Adaptation of diffusive gradients in thin films technique to sample organic pollutants in the environment: An overview of o-DGT passive samplers

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ABSTRACT

The adaptation of the diffusive gradients in thin films technique (DGT) to sample organic pollutants in the environment, called o-DGT has been performed since 2011 for various types of organic compounds (*e.g.* pesticides, pharmaceuticals, hormones, endocrine disrupting chemicals, household and personal care products). To sample these different compounds, configuration of the samplers (mainly receiving phase and diffusive gel) has to be adapted. Up-to-date, sampling of 142 organic compounds by this passive sampler have been tested. This review provides the state-of-art of o-DGT passive sampler development, describing theory and modelling, calibration, configuration of the devices, and field applications. The most used configurations were agarose-XAD-18 and agarose-HLB configuration. o-DGT can be used to sample soils and most of natural waters (range of pH 4-9 and ionic strength 0.001-0.1 M).

This review discusses current limitation of o-DGT in light of the feedback of DGT use to sample inorganic contaminants. It mainly concern the low sampling rates currently obtained by o-DGT compared to other passive samplers. This weakness could be compensated in the future with new sampler's design allowing an increase in exposure area.

KEYWORDS

o-DGT; passive sampler; organic compounds; diffusive gradients in thin films (DGT); monitoring

INTRODUCTION

Considering its low cost and simplicity, grab sampling is commonly performed to estimate concentration of micropollutants in waters (Allan et al., 2006). However, this technique has some limitations such as the large volume of water required for concentration of trace pollutants in order to comply with analytical sensitivity or the lack of temporal representativeness (Allan et al., 2006). Complementarily to this technique, passive sampling provides *in situ* pre-concentrated samples and allows access to time-weighted average concentration (TWAC), also called C_w (concentration in water). Passive samplers consist basically in a binding phase able to concentrate targeted compounds within various devices deployed in the environment. Organic contaminants in waters can be sampled by Polar Organic Chemical Integrative Sampler (POCIS) (Alvarez et al., 2004), Chemcatcher® (Kingston et al., 2000), Semi-Permeable Membrane Device (SPMD) (Huckins et al., 1990) or Membrane-Enclosed Sorptive Coating (MESCO) (Paschke et al., 2006). However, as shown for some devices (*e.g.* POCIS or SPMD), passive sampling can be affected by environmental factors (Fauvelle et al., 2017; Harman et al., 2012) such as temperature, biofouling or water flow velocity. Consequently, sampling rates (R_s) needed for TWAC estimations can vary between the studied systems (Alvarez et al., 2004; Buzier et al., 2019; Li et al., 2010; Togola and Budzinski, 2007). Given that sampling rates calibration is expensive and time consuming, their determination is not optimized for each targeted system. Consequently, laboratory-determined sampling rates corresponding to generic conditions are usually used for TWAC estimation and inaccuracies may arise (Buzier et al., 2019). Indeed, Poulier et al., (2014) demonstrated that POCIS passive sampling technique is a semi-quantitative method with an error on TWAC of a factor *c.a.* 2.

Similarly to DGT (diffusive gradients in thin films technique) passive sampler for inorganic compounds (Davison and Zhang, 1994), Bondarenko et al., (2011) firstly published the introduction of a diffusive layer in a device to passively sample organic compounds. The presence of a diffusive layer (hydrogel) constrains compounds mass transfer during sampling mostly to diffusion within this layer. Consequently, the device's sampling rate mostly derive from the mass transfer rate imposed by this limiting step. The influence of environmental conditions on sampling rates using such device configuration are therefore limited, compared to standard configurations not using a diffusive layer. The first use of passive sampler devices incorporating a diffusive hydrogel to sample organic compounds in water was reported in 2012

(Chen et al., 2012), under the name "o-DGT". This adaptation of DGT to organic compounds sampling mainly consists in changing the binding phase. Since the first adaptation, there is a growing interest for o-DGT (**Figure 1**) and adaptation to various organic compounds have been proposed (pesticides, pharmaceuticals, hormones, endocrine disrupting chemicals and household and personal care products). Among these published articles, 75% of studies concern devices development (tests on binding phases, elution, robustness or analyte conservation). Application of o-DGT in waters or soils is the aim of 17% of other articles and comparison between POCIS and o-DGT samplers is performed by two articles. A review (Gong et al., 2018), published in January 2018, compared the efficiency of three passive samplers for organic compounds: POCIS, o-DGT and Chemcatcher® but with only 12 articles discussed on o-DGT.

This review proposes an overview of o-DGT passive sampler from its first report in 2011 to the present. Theory, configurations, calibrations, robustness and field applications of the sampler are extensively detailed. This review also discusses its current limitations and future development needed in light of the knowledge already accumulated for inorganic compounds.

THEORY AND MODELLING

Similarly to the initial DGT samplers, o-DGT are usually composed of two hydrogels: a diffusive gel covering a binding gel. A microporous membrane can be added to protect the diffusive gel against particles from the sampled medium. The binding gel is separated from the solution by the diffusive gel and a diffusive boundary layer (DBL) is created at the water/sampler interface due to water viscosity (**Figure 2**). Mass transfer from solution to the binding gel is constrained to diffusion only and can be modeled using Fick's first law. For simplicity, modelling is commonly made under five assumptions: i) absence of interaction between analyte and diffusive gel, ii) concentration at the interface between the binding and diffusive gel is negligible (*i.e.* total and irreversible binding within the receiving phase), iii) time to reach steady-state is negligible, iv) diffusive boundary layer thickness is negligible and v) lateral diffusion is negligible. In these conditions, the flux density (φ) can be expressed by Eq. 1 (Davison and Zhang, 1994):

$$\varphi = \frac{D \times TWAC}{\Delta_g} \qquad \textbf{Equation 1}$$

where D is the diffusion coefficient of the analyte in the diffusive gel (compound and temperature dependent) and TWAC is the concentration of the targeted analyte in studied environment (water). Flux density can also be defined by the following equation Eq. 2:

$$\varphi = \frac{m}{\mathcal{A} \times t} \qquad \textbf{Equation 2}$$

where m is the mass of the analyte in the binding gel, $\mathcal{A}$ is the exposure area between diffusive gel and solution and t is the exposure time. Combining equations (1) and (2), the concentration in the studied environment (water) can be quantified by Eq. 3:

$$TWAC = \frac{m \times \Delta_g}{t \times D \times \mathcal{A}} \qquad \textbf{Equation 3}$$

Given that flux density in the sampler will vary proportionally with the analyte concentration variations in the exposure medium (Eq. 1), any exposure concentration determined with Eq. 3 is in fact a TWAC.

Considering exposure area, exposure time and diffusion layer thickness are known parameters and mass of the analyte is determined following elution of the binding gel, diffusion coefficient within the diffusive gel is the only parameter requiring calibration (see next section) for TWAC estimation. Such modelling allows therefore to free TWAC calibration from any environmental condition not affecting diffusion within the sampler such as flow velocity.

Eq. 3 should be convenient for most cases. Indeed, assumption i) and ii) are not environment dependent and are usually checked previously during the initial development of the sampler. Assumption iii), iv) and v) have never been validated for organic compounds but their behavior should be similar to inorganic compounds, considering their diffusion coefficient is about one order of magnitude different at worst in most cases (*i.e.* values of ≈ 10^{-7}-10^{-6} cm^2 s^{-1} for organics, see **Appendix 1**, *versus* values of ≈ 10^{-6} cm^2 s^{-1} for most inorganics according to DGT Research website). For inorganic compounds, assumption iii) was shown to holds for deployments ≥ 24h (Davison and Zhang, 2012). Warnken et al., (2006) shows that assumption iv) and v) are not strictly valid but the errors from each cancel each other out for standard devices as long as DBL (Diffusive Boundary Layer) thickness remains limited (*i.e.* valid for flow velocity > 2cm s^{-1}, (Gimpel et al., 2001)). Therefore, **Equation 3** should fail only for a limited number of systems, mostly the ones displaying very low flow conditions. Indeed, Belles et al., (2018) and Buzier et al., (2019) demonstrated for various organic compounds the validity of Eq. 3 in flowing conditions (reported flow

velocities ≥ 2.5 cm s^{-1} for the latter). However, Buzier et al., (2019) reported significant inaccuracies in quiescent conditions (between 30 and 70% depending on the analyte), arising from the formation of a significant DBL. To avoid such inaccuracy, more sophisticated models have been developed for inorganic compounds to consider both DBL thickness and lateral diffusion in order to avoid making assumption iv) and v) (Garmo et al., 2006; Santner et al., 2015). An advanced estimation of TWAC could be calculated using Equation 4 that considers the thickness of the DBL (δ) and lateral diffusion within the sampler (Santner et al., 2015):

$$TWAC = \frac{\mathrm{m}}{k_{ld} A_g t}\left(\frac{A_g}{D} + \frac{\delta}{D^w}\right) \qquad \textbf{Equation 4}$$

where k_{ld} is the lateral diffusion flux increase coefficient and D^w is the diffusion coefficient in water.

However, their use requires deployment of devices with various diffusive gel thickness and adaptation of data treatment. An evaluation of such models for organic compounds is found in Buzier et al., (2019) and suggests that their use currently allows limiting inaccuracies for some compounds in quiescent systems but also increase inaccuracies for flowing systems. Such limitation was attributed to limited accuracy of the additional parameters required compared to Eq. 3 (*i.e.* lateral diffusion, diffusion coefficient in water). Such procedure is therefore promising but still required further developments for organic compounds.

DETERMINATION OF DIFFUSION COEFFICIENTS

Diffusion coefficient accuracy is a key factor for o-DGT as it induces most part of TWAC's uncertainty (estimated at ≈ 23%) (Belles et al., 2018). Experimental determination of diffusion coefficients in the diffusive gel can be performed using three method: i) the diffusion cell method, ii) by fitting **Equation 3** following devices deployment in controlled solution, iii) the stack of gels method. The first two methods have been used for long for inorganic compounds (Zhang and Davison, 1999) whereas the last one is a method adapted from Rusina et al., (2010).

The diffusion cell method was the most use (80%). A diffusion cell device (see **Figure 3**) is composed of two separated compartments connected with an opening where a diffusive gel is intercalated and allows mass transfer between the two compartments by diffusion. One of the compartments ("source" compartment) is filled with a solution spiked with the analyte of interest whereas the other compartment

("receiving" compartment) is filled with the same solution but not spiked with the analyte. The analyte diffuse through the diffusive gel and a steady state is established after few minutes. Concentration in the receiving compartment is determined over time in order to determine the analyte flux through the diffusive gel and to derive the corresponding diffusion coefficient using Fick's first law (**Equation 1**).

The second method (ii) uses time series deployment of o-DGT samplers in known spiked solution. Accumulation of analyte into the binding gel *versus* time is determined allowing back calculation of the diffusion coefficient using **Equation 3**. In contrast to the first method, this one allows the use of lower concentrations (μg L^{-1} or less) that are more relevant compared to the targeted environmental applications. However, it includes the sorption step on the binding phase and allows determination of an "effective" diffusion coefficient rather than a "physical" diffusion coefficient. Guibal et al., (2017) compared the two methods for four anionic pesticides. They found good agreement between the two methods for two compounds whereas for the two others they measured higher *D* values (25 and 35%) with the diffusion cell method. Zou et al., (2018) and Guan et al., (2018) found good agreement (4 – 11%) between the two methods for all compounds tested (6 organophosphorus flame retardants and two perfluoroalkyl substances, respectively). When inorganic compounds are considered, Shiva et al., (2015) also reported good agreement between the two methods for nine elements over thirteen. Finally, they advise to favor the second method because of the issue of concentration level relevance.

The last method (iii), adapted from Rusina et al., (2010), was only recently used by Amato et al., (2018) and Belles et al., (2017). Unspiked diffusive gels are stacked with one spiked with the targeted analytes. Analytes diffuse from spiked to unspiked gels and are quantified over time (analyze of unspiked diffusive gels). In contrast, to the two previous methods, the system used do not reach a steady state and Eq. 1 is not valid. Diffusion coefficients are therefore derived using known solutions to Fick's first law for the specific boundary conditions imposed with this method (*e.g.* analyte initially homogeneously distributed across a section of constant surface area, **Equation 5**, (Amato et al., 2018)).

$$C(x,t) = \frac{m}{A\sqrt{4\pi D}} e^{-\left(\frac{x^2}{4Dt}\right)} \qquad \textbf{Equation 5}$$

Where *C (x, t)* is the analyte concentration in unspiked diffusive gels at a distance x from spiked diffusive gel after a time t. This method allows determination of diffusion coefficient without involving the sorption step similarly to the diffusion cell method but requires no specific material (*i.e.* diffusion cell device). Amato et al., (2018) compared this method and diffusion coefficient measurement by diffusive cell for carbamazepine, diuron and isoproturon. They measured higher D values (30, 18 and 25%, respectively) compared to the diffusion cell method.

Modeling of diffusion coefficient has also been tested. Chen et al., (2013) and Challis et al., (2016) derived diffusion coefficient from molecular weight and diffusive gel porosity but found that modelled values were overestimated compared to measured values. A simple linear relationship between LogP and diffusion coefficient was obtained by Zou et al., (2018) for organophosphorus flame retardants with a good determination coefficient (0.98). However, only 5 diffusion coefficients were used to determine the linear relationship and extrapolation to other compounds is questionable. Modelling of D values, although interesting since it can avoid time consuming laboratory work, still requires some developments.

Diffusion coefficients are temperature dependent and can be corrected using the Stoke-Einstein equation (Eq. 6):

$$\frac{D_1 T_1}{\eta_1} = \frac{D_2 T_2}{\eta_2} \qquad \textbf{Equation 6}$$

where T is the temperature and η the water viscosity. When 25°C is taken as the reference condition, Eq. 6 is derived into equation (7) and used to calculate diffusion coefficient at the desired temperature (Zhang and Davison, 1995) :

$$logD_{T_2} = \frac{1.37023\times(\mathrm{T}_2-25)+8.36\times10^{-4}\times(T_2-25)^2}{109+t_2} + \log\frac{D_{25}\times(273-T_2)}{298} \qquad \textbf{Equation 7}$$

Challis et al., (2016) reported for various organic compounds good agreement (typically within 20%) between measured diffusion coefficients and corrected ones with Eq. 7.

STUDIED COMPOUNDS

Sampling of 142 compounds from different action families have been tested: pharmaceuticals, hormones, illicit drugs, bisphenol, household products, personal care products, organophosphorus flame retardants, nitrophenols, perfluoroalkyl substances, endocrine disrupting chemicals and pesticides. Pharmaceuticals

were the most studied compounds (50% of the studied compounds) followed by pesticides with 20% of studied compounds. The list of compounds is presented in **Appendix 1**. They display a wide diversity of chemical properties. Acidic (*e.g.* glyphosate with pKa = - 0.6 (Weng et al., 2019), mecoprop with pKa = 3.5 (Guibal et al., 2017)), neutral (*e.g.* bisphenol (Chen et al., 2018), propranolol (Challis et al., 2016)) and basic (*e.g.* estriol with pKa = 10.3 (Chen et al., 2018), amphetamine with pKa = 10.0 (C. Guo et al., 2017)) compounds have been sampled by o-DGT. Compounds with a wide range of hydrophobicity (-4.54 < LogP < 7.51) and a wide range of molecular weight (128.17 g mol^{-1} for naphthalene to 916.11 g mol^{-1} for tylosin) were investigated; oxytetracycline being the most polar and salinomycin the most hydrophobic compound. Given the wide range of chemical properties displayed by the targeted compounds, it is necessary to check their ability to bind to the receiving phase and to diffuse through the diffusion gel. Moreover, considering the low solubility of the most hydrophobic compounds, adequacy between sampling rate and targeted concentrations has to be considered to allow their quantification.

HLB and XAD18 binding phases were studied for a wide range of compounds with investigations on sampling of 64 and 52 different compounds, respectively. The most studied compound was the antibiotic sulfamethoxazole (13 articles), sulfonamide family being the most widely studied with 19 compounds. For this pharmaceutical family, five receiving phases were found suitable: XAD18, HLB, XDA-1, Sepra ZT and porous carbon material (PCM).

Sampling of each compound with o-DGT will be characterized by a diffusion coefficient within the diffusive gel. These diffusion coefficients are detailed in **Appendix 1**. Compared to metals, diffusion coefficients of organic compounds are usually lower because of volume difference but are about one order of magnitude different at worst (*i.e.* 10^{-7}-10^{-6} cm^2 s^{-1}). For a given compound, with an identical sampler configuration, difference between diffusion coefficients determined by two different authors was lower than a factor 1.4 (except for ciprofloxacin with 2.4 factor difference). Average difference for diffusion coefficients of a given compound was about 1.2.

SAMPLER CONFIGURATION

o-DGT samplers are basically prepared with up to three constituents: a binding gel, a diffusive gel and an optional protective membrane. A broad range of targeted analytes were tested to be sampled by o-DGT and the sampler configuration mainly depends on the analytes of interest (see appendix 1). All published configurations are displayed in Table 1 and detailed below.

Binding phase.

For pharmaceutical compounds, 14 binding phases have been tested (listed in Table 2). Only 6 binding phases were finally used: XAD18, HLB, Sepra ZT, PCM, XDA-1 and nanoZnO. The XAD18 was the most used as binding phase for o-DGT to sample pharmaceutical compounds. This binding phase was used in 8 articles (Chen et al., 2015b, 2015a, 2014, 2013, 2012; D'Angelo and Martin, 2018; D'Angelo and Starnes, 2016; Zhang et al., 2018). Among four different binding phases (Oasis® HLB, activated charcoal, MCX and XAD18), XAD18 was selected by Zhang et al., (2018). The others binding phases were not selected because poor adsorptions were obtained for HLB phase and elutions from activated charcoal or from MCX gels were not efficient for some analytes (methcathinone and ephedrine).

The second binding phase the most used to sample pharmaceuticals was HLB (6 articles (Amato et al., 2018; Buzier et al., 2019; Challis et al., 2018b, 2018a, 2016; Stroski et al., 2018)). Four others binding phases were used by four authors (Sepra ZT (Stroski et al., 2018), PCM (Ren et al., 2018), XDA-1 (Xie et al., 2018a) and nanoZnO (You et al., 2019b)). Before selecting XDA-1, Xie et al., (2018a) have tested 8 binding gels: non-polar phases: XDA-1, LX-1180, XDA-600, LX-4027 and XAD18; ion exchange resin: D296; polar phases: NKA-9 and medium polar phases CAD-40. XDA-1 and LX-4027 had greater binding capacity than the others receiving phases. However, LX-4027 did not distribute evenly in the hot agarose was consequently not selected.

For pesticides, 9 binding phases have been tested (Table 2) and 7 were finally used: TiO_2, cyclodextrine polymer, XDA-1, Strata-X, HLB, activated carbon and Sepra ZT. Only three authors have tested different binding phase. Guibal et al., (2017) tested two phases (Oasis® HLB and Oasis® MAX). Oasis® HLB phase was slightly better than Oasis® MAX when o-DGT were deployed in natural waters. Stroski et al., (2018) compared HLB and Sepra ZT binding phases and concluded that Sepra ZT binding phase was easy to set up because it offered improvements on current-use designs and a more cost effective and widely available

245 binding resin. The same arguments were used by Bondarenko et al., (2011) to support the use of liquid
246 receiving phase (cyclohexane) that allowed convenient working conditions.
247 For hormones, 4 binding phases were selected out of 5 tested (Table 2). Four authors used Oasis® HLB as
248 binding phase whereas three authors used three other binding phases. Stroski et al., (2018) concluded, as
249 for pesticides, that the Sepra ZT binding phase was easy to set up. Chen et al., (2018) had tested three
250 binding phases (HLB, XAD18 and Strata-XL-A). Their investigations have demonstrated that the devices
251 with HLB or XAD18 as binding phases can measured hormones with high accuracy, high sensitivity and
252 good precision.
253 For bisphenols, 4 binding phases were selected out of 5 tested (activated carbon, XDA1, HLB, XAD18
254 and Strata-XL-A). Only Chen et al., (2018) tested different binding phases to sample bisphenol A and
255 concluded that both HLB and XAD18 can be efficiently used.
256 Other classes of compounds have been tested: illicit drugs, organophosphorus flame retardants,
257 perfluoroalkyls, household and personal care products, nitrophenols and miscellaneous organic
258 compounds. For illicit drugs and perfluoroalkyl, C. Guo et al., (2017) and Guan et al., (2018) used
259 XAD18. For organophosphorus flame retardants, Zou et al., (2018) used HLB. According to Chen et al.,
260 (2017), household and personal care products could be sampled using HLB and XAD18. According to
261 Belles et al., (2018, 2017), endocrine disrupting chemicals (*e.g.* tris(n-buthyl)phosphate,
262 tris(phenyl)phosphate) could be sampled using strata-X sorbent. According to You et al., (2019a) and
263 Dong et al., (2014), nitrophenols or 4-chlorophenol, could be sampled by HSAC (lignocellulose hazelnut
264 shell-derived activated carbons) and MIP (molecularly imprinted polymers), respectively.
265 Quantities of binding phase incorporated into binding gel varied from 0.25 to 20% (wet mass:volume)
266 with an average of 13% (Table 1). Protocols were adapted from Zhang and Davison, (1995) where
267 Chelex-100 binding gel was prepared using 2g of resin Chelex-100 in 20 mL of gel solution. The less
268 concentrated was Oasis® HLB receiving phase prepared by Guibal et al., (2017). The effective binding
269 capacity calculated with this concentration was sufficient for a long-term deployment (weeks to months).
270 Among the 6 materials successfully used for binding phase preparation, a mixed binding layer combining 2
271 or more material could be developed similarly to what have been done for inorganic compounds (Huynh

et al., 2012). It could be an interesting way to sample a wider range of organic compounds with a limited number of samplers.

Diffusive layer.

The reported diffusive layers that control mass transfer in the sampler were hydrogels or filter membranes. This last diffusive layer is the less used since only 10% of the published papers concern filter membranes (Dong et al., 2014; You et al., 2019b, 2019a). Regarding hydrogels, two different types were used. 80% of the studies used agarose whereas only 10% used polyacrylamide (**Table 1**). The choice between agarose and polyacrylamide is based on two criteria: i) no analyte adsorption on the diffusive gel and ii) greater diffusion coefficient (Chen et al., 2012, 2018, 2017; Fauvelle et al., 2015; Guibal et al., 2017; W. Guo et al., 2017).

To sample pharmaceuticals by o-DGT, agarose diffusive layer was used by 90% of studies because limited adsorption (<5%) has been observed (Chen et al., 2012; Zhang et al., 2018). However, Stroski et al., (2018) sometimes observed degradation of agarose diffusive gel whereas polyacrylamide shown to be more resistant during field deployment. Agarose degradation was also observed by Challis et al., (2018b) with sometimes a diffusive gel completely destroyed due to aquatic insects grazing. PES membranes could be used also as diffusive gel. This configuration was used by You et al., (2019b) to sample tetracyclines which shown low interaction with PES membranes.

For pesticides, agarose was the most used diffusive layer (64% of studies). The second most used diffusive layer was polyacrylamide (29%). Polyacrylamide diffusive gel was chosen by Fauvelle et al., (2015) because higher diffusion coefficients were obtained (higher than a factor 1.5 compared to agarose gels). This difference between diffusion coefficients in polyacrylamide and agarose gels was attributed to the pore size difference between the two types of gels. Such explanation is however surprising since Zhang and Davison, (1999) and Scally et al., (2006) showed that polyacrylamide contains smaller pore sizes compared to agarose gels, reducing diffusion coefficient of metals. Polyacrylamide was also used by Guibal et al., (2017) because they have observed significant adsorption of anionic pesticide on agarose (15%) whereas only 5% adsorption was observed on polyacrylamide. Contrarily, little adsorption (< 5%) was observed two non-ionic pesticides by Xie et al., (2018b) on agarose diffusive gel. The last diffusion layer used to sample pesticide was water Bondarenko et al., (2011). Diffusion coefficients in water were higher compared to hydrogels (agarose or polyacrylamide).

For hormones, agarose gel was used as diffusion layer by all authors, Stroski et al., (2018) using both agarose and polyacrylamide gels. Authors used agarose gel because poor adsorption of hormones was observed (<10%) (Chen et al., 2018; W. Guo et al., 2017; Xie et al., 2018b).

For bisphenols, illicit drugs, perfluoroalkyl, household and personal care products, and organophosphorus retardant flame, agarose gel was used as diffusive gel. This diffusive gel showed poor adsorption of bisphenols (Chen et al., 2018; Xie et al., 2018b; Zheng et al., 2015), illicit drugs (C. Guo et al., 2017), perfluoroalkyl (Guan et al., 2018), household and personal care products (Chen et al., 2017) and organophosphorus retardant flame (Zou et al., 2018). For Chen et al., (2017), the two type of diffusive gels (agarose and polyacrylamide) showed poor or no adsorption of household and personal care products but agarose had better stability. To sample phenols (4-chlorophenol and nitrophenols), authors used nylon membrane as diffusive layer (Dong et al., 2014; You et al., 2019a).

The protocols for the manufacture of agarose and polyacrylamide diffusive gels are the same for all authors and were adapted from (Zhang and Davison, 1999).

Outer protected layer.

Optional addition of membranes beyond the diffusive layer plays the role of physical protection of the diffusive gel against degradation. Whatever the membranes used, pore size was 0.45 μm. In DGT theory, membrane is considered as inert regarding the analytes and constitutes only a part of the diffusion path in the device.

Consequently, the choice between different membranes was made after evidencing the absence of adsorption of targeted compounds on the chosen membrane. However, such verification was not systematic and assumption of non-interactions between the analytes and the selected membrane was made by some studies.

A total of 11 types of membranes were tested for o-DGT (list of membranes tested are available in **Table 3**). Finally, polyethersulfone (PES) membranes are the most popular for sampling polar organic compounds and were used in 10 studies. Chen et al., (2012) and Zhang et al., (2018) did not observed adsorption (< 5%) for pharmaceuticals (sulfamethoxazole, methcathinone, ephedrine and tetracyclines). The same observation was obtained by C. Guo et al., (2017) for hormones. However, for four authors,

targeted compounds (pesticides (Challis et al., 2016; Chen et al., 2017), pharmaceuticals (Challis et al., 2016), hormones (Challis et al., 2016), bisphenols (Xie et al., 2018b; Zheng et al., 2015) and organophosphorus retardant flame (Zou et al., 2018)) were significantly adsorbed (from 10 to 100%) by this membrane.

PTFE (polytetrafluoroethylene) were also used as protective membranes for the sampling of bisphenols (Zheng et al., 2015) and organophosphorus retardant flame (Zou et al., 2018). No significant adsorption (<5%) was observed for bisphenols contrarily to organophosphorus retardant flame (0 to 50%).

Other protective membranes were used such as nucleopore track-etch ((bisphenols (Chen et al., 2018) and household and personal care products (Chen et al., 2017)), PVDF (polyvinylidene fluoride) (hormones (W. Guo et al., 2017)) and nylon ((pharmaceuticals) (D'Angelo and Martin, 2018)). Adsorption on these membranes was tested by the authors and, whatever the membrane, no significant adsorption (<5%) was observed.

Glass microfiber and nitrocellulose were also used as outer protective membranes for, respectively, the sampling of pesticides (Bondarenko et al., 2011; Wei et al., 2019) and nitrophenol (You et al., 2019a). However, no analyte adsorption test was performed.

To avoid the analyte sorption issue, nine studies (Table 1) use naked o-DGT, making this strategy the second most used. Moreover, Challis et al., (2018b) reported for certain organic compounds a signal suppression induced by PES membranes and then, preconized the use of naked o-DGT. As it was shown with PES membrane used in POCIS, the signal suppression during compounds analysis may be due to release of polyethylene glycol (PEG) by PES membrane (Guibal et al., 2015). Another alternative to conventional membranes to avoid sorption issue was to use aluminum screen (28% open area) as the outer protective layer (Belles et al., 2017).

The use of an outer membrane raises questions. Its use has an undeniable advantage for the protection of the diffusive gel against biofouling or damaging of the diffusive gels by particles and bacteria. However, the impact of using a membrane such as signal suppression during analysis or compound-membrane interaction were shown in some studies. Before using a membrane, two points should be considered: (i) target analytes and their potential interaction with the membrane (several compounds are often targeted and there is no "universally" inert membrane) and (ii) knowledge of the site of field deployment (including

seasonal changes) to evaluate the risk of biofilm development and the relevance using naked o-DGT. Depending on these two points, use of membranes or naked o-DGT should be favored.

INFLUENCE OF ENVIRONMENTAL FACTORS: pH, IONIC STRENGTH, ORGANIC MATTER, BIOFOULING, TEMPERATURE and FLOW EFFECT

Considering environmental factors is important because it can influence sampling. Several authors tested the o-DGT robustness over pH, ionic strength, organic matter and flow effect. All these parameters could influence o-DGT sampling by modifying the analyte speciation, diffusion within diffusive gel and/or sorption onto the binding phase.

pH.

Depending on pH and their pKa, some organic compounds can be neutral or ionic. Change in their protonation will modify their properties and potentially their sampling. A wide range of pH has been tested by the authors (from pH 3 to 11). Considering 20% accuracy is acceptable, no influence of pH on o-DGT sampling is demonstrated for many of the studied compounds. Robustness over pH was demonstrated for 4 hormones (from pH 3.5 to 9.5 (Chen et al., 2018) from pH 7 to 9 (Xie et al., 2018b), from pH 5 to 8 (W. Guo et al., 2017), pH 5 and 8.5 (Stroski et al., 2018)), for some household and personal care products (from pH 3.5 to 9.5) (Chen et al., 2017), for 4-chlorophenol (from pH 3 to 7) (Dong et al., 2014), for nitrophenols (from pH 2 to 7) (You et al., 2019a), for illicit drugs for pH ranged from 4 to 9 (Guo et al. 2017a), for pharmaceuticals (for pH ranged from 5 to 9 (Chen et al., 2012; Ren et al., 2018; Xie et al., 2018a; You et al., 2019b), for pH ranger from4 to 11 (Zhang et al., 2018), for pH 5 and 8.5 (Stroski et al., 2018)), for pesticides (from pH 7 to 9 (Xie et al., 2018b), for organophosphorus flame retardants for pH ranged from 3.1 to 9.7 (Zou et al., 2018) and for bisphenols for pH ranged from 4 to 8 (Zheng et al., 2015), for perfluoroalkyl substances (from pH 4.2 to 7.8) (Guan et al., 2018).

However, sampling of some compounds was found to vary with pH, depending on compounds' pKa. A non-acceptable ratio C_{DGT} / C_{sol} (*i.e.* with more than 20 % of inaccuracy) was obtained by numerous authors. It was the case of Dong et al., (2014) with 4-chlorophenol at pH=8, for some pharmaceuticals

385 (norfloxacin, enrofloxacin, ofloxacin and sulfadimethoxine) when pH < 7.3 Xie et al., (2018a) and for two
386 anionic pesticides (chlorsulfuron and mecoprop) at pH ≥ 7 (Guibal et al., 2017).
387 The influence of pH on sampler uptake and diffusion was deepened by (Stroski et al., 2018) for 31
388 compounds (pharmaceuticals, hormones and pesticides). In this study, different sampler uptake was
389 obtained for 14 compounds (atenolol, clofibric acid, 2,4-D, fluoxetine, ibuprofen, ketoprofen, naproxen,
390 sulfacholoryridazine, sulfamedimethoxine, sulfamethazine, sulfamethoxazole, sulfapyridine, sulfisoxazole
391 and thiamethoxam) between pH 5 and 8.5. A higher sampling was obtained at pH 8.5 for all compounds
392 except for atenolol where accumulated mass was higher at pH 5. They hypothesized that alteration of
393 robustness over pH was caused by changes in sorption on the binding phase following changed with
394 speciation of analyte, in other words there are a change of analyte-sorbent interaction due to speciation
395 modification of analyte. This hypothesis is in accordance with the study on some anionic pesticides from
396 Guibal et al., (2017) who found, for a given compound, pH dependance for two different binding phases
397 (HLB or MAX). Consequently, Stroski et al., (2018) recommended to consider pH as an important factor
398 for future development and calibration of o-DGT.
399
400 **Ionic strength.**
401 Ionic strength can affect sampling by the "salting-out" effect reducing the analyte solubility (Togola and
402 Budzinski, 2007; Xie et al., 1997) and can reduces the electrostatic repulsions due to the screening effect
403 of the surface charge of the diffusive gel (Fontecha-Cámara et al., 2007; Joseph et al., 2011). Ionic strength
404 effect sampling by o-DGT was tested by 15 authors by varying ionic strength from 0.0001 to 1 M
405 (imposed with NaCl or $NaNO_3$). Sampling by o-DGT was found independent on ionic strength usually
406 from 0.001 to 0.5 M (You et al., 2019b, 2019a; Zhang et al., 2018; Zheng et al., 2015; Zou et al., 2018).
407 Effect of ionic strength was reported for some compounds when it raised to 0.2 – 0.5 M or above. It was
408 observed for the antibiotic sulfamethoxazole (Chen et al., 2012), for the hormone estrone (Chen et al.,
409 2018), for the household and personal care products butylated hydroxyanisole and triclosan (Chen et al.,
410 2017), for 4-chlorophenol (Dong et al., 2014), tetracycline antibiotics and nitrophenols (You et al., 2019b,
411 2019a). Alteration of sampling at high ionic strength could be attributed to the "salting-out" effect
412 reducing the analyte solubility (Togola and Budzinski, 2007; Xie et al., 1997).

413 Effect of ionic strength (I) on sampling was also observed at low ionic strength for some compounds.
414 Reduced sampling was reported for perfluorooctane sulfonate at I = 0.0001 M (Guan et al., 2018) and for
415 9 antibiotics (sulfapyridine, sulfadiazine, sulfamethoxazole, sulfathiazole, sulfachloropyridine, norfloxacin,
416 ciprofloxacin, thiamphenicol and florfenicol) at I = 0.01 (Xie et al., 2018a). Conversely, enhanced
417 sampling was reported for three macrolides antibiotics (erythromycin, clarithromycin and azithromycin) at
418 I= 0.01 by the same study (Xie et al., 2018a). Alteration of sampling at low ionic strenght can be explained
419 by modification of electrostatic repulsions with the diffusive gel due to the screening effect of the surface
420 charge as already demonstrated for metals (Fatin-Rouge et al., 2003; Warnken et al., 2005). Indeed, the
421 opposite behavior observed for antibiotics (Xie et al., 2018a) can be linked to their opposite charge at the
422 study's pH (cationic for the three macrolides and anionic for the others at pH 8) which as been shown for
423 trace element to condition reduced (anion) or enhanced (cation) diffusion (Shiva et al., 2015).
424 To conclude on ionic strength, o-DGT can be used to estimate contamination by organic compounds in
425 most freshwaters (Chen et al., 2012, 2017; Guibal et al., 2017; C. Guo et al., 2017; Zhang et al., 2018;
426 Zheng et al., 2015), providing diffusion coefficient are specifically determined for low ionic strength. This
427 passive sampler can be also used to estimate contamination in waters with high ionic strength such as
428 seawater of some antibiotics with PCM as binding phase (Ren et al., 2018; Xie et al., 2018a) or some
429 endocrine disrupting chemicals with XDA-1 as binding phase (Xie et al., 2018b).
430
431 **Dissolved Organic Matter.**
432 Dissolved Organic Matter (DOM) can have two type of effects that could alter analyte uptake by o-DGT
433 samplers. First, DOM can cause competition over analyte for sorption to the binding phase and secondly,
434 reactions between DOM and analytes can alter analyte diffusion (Davison et al., 2015; W. Guo et al.,
435 2017). Indeed, a significant 40% alteration of triclosan sampling was observed by Chen et al., (2017) for
436 DOM concentration higher than 2 mg DOM L^{-1}. This hydrophobic compounds binds to DOM making
437 diffusion trough diffusive gel more difficult. Dong et al., (2014) similarly observed alteration of 4-
438 chlorophenol sampling for DOM concentration ranging from 9.8 to 36.5 mgC L^{-1}. Conversely, sampling
439 of several compounds was found unaltered. This behaviour was for observed for some pharmaceuticals
440 (You et al., 2019b), perfluoroalkyl substances (Guan et al., 2018), hormones (Chen et al., 2018),

organophosphorus flame retardants (Zou et al., 2018) and household and personal care chemicals (Chen et al., 2017)).

It is likely that sampling alteration caused by DOM is compound dependent but also DOM dependent. Until more work is done to investigate DOM effect, interpretation of o-DGT derived concentration should be made with caution when DOM is significantly present.

Biofouling.

Only one article studied biofouling of o-DGT (Challis et al., 2016) and consequences on compounds accumulation during field deployment. Challis et al., (2016) with a long-term deployment (21 days) observed samplers were fouled but do not notice any effect on compounds accumulation. They observed that traditional deployment times (from 2 to 4 weeks) in surface waters allows a linear accumulation in o-DGT. Few authors have studied the impact of biofouling on sampling and therefore this topic is poorly documented. However, it is of particular concern given that interference of fouling on inorganic compounds accumulation in DGT was demonstrated in few articles (Devillers et al., 2017; Feng et al., 2016; Uher et al., 2012). It clearly needs improvements for organic compounds and is further discuss in the last past of this review "future needs for o-DGT deployment".

Temperature effect.

Temperature affects mainly water viscosity and molecular thermic agitation (Brownian motion) and as a consequence *D*. As discussed in section "Determination of diffusion coefficients", it is possible to determine a temperature corrected *D* (*cf.* Eq.7). Challis et al., (2016) had measured and calculated (Eq. 7) diffusion coefficients at different temperatures. Relative error was about 20% and the authors concluded that relationship (Eq. 7) is valid to estimate diffusion coefficient. TWAC for field deployments can be calculated based on the average temperature recorded. Commercial devices such as Tynitag can easily perform temperature record with relevant time frequencies (below 1h)

Flow effect.

DGT sampler is known to be poorly sensitive to environmental conditions such as hydrodynamic flow for metals (Gimpel et al., 2001) thanks to the thickness of its diffusive layer. However, DBL (**Figure 2**) may become significant in low flow conditions and alter DGT sampling by increasing the diffusion path length (Davison and Zhang, 2012). DBL thickness has been estimated by several authors for organic compounds. Values obtained are in the same order of magnitude in well stirred systems (average thicknesses from 0.22 to 0.25 mm) (Belles et al., 2018; Challis et al., 2016; Chen et al., 2013, 2018, 2017; Ren et al., 2018). A higher value was obtained by Challis et al. (2018b) with an estimated median δ = 0.34 mm. Measured DBL thicknesses for organic compounds are very close to those obtained for inorganic compounds in well stirred systems (≈ 0.2 mm, Davison and Zhang, 2012). Without taking into account this boundary layer, the estimate of the concentration should be 20% underestimated by **Equation 3**. Some authors recommended the use of diffusive gel with a thickness at least 1.0 mm (Chen et al., 2013) to limit the significance of the DBL thickness. A ticker diffusive gel (1.2 mm) was chosen by Belles et al., (2017) to have a gel thickness significantly higher than the DBL one. Other authors propose to include δ ≈ 0.20 mm in calculations to estimate TWAC (Challis et al., 2016). It has been demonstrated for metals (Warnken et al., 2006) that, when using standard devices, the error made by neglecting DBL thickness is cancelled by the error made by neglecting lateral diffusion. This phenomenon is likely to concern also organic compounds and incorporating DBL thickness in concentration calculation for well stirred systems could alter its accuracy. In unstirred solutions, DBL thickness is found to increase up to 0.76 mm (average values (Challis et al., 2016; Chen et al., 2012)). Such increase in the diffusion length will significantly alter sampling and concentration estimation as demonstrated by Buzier et al., (2019) for some pharmaceuticals. In unstirred solutions, increasing diffusive gel thickness or incorporating DBL thickness in concentration calculation should improve accuracy. For some pharmaceuticals, Buzier et al., (2019) estimated that a 2.5 mm gel thickness should allow keeping <25% accuracies. It should be noted that such increase in the diffusion length will proportionally decrease the sampling rate and alter the sensitivity.

APPLICATION & FIELD DEPLOYMENT

494 Different environmental matrixes were tested for field deployments. The first application was made in
495 soils (Bondarenko et al., 2011) but few studies currently concerns such field application (Chen et al.,
496 2015a, 2014; Lin et al., 2018).
497 The majority of studies concerns sampling in freshwaters. The first one was performed in a river in
498 United-Kingdom (Chen et al., 2012) to estimate contamination of sulfamethoxazole with 14-day
499 deployment of o-DGT. Deployments in rivers were also performed by Guibal et al., (2017), C. Guo et al.,
500 (2017), Stroski et al., (201), Zhang et al., (2018) and Zheng et al., (2015) for 7 days or in a lake for 12-33
501 days (Guan et al., 2018). These authors concluded that o-DGT devices were suitable to detect organic
502 pollution in freshwaters. Three authors have tested deployment in coastal waters (Ren et al., 2018; Xie et
503 al., 2018b, 2018a). After 3-day deployment of o-DGT (XDA-DGT), endocrine disrupting chemicals were
504 detected. For 3 compounds (estradiol, Bisphenol A and acetochlor), differences between concentration
505 determined by o-DGT and concentrations determined by grab sampling was observed (Xie et al., 2018b).
506 These differences were explained the different nature of sampling, spot sampling being unable to provide
507 TWAC (Xie et al., 2018b, 2018a).
508 o-DGT were also successfully deployed in non-natural waters. Deployments for 24h to 120h in industrial
509 wastewaters contaminated with nitrophenolic compounds (You et al., 2019a) showed no significant
510 difference in estimated concentrations compared to grab samples. Deployments of o-DGT were
511 performed in WasteWater Treatment Plant (WWTP) influent and effluent from 6h to 33 days (Challis et
512 al., 2018b, 2016; Chen et al., 2015b, 2013, 2018, 2017; Dong et al., 2014; Guan et al., 2018; C. Guo et al.,
513 2017; W. Guo et al., 2017; Ren et al., 2018; Zou et al., 2018). A 5-day field deployment in small pound
514 receiving pig breeding wastewater was performed by You et al., (2019b).
515 Deployment time appears a key factor to ensure accurate results during field deployments in waters. A 7-
516 day deployment was recommended by Chen et al., (2013). This duration allows to stay in kinetic uptake
517 regime and to avoid significant biofouling. Biofouling was also observed by Challis et al., (2016) with a
518 long-term deployment (21 days) but accumulation was still linear and indicated that sampler capacity was
519 sufficient for using traditional deployment times (from 2 to 4 weeks) in impacted surface waters.
520

521 **FUTURE NEEDS FOR O-DGT DEVELOPMENT**

This review collected studies which demonstrated the potential of o-DGT. The o-DGT is of particular interest compared to other passive sampler since it has a better robustness over flow variations (Buzier et al., 2019) and allows deployments in soils (Chen et al., 2015a, 2014; Lin et al., 2018). However, a current disadvantage of o-DGT compared to others passive samplers for organic contaminants is its lower ability to concentrate compounds because of lower sampling rates. A detailed comparison of passive samplers efficiency and deployment (*i.e.* o-DGT, POCIS and Chemcatcher®) is proposed by Gong et al. (2018). Compared to sampling rates of POCIS (Polar Organic Chemical Integrative Sampler) o-DGT's ones were about 25 (Challis et al., 2018b) or 50 (Buzier et al., 2019) times lower. These reduced sampling rates are mostly due to a reduced exposure area of o-DGT (3.1 cm^2 versus 41 cm^2 for POCIS) compared to other passive samplers (Buzier et al., 2019; Chen et al., 2013; Guibal et al., 2017). Therefore, an increase of o-DGT sampling area should allow increasing sampling rates and consequently improving sensitivity. Buzier et al., (2019) estimated for 10 pharmaceutical compounds that a 160 cm^2 sampling area (~7 cm radius) should allow similar sampling rates compared to POCIS. Such a theoretical o-DGT configuration must however be tested in the field, since physical constrains on these larger gels could be significant. A recent study investigated improved design of o-DGT sampler in order to increase sampling rates (Urík and Vrana, 2019). Similarly to POCIS, this new o-DGT sampler design has two side and increased size allowing sampling area to be seven times higher than the standard DGT design (22.7 cm^2). This new o-DGT sampler was successfully tested for polar organic compounds sampling (pharmaceuticals and personal care products). Sampling rates were higher than the one obtained with standard o-DGT in Guibal et al., (2017) (43 *versus* 13 mL day^{-1}).

o-DGT can also be currently impacted by other limitations concerning any passive sampler. In many cases, because of sensitivity and representativeness issues, long deployment times (*e.g.* several weeks) would be preferred. However, longer deployment in environmental systems will favor biofouling formation in front of the samplers as already observed by Challis et al., (2016) and Chen et al., (2013). Fouling of the device can be due to microorganisms (bacterial, algal or fungi development) or deposition of suspended matter. Although biofouling effect was not studied for organic compounds passive sampling, it is likely to alter analyte sampling as observed for inorganic compounds (Feng et al., 2016; Pichette et al., 2009; Uher et al., 2017, 2012). It was shown by Devillers et al., (2017) that some metals

were adsorbed onto biofouling resulting in decreasing compound concentration at the water/sampler interface and consequently in smaller diffusion rate into the sampler.

Given that several organic compounds have a high affinity for organic matter (Chen et al., 2017), it is not to exclude that some compounds will bind to biofouling and their passive sampling should be consequently altered. However, such behavior still has to demonstrated for organic compounds. Feng et al., (2016) found that the diffusion coefficient of orthophosphate decreased linearly with increasing fouling thickness, allowing a mathematical model to be proposed for diffusion coefficient correction over the formation of the fouling. Similar procedure for organic compounds could be investigated if their sampling was found to be altered by biofouling.

Finally, standardization of the calibration procedures (*i.e.* diffusion coefficient determination, see previous sections) would be valuable to favor reproducibility and reliability of o-DGT results. Indeed, determination of diffusion coefficients can be performed by three different methods. The time series deployments method allows using more environmentally relevant concentrations and could be considered as the most relevant method. However, it results from model fitting to not only diffusion process but also to compound binding within the sampler. Rather than a physical diffusion coefficient, it is a calibration parameter usually called "effective diffusion coefficient". Moreover, some authors did not take into account the entire diffusion path (diffusive gel and membrane). Considering that membranes were previously shown to alter diffusion coefficient of some metals (Buzier et al., 2014), it is possible that diffusion of some organic compounds is also altered. Indeed, significant sorption between some organic compounds and polyethersulfone membranes used with POCIS were demonstrated by Endo and Matsuura, (2018). Until it is demonstrated that the membrane used with o-DGT has no influence on the diffusion of the targeted compounds, it is advisable to incorporate the membranes in the calibration experiments.

CONCLUSION

This review investigated the current data available on o-DGT passive samplers. 22 possible configurations were developed (*i.e.* binding gel combined with diffusive gel and membranes) to enable sampling of organic compounds from different chemicals families with a wide range of physico-chemicals properties

(*e.g.* hydrophobicity with logP ranged from -4.54 to 7.51) in environmental water bodies or in soil systems. The two most commonly used configurations were agarose-XAD18 and agarose-HLB. However, it is important to adapt the configuration of the sampler to the known properties of the targeted compounds. These two configurations allow to sample organic compounds in a wide range of pH (4-9) and ionic strength (0.001 to 0.1 M). This robustness indicated that o-DGT can be used in most natural waters. Considering that, compared to other samplers, o-DGT is less influenced by flow variations and allows deployment in several environmental compartments (*e.g.* water, soil and sediment), it seems to have a great potential for monitoring a large class of organic pollutants in environment. However, this sampler cannot currently reach sensitivity offers by other passive samplers (*e.g.* POCIS). Depending on the targeted contamination levels, improvement of o-DGT sensitivity would be desirable.

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Table 1. Initial (2007) soil TE concentrations (mg kg^{-1} DW) for the PHYTOPOP plots, compared with natural pedogeochemical background values (NPBV) and local usual agricultural concentrations (UAC) given as ranges (Lamy et al. 2006).

	NPBV	**UAC**	**PHYTOPOP plots**	
			Min	max
Cd	0.014-0.02	0.19 - 0.42	1.98	4.44
Co	2.3 - 3.6	3.0 – 7.7	4	13.5
Cr	13.9 – 21.0	15 - 29	37	89
Cu	2.4 – 5.9	8 - 19	69	218
Hg	0.01 – 0.03	0.08 – 0.15	-	-
Ni	4.2 – 8.2	6 - 20	14	42
Pb	3.7 – 8.3	18 - 43	74.7	484
Zn	8.6 -19.4	34 - 63	314	692

Table 2. Ammonium nitrate-TE extractable fraction in Pierrelaye soils collected from under the various poplar genotypes. Values presented were measured in 2007 and 2011 and the changes occurring between the two samplings are indicated.

Genotype	Cd			Cu			Zn			pH		
	µg kg^{-1} DW		change (%)	µg kg^{-1} DW		change (%)	µg kg^{-1} DW		change (%)			change (%)
	2007	2011		2007	2011		2007	2011		2007	2011	
Bakan	21.3	16.5	-23	812	690	-15	1970	1620	-18	7.24	7.39	+2
Dorskamp	20.5	16.2	-21	639	525	-18	1620	1370	-16	7.27	7.31	+1
Dvina	39.1	26.2	-33	718	648	-10	2240	1350	-40	7.47	7.47	=
Flevo	24.6	19.3	-21	895	751	-16	2260	1880	-17	7.19	7.36	+2
Fritzi Pauley	17.9	13.9	-23	634	475	-25	165	137	-17	7.36	7.24	-2
l214	29.1	20.9	-28	801	726	-10	2130	1630	-23	7.27	7.52	+3
Koster	19.4	15.6	-20	723	611	-16	1910	1630	-15	7.34	7.34	=
Lena	20.0	15.7	-22	650	532	-18	1590	1280	-20	7.33	7.32	=
Muur	25.7	20.3	-21	839	766	-9	2300	1820	-21	7.29	7.45	+2
Skado	25.9	19.8	-24	758	642	-16	1680	1340	-20	7.38	7.51	+2
Soligo	19.8	16.0	-20	505	433	-15	1490	1210	-19	7.40	7.32	-1
Trichobel	19.0	15.5	-18	620	535	-14	1530	1310	-15	7.38	7.46	+1
Triplo	29.2	21.4	-27	761	726	-5	2010	1390	-31	7.30	7.54	+3
Vesten	22.0	17.1	-23	779	630	-19	1990	1590	-20	7.31	7.38	+1

Table 3. Estimated allometric parameters (standard error) of the power function and statistical outputs (data are for TrunkDW and BranchDW). Logarithm transformation of data and power form ($DW=a*dbh^{\wedge b}$) with a and b as regression coefficients were chosen as the best relevant models. The "a" regression coefficients was the same for all genotypes (a=10.12). The TrunkDW and BranchDW estimates were expressed with the Bakan genotype as the reference. D: *P. deltoides*; DN: *P. deltoides* x *P. nigra*; T: *P. trichocarpa*; TM: *P. trichocarpa* x *P. maximowiczii.* Levels of significance are indicated by asterisks : ***p < 0.001; **p < 0.01; *p < 0.05. ns : not significant.

Genotype	Species	n	TrunkDW estimate	t-value	b	BranchDW estimate	t-value	b	BranchDW Proportion (%)
Bakan (intercept)	TM	5	10.12 (2.65)	3.825 (***)	10.12	1.83 (1.65)	1.11 (ns)	1.83	26
Dorskamp	DN	5	-3.704 (3.49)	-1.06 (ns)	6.41	5.79 (2.22)	2.61 (*)	7.62	27
Dvina	D	5	-10.49 (3.48)	-3.01 (**)	-0.37	0.46 (2.22)	0.21 (ns)	2.29	34
Fritzi Pauley	T	6	-0.0035 (3.34)	-0.00 (ns)	10.11	-2.95 (2.13)	-1.38 (ns)	-1.12	25
Flevo	DN	5	-5.928 (3.48)	-1.70 (.)	4.19	0.63 (2.22)	0.29 (ns)	2.46	30
I214	DN	5	-9.116 (3.50)	-2.60 (*)	1.00	1.11 (2.23)	0.50 (ns)	2.94	33
Koster	DN	5	-8.78 (3.49)	-2.51 (*)	1.34	-1.58 (2.23)	-0.71 (ns)	0.25	31
Lena	D	6	-14.62 (3.33)	-4.38 (***)	-4.50	2.37 (2.13)	1.11 (ns)	4.19	40
Muur	DN	7	-8.914 (3.26)	-2.73 (**)	1.20	-1.05 (2.08)	-0.50 (ns)	0.78	31
Skado	TM	6	0.0242 (3.33)	0.01 (ns)	10.14	2.05 (2.12)	0.97 (ns)	3.88	27
Soligo	DN	7	-5.948 (3.24)	-1.84 (.)	4.17	-2.39 (2.06)	-1.16 (ns)	-0.56	29
Trichobel	T	5	-2.827 (3.49)	-0.80 (ns)	7.29	-1.82 (2.23)	-0.82 (ns)	0.00	27
Triplo	DN	6	-14.03 (3.33)	-4.20 (***)	-3.91	-3.43 (2.12)	-1.62 (ns)	-1.61	37
Vesten	DN	5	-10.65 (3.48)	-3.06 (**)	-0.53	-5.08 (2.22)	-2.29 (*)	-3.25	35

Table 4. Macronutrient concentrations (mg kg^{-1} DW) in wood and branches of the 14 poplar genotypes from the Pierrelaye site. Data represent the mean (± SE), resulting from samples taken at three different heights as described in the material and method section (see also Fig. S1). Levels of significance are indicated by asterisks : ***p < 0.001; **p < 0.01. Different letters represent significant differences for element content between the genotypes (one-way ANOVA, Tukey-Kramer HSD test). ns : not significant.

Genotype	**Ca**		**K**		**P**		**Mg**	
	Branch	Wood	Branch	Wood	Branch	Wood	Branch	Wood
	***	**	ns	***	***	***	***	***
Bakan	16273 (2171) b	1214 (53) ab	4891 (403)	1519 (152) ab	1732 (121) ab	570 (70) ab	1011 (88) ac	218 (12) ab
Dorskamp	13504 (1861) ab	1711 (182) b	6248 (890)	1989 (112) ac	2136 (186) ab	747 (42) bc	1222 (140) bc	366 (17) ef
Dvina	12125 (1337) ab	1437 (119) ab	5547 (548)	1550 (120) ac	1571 (158) ab	614 (24) ab	1331 (118) c	387 (12) f
Flevo	13787 (532) ab	1253 (76) ab	5731 (283)	1904 (118) ac	1659 (54) ab	543 (46) ab	1054 (26) ac	267 (12) bc
Fritzi Pauley	14025 (1464) b	1250 (118) ab	5107 (343)	1758 (146) ac	1985 (185) ab	576 (60) ab	897 (39) ab	248 (11) bc
I214	12572 (1569) ab	1381 (81) ab	6454 (647)	1795 (111) ac	1625 (150) ab	610 (31) ab	1052 (129) ac	299 (12) cde
Koster	9244 (960) ab	1206 (67) ab	5233 (418)	1511 (78) ab	1593 (91) ab	536 (26) ab	948 (79) ac	358 (21) df
Lena	10264 (1412) ab	1445 (105) ab	5844 (813)	2036 (120) bc	1613 (199) bc	557 (34) ab	935 (96) ac	302 (11) cde
Muur	11812 (1075) ab	1282 (105) ab	6047 (529)	1762 (66) ac	2026 (110) ab	883 (27) c	820 (47) ab	294 (17) cde
Skado	10184 (1161) ab	1227 (82) ab	4796 (466)	1494 (67) a	1904 (193) ab	542 (35) b	961 (115) ac	222 (10) b
Soligo	14794 (1836) b	1647 (136) b	6587 (537)	1717 (107) ac	2216 (137) ac	643 (45) ab	1113 (74) bc	373 (23) f
Trichobel	11662 (1141) ab	1306 (122) ab	6813 (491)	2114 (193) c	2345 (119) a	746 (53) ac	785 (35) ab	266 (13) bc
Triplo	13348 (1417) ab	1079 (60) a	6610 (625)	1857 (102) ac	2049 (153) ab	577 (38) ab	1303 (132) c	279 (7) bc
Vesten	9150 (403) a	1488 (108) ab	5483 (107)	1780 (91) ac	1602 (53) b	600 (52) ab	749 (20) a	286 (12) acd

Table 5. Trace element concentrations (mg kg^{-1} DW) in wood of the 14 poplar genotypes from the Pierrelaye site. Data represent the mean (± SE), resulting from samples taken at three different heights as described in the material and method section (see also Fig. S1). Levels of significance are indicated by asterisks : ***p < 0.001; **p < 0.01. Different letters represent significant differences for element content between the genotypes (one-way ANOVA, Tukey-Kramer HSD test). ns : not significant.

Genotype	Cd	Cr	Cu	Fe	Mn	Pb	Zn
	***	**	***	***	***	***	***
Bakan	1.6 (0.15) cd	0.1 (0.01) ab	4.0 (0.3) ab	12.4 (1.2) ab	16.1 (2.0) bd	0.4 (0.04) ab	132 (13) cdf
Dorskamp	1.7 (0.20) d	0.2 (0.02) ac	6.6 (0.9) cd	20.7 (3.0) cd	17.9 (2.6) bd	0.4 (0.03) ac	185 (25) f
Dvina	1.6 (0.18) cd	0.2 (0.06) c	6.6 (0.9) c	16.7 (1.7) ad	20.1 (2.9) d	0.4 (0.06) c	79 (8) abc
Flevo	1.1 (0.25) ad	0.1 (0.01) ac	5.8 (0.4) ac	19.9 (2.1) bd	19.3 (1.4) cd	0.6 (0.05) ac	93 (8) ad
Fritzi Pauley	1.0 (0.08) a	0.2 (0.01) ac	3.8 (0.3) a	10.9 (1.1) a	9.4 (0.9) ab	0.5 (0.09) ac	118 (11) bd
I214	0.9 (0.11) a	0.1 (0.01) ac	3.8 (0.4) ab	9.9 (1.1) a	7.3 (0.9) a	0.4 (0.06) ac	86 (8) abc
Koster	1.3 (0.09) ad	0.2 (0.01) ac	4.2 (0.4) ac	13.1 (1.4) abc	16.8 (2.0) ad	0.4 (0.04) ac	91 (8) ad
Lena	1.3 (0.19) ad	0.1 (0.01) ac	5.0 (0.6) ac	22.5 (3.2) d	13.9 (2.7) ad	0.5 (0.10) ac	72 (9) ab
Muur	1.4 (0.09) ad	0.1 (0.01) ac	5.2 (0.5) ac	15.3 (1.4) abc	15.2 (1.4) ad	0.3 (0.02) ac	126 (9) cde
Skado	1.09 (0.10) abc	0.1 (0.01) ac	5.7 (0.3) bc	12.3 (1.3) ab	13.7 (1.8) ad	0.3 (0.02) ac	143 (14) df
Soligo	1.7 (0.13) bd	0.2 (0.02) bc	5.6 (0.3) ac	13.4 (1.5) abc	13.5 (1.4) ad	0.3 (0.03) bc	101 (7) ad
Trichobel	1.2 (0.10) ad	0.1 (0.01) ac	4.1 (0.2) ab	10.5 (1.0) ab	9.6 (1.2) abc	0.5 (0.05) ac	172 (13) ef
Triplo	1.4 (0.15) ad	0.1 (0.01) a	4.7 (0.4) ac	14.4 (1.3) abc	16.6 (2.8) bd	0.3 (0.02) a	71 (8) a
Vesten	1.2 (0.03) ac	0.1 (0.01) ac	4.7 (0.1) abd	14.5 (0.4) abc	13.4 (0.4) ad	0.3 (0.03) ac	82 (3) ab

Table 6. Trace element concentrations (mg kg^{-1} DW) in branches of the 14 poplar genotypes from the Pierrelaye site. Data represent the mean (± SE), resulting from samples taken at three different heights as described in the material and method section (see also Fig. S1). Levels of significance are indicated by asterisks : ***p < 0.001; **p < 0.01. Different letters represent significant differences for element content between the genotypes (one-way ANOVA, Tukey-Kramer HSD test). ns : not significant.

Genotype	Cd	Cr	Cu	Fe	Mn	Pb	Zn
	***	ns	***	***	***	ns	***
Bakan	0.5 (0.04)	0.1 (0.01)	2.2 (0.2)	2.1 (0.2)	2.5 (0.1)	0.4 (0.08)	33 (2)
	bdf		abc	ac	bd		bd
Dorskamp	0.7 (0.05)	0.1 (0.02)	4.1 (0.3)	2.9 (0.3)	2.3 (0.2)	0.4 (0.05)	51 (2)
	f		e	bc	ad		e
Dvina	0.6 (0.05)	0.1 (0.01)	2.6 (0.2)	3.0 (0.3)	2.7 (0.3)	0.4 (0.05)	25 (2)
	ef		ad	c	cd		ab
Flevo	0.4 (0.05)	0.1 (0.01)	3.2 (0.3)	2.8 (0.2)	2.0 (0.1)	0.4 (0.04)	27 (2)
	ad		cde	bc	abc		ab
Fritzi Pauley	0.2 (0.02)	0.1 (0.01	1.7 (0.1)	1.9 (0.2)	1.6 (0.1)	0.4 (0.05)	28 (1)
	a		a	ab	a		ab
I214	0.4 (0.03)	0.1 (0.01)	2.0 (0.1)	1.6 (0.2)	2.1 (0.2)	0.4 (0.04)	36 (2)
	ad		ab	a	abc		cd
Koster	0.5 (0.05)	0.1 (0.02)	2.0 (0.1)	2.4 (0.2)	2.9 (0.1)	0.4 (0.05)	32 (1)
	bcde		ab	ac	d		bd
Lena	0.5 (0.06)	0.1 (0.01)	2.5 (0.2)	4.2 (0.5)	2.1 (0.3)	0.4 (0.05)	21 (2)
	bcde		ad	d	ad		a
Muur	0.4 (0.02)	0.1 (0.01)	2.0 (0.1)	2.3 (0.1)	2.1 (0.2)	0.3 (0.03)	32 (1)
	bcd		a	ac	abc		bc
Skado	0.3 (0.03)	0.1 (0.01)	2.9 (0.2)	2.1 (0.1)	1.8 (0.1)	0.5 (0.04)	31 (1.2)
	ac		cd	ac	a		bc
Soligo	0.5 (0.03)	0.1 (0.01)	3.2 (0.3)	2.4 (0.2)	1.6 (0.1)	0.3 (0.03)	32 (2)
	df		de	ac	a		bc
Trichobel	0.3 (0.04)	0.1 (0.02)	2.5 (0.3)	2.0 (0.3)	1.6 (0.1)	0.4 (0.05)	40 (2)
	ab		ad	ac	a		d
Triplo	0.4 (0.05)	0.1 (0.01)	2.0 (0.1)	2.1 (0.2)	1.9 (0.1)	0.3 (0.03)	23 (1)
	ad		a	ac	ab		a
Vesten	0.4 (0.03)	0.1 (0.02)	3.0 (0.3)	2.9 (0.2)	1.7 (0.1)	0.4 (0.05)	26 (2)
	bcd		bd	bc	ab		ab

Table 7. Element concentrations (mg kg^{-1} DW) in bark of the poplar Skado genotype from the site of Pierrelaye. Data represent the mean (± SE). The ratio bark/wood and branch/wood (data from tables 4 and 5) are indicated.

	Ca	**K**	**P**	**Mg**	**Mn**	**Cu**	**Fe**	**Zn**	**Cd**	**Cr**	**Pb**
Bark	17326 (471)	5923 (256)	1109 (57)	679 (23)	13.4 (0.4)	3.4 (0.2)	16.0 (1.7)	183.1 (9.5)	1.23 (0.08)	0.15 (0.03)	0.64 (0.16)
Ratio bark/wood	14	4	2	3	8	1	8	6	4	1	1
Ratio branch/wood	8	3	4	4	8	2	6	5	3	1	1

Table 8. Element export by wood and branches of the 14 poplar genotypes grown at the Pierrelaye site for 7 years. Data are means for the number of replicates, calculated from element content (mg kg^{-1} DW) provided in tables 4 and 5, and growth data provided in fig. 3 (Odt ha^{-1} $year^{-1}$).

Genotype		Ca	K	P	Mg	Mn	Cu	Fe	Zn	Cd	Cr	Pb
		kg^{-1} ha^{-1} $year^{-1}$				g^{-1} ha^{-1} $year^{-1}$						
Bakan	Branch	29.94	9.00	3.19	1.86	29.60	7.41	22.90	241.94	3.01	0.21	0.82
	Wood	6.36	7.96	2.98	1.14	13.00	11.65	10.96	172.38	2.71	0.54	2.33
Dorskamp	Branch	11.35	5.25	1.79	1.03	15.00	5.52	17.43	155.48	1.45	0.13	0.31
	Wood	3.90	4.54	1.71	0.83	5.24	9.38	6.62	116.39	1.64	0.30	0.92
Dvina	Branch	15.61	7.14	2.02	1.71	25.88	8.55	21.50	101.54	2.12	0.26	0.48
	Wood	3.53	3.81	1.51	0.95	6.54	6.32	7.47	61.52	1.56	0.33	0.92
Flevo	Branch	13.17	5.47	1.58	1.01	18.47	5.59	18.98	89.11	1.07	0.14	0.54
	Wood	2.82	4.28	1.22	0.60	4.42	7.22	6.40	61.38	0.82	0.25	0.84
Fritzi Pauley	Branch	20.04	7.30	2.84	1.28	13.37	5.36	15.62	168.02	1.43	0.22	0.74
	Wood	5.35	7.53	2.47	1.06	6.87	7.24	8.05	118.90	0.89	0.52	1.81
I214	Branch	22.31	11.45	2.88	1.87	12.91	6.72	17.58	152.62	1.62	0.21	0.75
	Wood	5.01	6.52	2.22	1.09	7.56	7.41	5.92	129.25	1.32	0.33	1.41
Koster	Branch	13.99	7.92	2.41	1.44	25.49	6.43	19.77	137.22	1.91	0.24	0.58
	Wood	4.01	5.03	1.78	1.19	9.55	6.59	8.01	107.47	1.56	0.39	1.28
Lena	Branch	21.70	12.36	3.41	1.98	29.29	10.59	47.56	153.24	2.74	0.28	1.11
	Wood	4.57	6.44	1.76	0.96	6.79	7.81	13.40	65.88	1.54	0.38	1.22
Muur	Branch	13.89	7.11	2.38	0.96	17.92	6.07	17.98	148.14	1.69	0.15	0.34
	Wood	3.36	4.61	2.31	0.77	5.39	5.27	6.05	84.17	1.05	0.28	0.68
Skado	Branch	19.03	8.96	3.56	1.80	25.68	10.68	23.02	267.66	2.04	0.25	0.53
	Wood	6.06	7.38	2.68	1.09	8.69	14.64	10.35	154.45	1.59	0.61	2.38
Soligo	Branch	17.31	7.71	2.59	1.30	15.80	6.56	15.67	117.83	1.97	0.22	0.38
	Wood	4.76	4.96	1.86	1.08	4.50	9.32	6.89	93.05	1.54	0.33	0.90
Trichobel	Branch	16.08	9.39	3.23	1.08	13.22	5.59	14.51	236.51	1.63	0.18	0.65
	Wood	4.95	8.02	2.83	1.01	6.12	9.44	7.50	152.33	1.19	0.47	1.42
Triplo	Branch	29.26	14.49	4.49	2.86	36.45	10.30	31.49	155.50	2.99	0.22	0.62
	Wood	4.08	7.02	2.18	1.06	7.26	7.45	8.07	87.36	1.44	0.36	1.16
Vesten	Branch	27.52	16.49	4.82	2.25	40.26	14.20	43.59	247.02	3.54	0.41	0.78
	Wood	8.13	9.73	3.28	1.56	9.53	16.45	16.00	143.53	2.33	0.67	2.34

Table 1: Configuration of o-DGT (*n.c.* not concerned, *n.i.* not indicated).

Binding phase	Targeted analytes	Diffusive phase	Membranes	Thickness of diffusive gel (mm)	Binding phase concentration in binding gel (% mass:volume)	References
Activated charcoal	Bisphenols	Agarose	PTFE	0.75	5	Zheng et al., (2015)
Activated charcoal	Naphtalene	Water	Glass microfiber	10.50	*n.c.*	Bondarenko et al., (2011)
Activated charcoal	Nitrophenols	Nylon membrane	Nitrocellulose	0.16	1	You et al., (2019a)
Cyclodextrine polymer	Biocides	Agarose	Glass microfiber	1.00	n.c.	Wei et al., (2019)
MIP	4-chlorophenol	Nylon membrane	*n.i.*	0.18	30	Dong et al., (2014)
n.i.	*Atrazine*	*n.i.*	*n.i.*	*n.i.*	*n.i.*	Lin et al., (2018)
NanoZnO partcicles	Pharmaceuticals	PES membrane	No membrane	0.16	0.25	You et al., (2019b)
Oasis HLB	Endocrine disrupting chemicals	Agarose	Nucleopore track-etch	0.35 – 2.00	20	Chen et al., (2018)
Oasis HLB	Household and personal care products	Agarose	Nucleopore track-etch	0.80	20	Chen et al., (2017)
Oasis HLB	Organophosphorus flame retardants	Agarose	PTFE	0.75	20	Zou et al., (2018)
Oasis HLB	Pesticides	Polyacrylamide	No membrane	0.77	3	Guibal et al., (2017)
Oasis HLB	Pharmaceuticals	Agarose	No membrane	0.16 – 0.84	7	Buzier et al., (2019)
Oasis HLB	Pharmaceuticals and pesticides	Agarose	*n.i.*	0.75	10	Amato et al., (2018)
Oasis HLB	Pharmaceuticals and pesticides	Agarose	No membrane	0.75	7	Challis et al., (2018a)
Oasis HLB	Pharmaceuticals, hormones and pesticides	Agarose	No membrane	1.00	7	Challis et al., (2016)
Oasis HLB	Pharmaceuticals, hormones and pesticides	Agarose	No membrane	0.75	8	Stroski et al., (2018)
Oasis HLB	Pharmaceuticals, hormones and pesticides	Agarose	No membrane	0.75	7	Challis et al., (2018b)

Oasis MAX	Pesticides	Polyacrylamide	No membrane	0.75	3	Guibal et al., (2017)
PCM	Pharmaceuticals	Agarose	PES	0.80	1	Ren et al., (2018)
Sepra ZT	Pharmaceuticals, hormones and pesticides	Polyacrylamide	No membrane	0.75	7	Stroski et al., (2018)
Strata-X	Pesticides, endocrine disrupting chemicals and others	Agarose	No membrane	1.20	10	Belles et al., (2017)
Strata-X	Pesticides, endocrine disrupting chemicals and others	Agarose	No membrane	2.00	0.5 to 10	Belles et al., (2018)
TiO_2	Glyphosate	Polyacrylamide	PES	0.91 (with prefilter)	8	Weng et al., (2019)
TiO_2	Herbicides	Polyacrylamide	PES	0.80	10	Fauvelle et al., (2015)
XAD-18	Endocrine disrupting chemicals	Agarose	Nucleopore track-etch	0.35 – 2.00	20	Chen et al., (2018)
XAD-18	Hormones	Agarose	PVDF	0.75	20	W. Guo et al., (2017)
XAD-18	Illicit drug	Agarose	PES	0.80	20	C. Guo et al., (2017)
XAD-18	Perfluoroalkyl substances	Agarose	PES	0.75	20	Guan et al., (2018)
XAD-18	Pharmaceuticals	Agarose	Nylon	0.80	20	D'Angelo and Starnes, (2016)
XAD-18	Pharmaceuticals	Agarose	PES	0.80	20	Chen et al., (2013)
XAD-18	Pharmaceuticals	Agarose	PES	0.80	20	Chen et al., (2014)
XAD-18	Pharmaceuticals	Agarose	PES	0.80	20	Chen et al., (2015a)
XAD-18	Pharmaceuticals	Agarose	PES	0.80	20	Chen et al., (2015b)
XAD-18	Pharmaceuticals	Agarose	PES	0.80	*n.i.*	Zhang et al., (2018)
XAD-18	Sulfamethoxazole	Agarose	PES	0.80	20	Chen et al., (2012)
XAD-18	Tetracycline	Agarose	Nylon	0.80	20	D'Angelo and Martin, (2018)
XDA-1	Endocrine disrupting chemicals	Agarose	No membrane	0.80	10	Xie et al., (2018b)
XDA-1	Pharmaceuticals	Agarose	PES	0.80	10	Xie et al., (2018a)

Table 2: List of binding gels tested by authors.

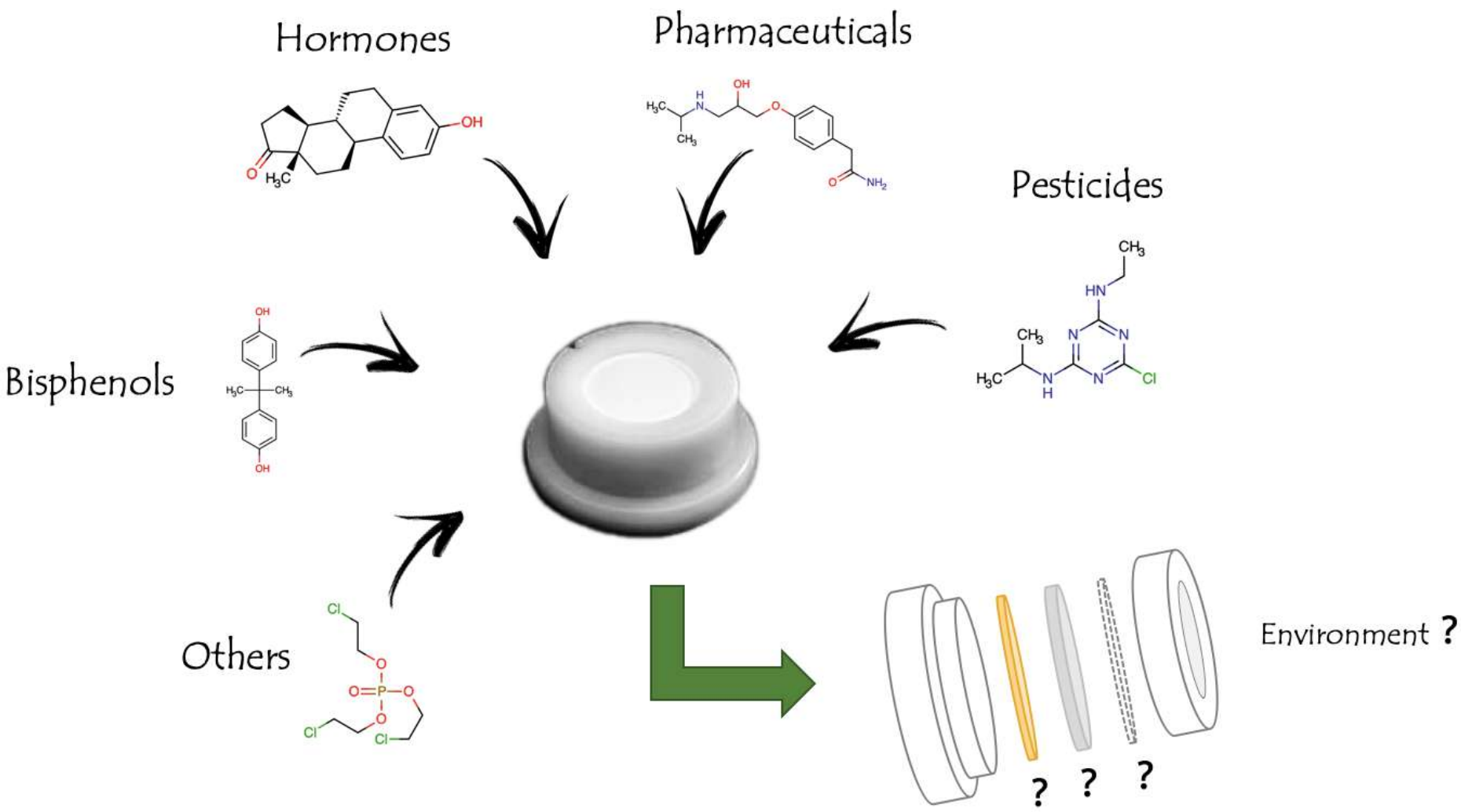
Compounds	Binding phase	Authors
Bisphenols	Activated carbon	Zheng et al., (2015)
Bisphenols	XAD18, HLB and Strata-XL-A	Chen et al., (2018)
Bisphenols	XDA-1	Xie et al., (2018b)
Hormones	HLB	Challis et al., (2018b, 2018a, 2016); Chen et al., (2018); Stroski et al., (2018)
Hormones	Sepra ZT	Stroski et al., (2018)
Hormones	Strata-XL-A	Chen et al., (2018)
Hormones	XAD18	Chen et al., (2018); W. Guo et al., (2017)
Hormones	XDA-1	Xie et al., (2018b)
Household and personal care produc	XAD18, HLB and Strata-XL-A	Chen et al., (2017)
Illicit Drug	XAD18	C. Guo et al., (2017)
Organophosphorus flame retardants	HLB	Zou et al., (2018)
Other	HSAC	You et al., (2019a)
Other	MIP	Dong et al., (2014)
Other	Strata-X	Belles et al., (2018, 2017)
Other	XAD18	Chen et al., (2018)
Perfluoroalkyl	XAD18	Guan et al., (2018)
Pesticides	Activated carbon and cyclohexane	Bondarenko et al., (2011)
Pesticides	CDPM	Wei et al., (2019)
Pesticides	HLB	Amato et al., (2018); Challis et al., (2018b, 2018a, 2016); Guibal et al., (2017); Stroski et al., (2018)
Pesticides	MAX	Guibal et al., (2017)
Pesticides	n.i.	Lin et al., (2018)
Pesticides	Sepra ZT	Stroski et al., (2018)
Pesticides	Strata-X	Belles et al., (2018, 2017)
Pesticides	TiO_2	Fauvelle et al., (2015); Weng et al., (2019)
Pesticides	XDA-1	Xie et al., (2018b)

Pharmaceuticals	HLB	Amato et al., (2018); Buzier et al., (2019); Challis et al., (2018b, 2018a, 2016); Stroski et al., (2018); Zhang et al., (2018)
Pharmaceuticals	MCX and activated carbon	Zhang et al., (2018)
Pharmaceuticals	nanoZnO	You et al., (2019b)
Pharmaceuticals	PCM	Ren et al., (2018)
Pharmaceuticals	Sepra ZT	Stroski et al., (2018)
Pharmaceuticals	Strata-X	Belles et al., (2017)
Pharmaceuticals	XAD18	Chen et al., (2015b, 2015a, 2014, 2013, 2012); D'Angelo and Martin, (2018); D'Angelo and Starnes, (2016); Xie et al., (2018a); Zhang et al., (2018)
Pharmaceuticals	XDA-1, LX-1180, XDA-600, LX-4027, D296, NKA-9 and CAD-40	Xie et al., (2018a)

Table 3: Outer protected layer tested by authors.

Compounds	Utilisé	References
Bisphenol	No membrane	Xie et al., (2018b)
Bisphenol	Nucleopore track-etch	Chen et al., (2018)
Bisphenol	PES	Xie et al., (2018b)
Bisphenol	PTFE	Xie et al., (2018b)
Bisphenols	Mixed cellulose ester (MCE)	Zheng et al., (2015)
Bisphenols	Nylon	Zheng et al., (2015)
Bisphenols	PES	Zheng et al., (2015)
Bisphenols	PTFE	Zheng et al., (2015)
HCPP	Cellulose nitrate	Chen et al., (2017)
HCPP	Cyclopore track-etch	Chen et al., (2017)
HCPP	Nucleopore polycarbonate	Chen et al., (2017)
HCPP	Nucleopore track-etch	Chen et al., (2017)
HCPP	Nucleopore track-etch	Chen et al., (2017)
HCPP	PES	Chen et al., (2017)
Hormones	No membrane	Challis et al., (2018b, 2018a, 2016); Stroski et al., (2018); Xie et al., (2018b)
Hormones	Nucleopore track-etch	Chen et al., (2018)
Hormones	PES	Challis et al., (2016); Xie et al., (2018b)
Hormones	PTFE	Xie et al., (2018b)
Hormones	PVDF	W. Guo et al., (2017)
Illicit drug	Mixed cellulose ester (MCE)	C. Guo et al., (2017)
Illicit drug	Nylon	C. Guo et al., (2017)

Illicit drug	PES	C. Guo et al., (2017)
Illicit drug	PTFE	C. Guo et al., (2017)
Organophosphorus flame retardants	PTFE	Zou et al., (2018)
Other	No membrane	Belles et al., (2017)
Other	Nucleopore track-etch	Chen et al., (2018)
Perfluoroalkyl	PES	Guan et al., (2018)
Pesticides	Glass-fiber	Bondarenko et al., (2011); Wei et al., (2019)
Pesticides	No membrane	Amato et al., (2018); Belles et al., (2018, 2017); Challis et al., (2018b, 2018a, 2016); Guibal et al., (2017); Stroski et al., (2018); Xie et al., (2018b)
Pesticides	PES	Challis et al., (2016); Fauvelle et al., (2015); Weng et al., (2019); Xie et al., (2018b)
Pesticides	PTFE	Xie et al., (2018b)
Pharmaceuticals	Mixed cellulose ester (MCE)	Zhang et al., (2018)
Pharmaceuticals	No membrane	Amato et al., (2018); Belles et al., (2017); Buzier et al., (2019); Challis et al., (2018b, 2018a, 2016); Stroski et al., (2018); You et al., (2019b)
Pharmaceuticals	Nylon	D'Angelo and Martin, (2018); D'Angelo and Starnes, (2016); Zhang et al., (2018)
Pharmaceuticals	PES	Challis et al., (2016); Chen et al., (2015b, 2015a, 2014, 2013, 2012); Ren et al., (2018); Xie et al., (2018a); Zhang et al., (2018)
Pharmaceuticals	PTFE	Zhang et al., (2018)
Phenols	Nitrocellulose	You et al., (2019a)


Hormones
Pharmaceuticals
Pesticides
Bisphenols
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