenheim 08/04-15/04	Ohnenheim 29/04-06/05	Ohnenheim 13/05-20/05	Ohnenheim 30/06-07/07	Ohnenheim 16/07-23/07	Kintzheim 08/04-15/04	Kintzheim 29/04-06/05	Kintzheim 13/05-20/05	Kintzheim 23/06-30/06	Kintzheim 07/07-15/07
Chlorfenvinphos	15.6	< LOQ				5.6				
Diflubenzuron										< LOQ
Diflufenican	3.4	2.5		2.4			348.8	0.9	2.9	
Dimethenanid-p	10.7									
Diuron								846.7		
Flufenoxuron		288.3								
Isoproturon	13.4			22.3						
Isoxadifen										
Lufenuron	351.2	66.0								
Metalaxyl-M		2.3							2.2	
Pendimethalin		146.5	22.9	167.2				33.6	20.6	
Propiconazole						0.9			< LOQ	
Pymetrozin			2,467.2	3,983.0					3,498.8	
Pyraclostrobin		39.8				4.3		4.3		
Spinosyn A										
Tebuconazole	3.3									

N-C SiC foam (ng.sampler^{-1})

LC pesticides	Sigolsheim 08/04-15/04	Sigolsheim 29/04-06/05	Sigolsheim 13/05-20/05	Aspach-le-haut 29/04-06/05	Aspach-le-haut 13/05-20/05	Aspach-le-haut 23/06-30/06	Aspach-le-haut 07/07-15/07	Aspach-le-haut 15/07-23/07	Niederau 08/04-15/04	Niederau 21/04-26/04	Niederau 01/07-08/07	Niederau 08/07-15/07
Chloridazon							67.5					
Diflubenzuron									15.3			
Diflufenican		50.9				12.7		0.7	14.9			4.6
Dimethenanid-p		1.4				0.6			9.3			
Diuron			808.0									
Epoxiconazole		11.0	0.8									
Isoxadifen									23.6			
Lufenuron												
Metalaxyl-M	132.4	17.1	9.6				2.0		138.3			
Penconazole	1.4											
Pendimethalin		280.6	14.0			13.2						
Propiconazole												
Pymetrozin			614.6									
Pyraclostrobin		148.2	4.4	2.5	32.0			0.3	71.4			
Tebuconazole		4.7	0.6						11.6	0.5		
Terbutryn									35.0			
Triflusulfuron methyl	< LOQ								16.0			

N-CNT SiC foam (ng.sampler^{-1})

LC pesticides	Sigolsheim 08/04-15/04	Sigolsheim 29/04-06/05	Sigolsheim 13/05-20/05	Aspach-le-haut 29/04-06/05	Aspach-le-haut 13/05-20/05	Aspach-le-haut 23/06-30/06	Aspach-le-haut 07/07-15/07	Aspach-le-haut 15/07-23/07	Niederau 08/04-15/04	Niederau 21/04-26/04	Niederau 01/07-08/07	Niederau 08/07-15/07
Chlorfenvinphos												
Diflubenzuron									9.6			
Diflufenican			< LOQ		0.8		1.9		9.0		1.1	
Dimethenanid-p					0.3					2.2		
Diuron												
Flufenoxuron												
Isoproturon												
Isoxadifen									13.2	1.0		
Lufenuron		59.0										
Metalaxyl-M					0.5		0.4		71.3			
Pendimethalin							8.2	14.2				
Propiconazole					< LOQ	1.0			9.8			
Pymetrozin						< LOQ		< LOQ			1,615.6	
Pyraclostrobin		14.2	0.9		3.5	< LOQ		0.8	31.5	3.3		
Spinosyn A								213.4				
Tebuconazole								0.3	14.3			

Marine LÉVY

Developing new adsorbents for the passive sampling of organic pollutants in the atmosphere – comparison with existing systems

Résumé

Les matériaux actuellement utilisés comme capteurs passifs de polluants atmosphériques, la mousse de polyuréthane et la résine XAD®-2, ne sont optimisés ni pour l'adsorption de composés polaires ni pour le captage de particules. Pour remédier à ces limitations, la mousse de carbure de silicium (SiC) est proposée comme alternative. Plusieurs campagnes de mesures ont été mises en place pour comparer SiC et XAD®-2. Les composés recherchés étaient des HAP, des PCB et des pesticides.

Une méthode d'analyse combinant ASE, SPE et SPME a été développée et optimisée pour ces polluants. Celle-ci permet d'atteindre de faibles limites de détection et quantification pour les composés recherchés.

Les campagnes réalisées montrent que la mousse de SiC est toujours plus efficace que la résine XAD®-2 pour le piégeage de composés particulaires et polaires. De plus, la SiC peut être greffée avec du carbone ou des nanotubes de carbone pour augmenter sa surface spécifique, ce qui la rend également plus performante pour l'adsorption de composés volatils. Les débits d'échantillonnage moyens de la mousse ont été calculés et sont comparable aux valeurs rapportées dans la littérature pour la résine XAD®-2.

Mots-clés : échantillonnage passif de l'air, ASE, SPE, SPME, HAP, PCB, pesticides, mousse de SiC, débit d'échantillonnage

Abstract

Materials currently used as passive samplers for atmospheric pollutants, polyurethane foam and XAD®-2 resin, are not suited to trapping polar compounds nor particles. To overcome these limitations, silicon carbide (SiC) foam is presented as an alternative. Several sampling campaigns monitoring PAH, PCB and pesticides were done to compare SiC and XAD®-2.

An analytical method coupling ASE, SPE and SPME was developed and optimised for these pollutants. It allowed low limits of detection and quantification to be reached for all compounds of interest.

Sampling campaigns showed that SiC foam is consistently more efficient than XAD®-2 resin at trapping particulate and polar compounds. Moreover, SiC foam can be grafted with carbon or carbon nanotubes to increase its specific surface area, which also makes it better at adsorbing volatile compounds. Average sampling rates were calculated for SiC foam and they are comparable to the values reported in the literature for XAD®-2 resin.

Keywords: passive air sampling, ASE, SPE, SPME, PAH, PCB, pesticides, SiC foam, sampling rate